Russian Chemical Reviews **65** (10) 865–913 (1996) © 1996 Russian Academy of Sciences and Turpion Ltd

UDC 541(15 + 64):537.5

The structure and properties of block poly(vinylidene fluoride) and systems based on it

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Abstract. The influence of external factors on the formation of various polymorphic modifications of poly(vinylidene fluoride) (PVDF) and the copolymers and blends based on it is examined. It is shown that the formation of a particular conformational structure of the PVDF chains may be controlled by regulating, for example, the fraction of irregular 'head to head' ('tail to tail') attachments and by selecting a suitable comonomer or component of the blend. It is shown that polar modifications of PVDF may be obtained by its crystallisation from solutions in specific solvents. The important role of high pressures was noted in block crystallisation. Solid-phase transformations may be initiated with the aid of tensile and compressive deformations (within certain temperature ranges), high electric fields, and exposure to radiation. It is shown that both the type of the lattice and the variety of the morphology of the PVDF change on crystallisation in a blend with amorphous poly(methyl methacrylate). The characteristics of the dynamics of the block PVDF chains, obtained predominantly with the aid of dielectric spectroscopy, have proved sensitive to the polymorphism and the kind of morphology and may yield additional information about the structure of the noncrystallising regions of the polymer under consideration. The bibliography includes 383 references.

I. Introduction

A systematic treatment of the structure and properties of poly(vinylidene fluoride) (PVDF) is of interest because it has effective piezoelectric and pyroelectric properties.[1,2] It is one of the most promising polymeric ferroelectrics. It is used for practical purposes in the polarised state (for example, in various kinds of transducers[3]), so that knowledge of the mechanism of the structural changes in strong electric fields is obligatory. Analysis of published studies has shown that polarisation processes depend on the characteristics of the structure and the nature of the molecular mobility in crystalline and amorphous regions.

One of the most informative methods for the study of the microstructure of PVDF chains is high-resolution nuclear magnetic resonance, NMR spectra of polymer solutions being recorded. A series of peaks, associated with defects in the 'head to head' or 'tail to tail' attachment, may be distinguished for ^{19}F nuclei.[4] As the apparatus improved, it became possible to obtain spectra at higher frequencies,[5–8] which yield detailed information about the microstructure of the PVDF chain. In particular, the influence of the suspension (or emulsion) polymerisation method on the microstructure of the PVDF chain has been discussed.[7] In order to obtain additional information, data on the ^{13}C resonance[9–10] or the resonances involving all three nuclei entering into the composition of the chain (^1H, ^{13}C, and ^{19}F) at once[11] are resorted to. The application of two-dimensional NMR spectroscopy[12,13] has also expanded the existing ideas about the microstructure of the PVDF chain. This method is used in the study of the microstructure of the chains in vinylidene fluoride (VDF) copolymers with perfluoroalkyl trifluorovinyl ethers,[14] trifluoroethene (TrFE),[15] tetrafluoroethene (TFE), or hexafluoropropene.[16,17] Having estimated the spin-spin coupling constants for neighbouring sections of PVDF in the *trans*-(*T*) or *gauche*-conformations (*G*), it is possible to estimate their proportions. For example, the fraction of the *TT* conformations for the monochlorobenzene–dimethyl sulfoxide solvent mixture increases significantly when the fraction of monochlorobenzene is reduced.[18] It is assumed that there must exist a correlation between the conformations of the VPDF chains in solution and in the block state.

The crystalline phases of PVDF and of its copolymers are characterised by the presence of at least four polymorphic modifications [α (II), β (I), γ (III), and α (IV)]. These modifications are distinguished by the conformational structure of the chain and by the nature of the packing of the macromolecules in the unit cell of the crystallites. The characteristic conformational

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Received 23 October 1995
Uspekhi Khimii **65** (10) 936–987 (1996); translated by A K Grzybowski

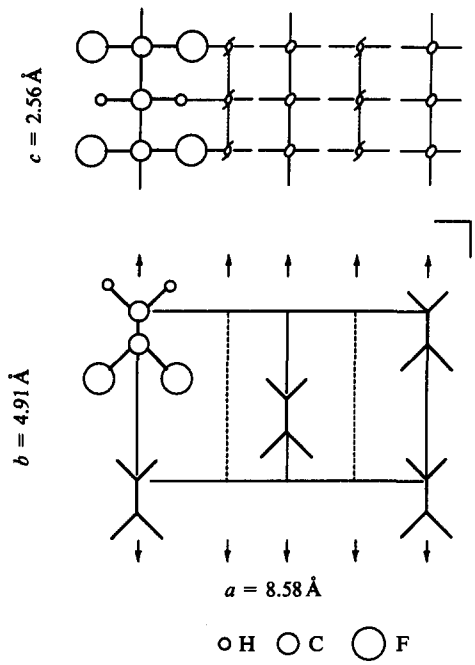


Figure 1. The structure of the crystal lattice of the β modification of PVDF.[19,36]

chain structures for three of the modifications listed above are presented in Figs 1–3. Evidently conformations of the $TGT\bar{G}$, $T_3GT_3\bar{G}$, and 'planar zigzag' types are characteristic of the α phases, γ phases, and β phases respectively.[19] One may note that, owing to the phenomenon of rotational isomerism involving the hydrocarbon skeleton of the chain, the transition from the 'planar zigzag' conformation to the $TGT\bar{G}$ conformation is accompanied by an almost twofold increase in the identity period along the chain (*c* axis of the cell).

The Raman and IR spectroscopic methods are known to be 'sensitive' to the short-range order, i.e. they should be more informative as regards the chain conformation. Numerous literature data on the vibrational spectra of PVDF have confirmed this.[19–35] Table 1 presents the results of the study of PVDF crystallised in three different modifications — their symmetries and characteristic vibrational frequencies. It follows from the tabulated data that there exist a series of characteristic absorption bands for each conformation and that this can be used to identify a particular PVDF conformation.

Since Table 1 presents mainly the characteristics of localised vibrations, it should be supplemented by data on the low-frequency vibrations characterising as a rule the lattice modes of motion. Thus, according to Latour et al.,[20] these modes for PVDF crystallised as the α, β, and γ phases are characterised by absorption bands at 100, 70, and 90 cm^{-1} respectively.

The need to characterise PVDF and its copolymers by the degree of crystallinity α frequently arises. The so called 'crystalline' or 'amorphous' bands are usually found for this purpose in spectroscopic practice for crystallisable polymers. Such bands have been found also for PVDF. The bands at 600, 740, and 905 cm^{-1} have been classified as amorphous and those at 1180 and 1235 cm^{-1} have been classified as crystalline.[34,35] According to Kobayashi et al.,[25] the 489 cm^{-1} band for PVDF crystallised in the β and γ modification should also characterise the nonordered phase. The 442 cm^{-1} band characterises the chain vibrations in the 'planar zigzag' conformation present in the crystal whereas the 510 cm^{-1} band is characteristic of such conformers in the crystalline and amorphous phases.[15] The conclusion that bands sensitive to the presence of fragments with long *trans*-sequences is useful for practical purposes: these are vibrations with frequencies of 840 and 1275 cm^{-1}.[27] Regions which may yield information

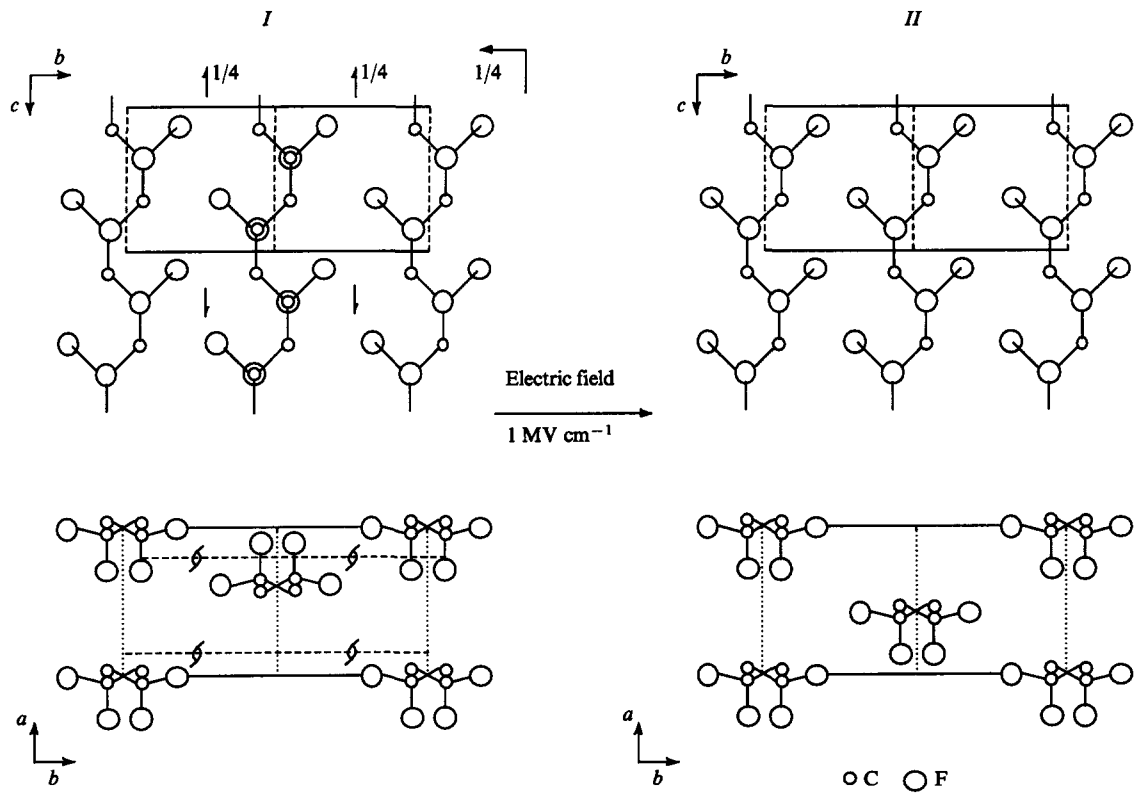


Figure 2. The structure of the crystal lattice of the α modification of PVDF with parallel chains (*I*) and the phase transition to the α_p phase on 180 ° rotation and translation by *c*/2 of the central chain (*II*).[19]

Table 1. The assignments of the IR absorption bands for the α, β, and γ phases.[19]

α Phase ($TGT\bar{G}$)			γ Phase ($T_3GT_3\bar{G}$)			β Phase (TT)		
I	II	III	I	II	III	I	II	III
3026	A'	$\nu_a CH_2$	3023	A'	$\nu_a CH_2$	3020	B_1	$\nu_a CH_2$
	A''			A''				
2986	A''	$\nu_s CH_2$	2981	A''	$\nu_s CH_2$	2978	A_1	$\nu_s CH_2$
	A'			A'				
1425	A	$\delta CH_2-\omega CH_2$	1431	A'	$\delta CH_2-\omega CH_2$	1430	A_1	δCH_2
1404	A'	$\delta CH_2+\omega CH_2$	1406	A'	$\delta CH_2+\omega CH_2$	1400	B_1	$\omega CH_2-\nu_a CC$
1385	A''	$\delta CH_2+\omega\ CH_2$						
1294	A'	$\nu_a CF_2-rCF_2$						
1213	A''	$\nu_a CF_2+\omega\ CH_2$	1234	A''	$\nu_a CF_2+\omega CH_2$			
1185	A''	$\nu_s CF_2+l CH_2$	1176	A''	$\nu_s CF_2+l CH_2$	1180	B_2	$\nu CF_2-rCF_2+rCH_2$
1150	A''	$\nu_a CC-\nu_s CF_2$	1140	A''	$\nu_a CC-\nu_s CF_2$			
976	A'	$l CH_2$						
874	A'	$\nu_a CC+\nu_s CF_2$	880	A''	$\nu_a CC+\nu_s CF_2$	880	A_1	$\nu_s CF_2+\nu_s CC$
855	A'	rCH_2	838	A'	rCH_2	840	B_2	$rCH_2-\nu_a CF_2$
			813	A'	rCH_2			
796	A'	rCH_2	792	A''	$r\ CH_2$			
765	A''	$\delta\ CF_2+\delta CCC$	776	A'	$\delta\ CF_2$			
			723	A''	$\delta\ CF_2$			
			688	A''	$\delta\ CF_2$			
			656	A''	$\delta\ CF_2$			
615	A'	$\delta\ CF_2-\delta' CCC$						
			552	A'	$\delta\ CF_2$			
532	A''	$\delta\ CF_2$	511	A''	$\delta\ CF_2$	508	A_1'	$\delta\ CF_2$
490	A'	$\delta\ CF_2+\ \omega CF_2$	482	A'	$\delta\ CF_2+\omega\ CF_2$	490		
410	A'	$r\ CF_2$	430	A'	$r\ CF_2$	470	B_1	$\omega\ CF_2$
			400	A''	$r\ CF_2$	445	B_2	rCF_2+rCH_2
355	A'	lCF_2+rCF_2	348	A''	lCF_2+rCF_2			
287	A'	$lCF_2+\omega\ CF_2$	300	A'	$lCF_2+\omega\ CF_2$			

Note. Designations adopted: I – band (cm^{-1}); II – symmetry; III – type of vibration.

about the defects of 'head to head' attachment have been differentiated by calculating the densities of vibrational states in PVDF chains.[31]

We shall consider certain crystallographic aspects of the packing of the chains in the unit cell. Fig. 1 presents the unit cell parameters for β-phase crystals. According to Servet et al.[19] and Lando and Doll[36], this is an orthorhombic cell belonging to the $Cm2m$ space group and the density of the crystal is 1.97 g cm^{-3}. Fig. 2 presents a schematic illustration of the unit cell of the α phase with a parallel arrangement of the chains in the lattice. In this case, the cell is monoclinic with the Cc space group, whereas for antiparallel chains it is orthorhombic with the space group $P2_1cn$. In both cases, the cell is found to be nonpolar, since the two chains in the repeat unit have opposite dipole moments. The α_p phase† differs from the α phase only by the fact that the overall dipole moment per cell is not zero. The appearance of additional extinctions of the reflections in the case of the α_p phase indicates its greater symmetry compared with the α phase.

The nature of the packing of the chains in the PVDF γ phase is illustrated in Fig. 3. The workers who have studied systematically

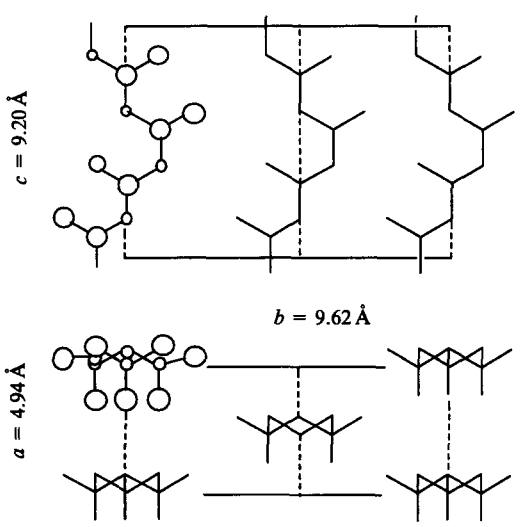


Figure 3. The structure of the crystal lattice of the γ modification of PVDF.[19]

† The mechanisms of the formation of this form will be discussed below.

Table 2. X-Ray reflections and structure factors F_{hkl} for the PVDF β phase.[38]

hkl	d' /Å	θ /deg	F_{hkl}
200	4.29	10.35	9.31
110	4.26	10.42	16.6
001	2.56	17.53	7.2
310	2.47	18.18	5.15
020	2.46	18.3	5.4
201	2.20	20.53	1.1
411	2.19	20.57	5.7
400	2.15	21.06	1.5
220	2.13	21.21	0.24
311	1.78	25.69	
021	1.77	25.79	
401	1.64	27.96	

Table 3. X-Ray reflections and structure factors F_{hkl} for the α and α_p phases of PVDF.[38]

hkl	*d'*/Å	θ /deg	F_{hkl}	
			α	α_p
100	4.96	8.94	36	0
020	4.82	9.20	52	52
110	4.41	10.07	83	100
011	4.17	10.66		
120	3.46	12.89	56	0
021	3.34	13.36	72	72
111	3.19	13.98	48	52
121	2.77	16.17	39	0
130	2.7	16.61	45	56
031	2.64	16.99		
200	2.48	18.11	42	64
040	2.41	18.66	9	9
210	2.4	18.72	49	0
131	2.33	19.33		
002	2.31	19.49	47	47
012	2.25	20.07		
220	2.21	20.46		
140	2.17	20.83		
041	2.14	21.15		
211	2.13	21.21		
102	2.09	21.6		
022	2.08	21.72		
112	2.05	22.13		
221	1.99	22.79		
230	1.96	23.12		
141	1.96	23.13		
122	1.92	23.66		
032	1.88	24.27		

Table 4. The calculated and experimental interplanar spacings and the indexing of reflections for γ phase crystals.[19]

hkl	*d*/Å		*hkl*	*d*/Å	
	experiment	calculation		experiment	calculation
020	4.81	4.81	024	2.07	2.07
110	4.38	4.39	114		2.04
			133		2.04
021		4.26	150	1.76	1.79
022	3.34	3.32	223		1.79
			151		1.76
130	2.69	2.69	134		1.75
			240		1.72
023	2.58	2.59			
131		2.58	241	1.63	1.69
			204		1.68
200	2.46	2.47	152		1.67
			044		1.66
041	2.30	2.32	310		1.62
132		2.32	241		1.61
004		2.30	060		1.60
221	2.14	2.14	311		1.60
042		2.13	224		1.59
			061		1.58

the PVDF structure hold different views concerning the crystallographic identification of the γ phase. One of the reasons for this is the difficulty of obtaining the γ phase in the oriented state. Another one is the possibility of the formation of two modifications of the γ phase. According to Weinhold et al.[37] this may be the cause of the assignment of the γ phase to the orthorhombic system with the *C2cm* space group, on the one hand, and to the monoclinic system with the *Cc* space group, on the other. Tables 2–4 present the angular positions of the principal reflections with their identifications and their structure factors (F_{hkl}) for all four polymorphic modifications of PVDF considered.

II. The specific effect of solvents on the conformational characteristics of the chains of poly(vinylidene fluoride) obtained by polymerisation or crystallisation from solution

An attempt has been made[39] to obtain PVDF single crystals by crystallisation from solution. A 90:10 mixture of monochlorobenzene and dimethylformamide was used as the solvent. At a solution concentration of 0.01%–0.1% and with the solutions cooled slowly, crystals of the α phase were obtained with a thickness of the lamellae of 90 Å, the chain axis being arranged at right angles to the surface of the crystal. According to the assignment, crystals with a monoclinic lattice in the β modification were obtained as a result of precipitation from dimethyl sulfoxide. This can hardly be regarded as reliable, since later this conclusion was not confirmed by any investigator using the same solvent. Crystallisation from an good solvent such as dimethyl sulfoxide is most likely to result in the γ phase. For example, Makarevich and Sushko[35] and Gal'perin et al.[40] arrived independently at this conclusion. The crystallisation conditions apparently play a by no means secondary role. Thus, according to the results of Gal'perin et al.,[40] crystallisation from solution in an good solvent (dimethyl sulfoxide or dimethyl formamide) affords the γ modification of PVDF only at a temperature of the support below 140–150 °C. Analysis of the formation of films from solutions in variable solvents showed that the crystals of the γ phase are obtained from solutions in acetone, dimethyl sulfoxide, and ethyl methyl ketone, whilst those of the α phase are obtained from solutions in methyl propyl ketone, dipropyl ketone, butyl methyl ketone, acetophenone, cyclohexanone, or their mixtures.[35] The presence of the α phase on crystallisation from solution in cyclohexanone (on the surface of water) has been confirmed indirectly by the presence of spherulites in the crystallised films[41] which are usually produced by crystals of this modification.

The conclusion that the γ phase is formed on crystallisation from a mixture of good and poor solvents for PVDF[39] has been confirmed by the results of a study[42] where monochlorobenzene was again used as the poor solvent, whilst the good solvent was dimethylacetamide. According to this study,[39] the γ phase crystallises at a concentration of 0.1%, whereas at a concentration of ~ 0.5% the α modification is actually produced. It has been noted that the crystals of the γ phase are very resistant to an electron beam, i.e. they are not converted into an amorphous form in the course of 10 min and longer (for comparison, we may note that the crystals of the α phase are preserved for 0.5 min and those of polyethylene for 1.5 min).

The influence of ionogenic impurities (in the polymer and in the solvent) on the characteristic features of the crystallisation process may be traced in relation to solutions of PVDF in cyclohexanone. Thus crystallisation from a 0.02% solution of PVDF in cyclohexanone is accompanied by the formation of a pseudohexagonal structure.[43] This was inferred from the ratio of the unit cell parameters: $a/b = 1.73$ (for the pseudohexagonal structure, $a/b = \sqrt{3}$). Taking into account literature data, Miller and Raisoni[43] concluded (in contrast to Makarevich and Sushko[35]) that PVDF crystallises as a mixture of β and γ phases. However, it was established with the aid of a series of methods for monitoring the crystal structure that crystallisation from this solvent is accompanied by the formation of the α phase or its mixture with the γ phase.[44] In the latter case, the X-ray method did not permit the estimation of the contributions of each phase and their fractions were therefore calculated from IR spectroscopic data: the γ phase was assumed to be associated

with the presence of absorption bands at 430 and 776 cm^{-1} in addition to others.

Comparison of the published data permits the conclusion that the polymorphic modifications deduced by different investigators for solutions of PVDF in the same solvents are poorly reproducible. This forced Grubb and Choi[44] to postulate the important role of ionogenic impurities in crystallisation processes. The same workers confirmed this hypothesis later[45] in relation to dilute (0.01%) and concentrated (5%–9%) solutions of PVDF in dimethylacetamide (or in its mixture with monochlorobenzene). It was observed that an increase in the concentration of ionogenic impurities leads to an increase in the fraction of the γ phase if the polymer crystallises as a mixture of the α and γ phases. This is explained by the fact that, under the conditions governing the formation of crystals with intrinsic polarisation, the latter possess an appreciable electrostatic energy. For example, on the assumption that the perpendicular and parallel components of the dipole moment for the orthorhombic lattice of the γ phase crystal are 4×10^{-30} and 3.4×10^{-30} C m respectively, the surface charge densities on the 100 and 001 planes were found to be $P_a = 0.073$ and $P_c = 0.062$ C m^{-2}. As a result of an increase in the concentration of ionogenic impurities, the latter are deposited on a plane having the opposite charge and give rise to a depolarising field. An appreciable decrease in electrostatic energy thus has a favourable effect on the crystallisation of the polymer in a polar phase.

The high energy of the electrostatic interaction between the PVDF chains is apparently one of the causes of an unusual phenomenon — the displacement of the solvent from the bulk phase in experiments on the swelling of PVDF in various solvents, including those having a high affinity for the polymer (for example, in dimethylformamide).[46] Experiments on the swelling of biaxially oriented PVDF film in various solvents (or their mixtures) have shown that the equilibrium swelling tends to decrease with increase in the amount of precipitant in dimethylformamide — water and acetonitrile–water mixtures. It was noted that even the best solvents have a low affinity for the polymer, which is approximately the same for the α and β modifications. The remark by Chapiro et al.[46] that all solvents are spontaneously desorbed from the film after its removal from the medium (liquid or gaseous) owing to the higher energy of the polymer–polymer interaction is significant.

Yet another contradiction, noted when data on the crystallisation of PVDF from acetone were compared, can probably also be accounted for by the influence of ionogenic impurities on the nature of the polymorphic modification formed when PVDF crystallises from solutions. According to the data of Makarevich and Sushko,[35] this process results in the formation of the γ phase, whilst according to those of Kochervinskii et al.[47] this should be the α phase, since bands typical of the $TGT\bar{G}$ conformers were observed in the IR spectrum: 100, 214, 287, 411, and 530 cm^{-1}, etc. It is noteworthy that the crystallisation from acetone in the latter study[47] was accompanied also by a significant change in the nature of the morphology. If the polymer crystallises from the melt, spherulites with a high birefringence coefficient are formed. In contrast to this, spherulites were hardly noted in the film crystallised from acetone.

Yet another cause of the contradictions noted in different investigations may be failure to take into account other factors, for example, the molecular mass, the characteristics of the molecular mass distribution (MMD), the number of 'head to head' defects, the form of the end groups, etc., data on which are not always reported. One should apparently consider separately the characteristics of crystallisation from solutions not of the homopolymer but of the VDF–TFE 94/6 copolymer, which, in contrast to the homopolymer, crystallises from the melt at once mainly as the β phase.[32,48] It has been observed that the crytallisation of this copolymer from an 8% solution in pure dimethylformamide leads to the formation of the β phase with a morphology comprising spherulites with an average size of 2–3 μm.[48] The crystallisation of the same copolymer from solution in a 76:24 dimethylformamide–ethyl acetate mixture leads to an appreciable alteration of the morphology of the β phase formed. In this case, the spherulites are no longer formed and the film (in contrast to the film obtained from pure dimethylformamide) is characterised by an optical transparency which is several times greater. Analysis of the results of X-ray analysis has shown[32] that the size of the crystallites for the coexisting ferroelectric and paraelectric phases is smaller in the case of crystallisation from the solvent mixture and the fraction of the paraelectric phase is also reduced.

It appears attractive to use the phenomenon of epitaxy for the formation of the required polymorphic PVDF modification. In this case, one should consider the results of several studies in which the crystallisation of PVDF from solution onto a support of a particular crystal was investigated. Thus the crystallisation of the homopolymer of the Kynar 460 type ($M_\omega = 451\,000$, $M_n = 160\,000$) from 6.3 vol.% solution in dimethylacetamide on the surface of a KBr crystal at 60 °C leads to the formation of a nonoriented γ phase,[26] while crystallisation of the same crystal (on the 001 plane) from a dilute solution (0.1%) of PVDF in dimethylformamide at a temperature of the support of 165 °C leads to the formation of lamellar crystals of the β phase oriented along two directions in the 110 plane of the support.[49] An exact correspondence of the lattices in epitaxial crystallisation is not obligatory, since the difference between the identity periods of the substrate and support ranges from 4.3% to 5.6%. Analysis of electron diffraction patterns has shown that the *bc* plane of the unit cell of the PVDF β phase grows parallel to the plane of the support, the growth being directed predominantly along the *b* axis. Crystallisation from a dilute solution of PVDF in dimethylformamide onto the 001 plane on the surface of muscovite or NaCl at 180 °C has been investigated.[50] The γ phase formed is characterised by a monoclinic cell with a 93 °C angle and the $T_3GT_3\bar{G}$ conformation of the chain. The possibility of the formation on NaCl of two lattices with mirror symmetry relative to the 001 plane of the substrate has been demonstrated. According to the ideas developed, the possibility of the formation of a modification of the γ phase with antiparallel packing of the dipoles in the cell is not ruled out. Epitaxial crystallisation of a copolymer of vinylidene fluoride and vinyl fluoride (molar ratio 95/5) has been investigated.[51] The crystallisation was carried out from a 0.1% solution in nitrobenzene at 90–105 °C onto the 001 planes of NaCl and KCl crystals. Lamellar crystals with a rod-like morphology are formed in both cases (according to electron microscope data). Electron diffraction patterns have shown that more perfect crystals are formed on the KCl support than on the NaCl support, although their size is greater in the latter case.

The differences are explained by the unequal concentrations of specific defects on the surface of the support, which are the nucleation sites. The above copolymer crystallises as the orthorhombic β phase, which has been confirmed by electron diffraction data. The reflections have been indexed as *0kl*, which implies that the *bc* plane of the cell grows parallel to the plane of the support.

The studies of the influence of the conditions of the synthesis of PVDF on its crystallographic and conformational characteristics must be analysed in the light of the data considered. In one of the early studies,[52] the characteristics of the polymer obtained for different methods of initiating the polymerisation of VDF were compared. It was shown that the change from chemical to radiation-induced initiation is accompanied by a transition from the β phase crystals to those of the weakly ordered α phase. It was observed later that the decisive factor in the formation of a particular polymorphic modification is nevertheless the medium and not the initiation method.[53] Indeed, whereas the radiation-induced initiation in the gas phase is characterised by the formation of the relatively imperfect α phase, the transition in an aqueous medium is accompanied by the appearance of β crystals, i.e. the 'planar zigzag' conformation of the chain proves to be more favourable for the chain in a polar condensed medium in which the polymerisation takes place.

The study of the influence of the initiation method on the nature of the morphology of the films obtained on crystallisation from solution of the polymerisation products has shown that, regardless of the molecular mass of the polymer, chemical initiation always results in the formation of spherulites with an average size of 1–12 μm.[53] On radiation-induced initiation, the spherulites are formed in the film only for molecular masses below 2×10^5. With increase in molecular mass, dendritic crystals appear initially and then atructures of the 'shish-kebab' type. PVDF obtained by the radiation-induced cross-linking has been characterised in greater detail by Doll and Lando.[54] Analysis showed that the polymerisation conditions do not affect significantly the number of 'head to head' defects, which varied in the range from 6.8% to 9.7%, but may be reflected appreciably in the molecular mass of the chain formed. For example, the radiation polymerisation of VDF in acetone is accompanied by an appreciable decrease in the intrinsic viscosity of the product compared with that of the commercial polymer obtained by suspension polymerisation. At the same time, this leads to an increase in the melting point of the former by 15–17°.

Polymerisation in dimethylacetamide, dimethylformamide, and dimethyl sulfoxide is accompanied by the crystallisation of the polymer with the 'planar zigzag' conformation (β phase), but the polymers are distinguished by instability and are degraded on heat treatment. Polymerisation in fluorine-containing solvents (trifluoroacetic acid, etc.) leads to a high-molecular-mass product, which may ensure the formation of a well oriented state under the conditions of uniaxial stretching. Fairly unusual properties have been reported for PVDF obtained by a special type of polymerisation ensuring single additions of the repeat units to the chain.[55] The polymer obtained exhibits a weak absorption of water and has enhanced electrical parameters (specific volume resistance, breakdown potential, etc.) The effective electret characteristics of the films obtained from the above polymer are also included among its quite unusual properties (admittedly these were not subsequently confirmed by any investigator). Thus it has been noted that the electret charge (with a surface density of 10–20 CGSE charge units per cm^2) may be retained for ten years and does not require preliminary protection by 'short circuiting' the charged surfaces. The electret charge is also more resistant to the effect of temperature and various media (air, oil, solvents).

Certain properties of polymer with a reduced number of 'head to head' defects in the chains (2.7%–3.2%) have been reported.[56] New types of initiators and catalysts (for example, Ziegler–Natta catalysts) were employed in this investigation. Comparison of the characteristics of this polymer and those of commercial PVDF (having 6% of irregular attachments) showed that the extinction of the absorption bands characteristic of the different polymorphic modifications of the polymer varies in the sequence $\alpha > \beta > \gamma$, whereas for the commercial product it varies in the sequence $\alpha < \beta < \gamma$. According to the results of Liepins et al.,[56] the crystallisation of the new polymer from hot dimethylformamide results in the formation of crystals of the α phase‡ whilst the crystallisation of the commercial PVDF affords crystals of the β phase. Thus, when the concentration of the chemical irregularities along the PVDF chain is reduced, the $TGT\bar{G}$ conformation becomes energetically more favourable than the $T_3GT_3\bar{G}$ or 'planar zigzag' conformation.

In a number of studies,[57–61] attention was concentrated on the investigation of the influence of the end groups in the PVDF chains on the properties of the polymer, including its properties in the block state. It was noted that the radical polymerisation of VDF in an aqueous medium under the influence of two different initiators — potassium persulfate (PPS) and β-hydroxyethyl *tert*-butyl peroxide (HETBP) — is accompanied by a significant change in the properties of the polymer obtained. When PPS was used, the number of volatile substances in the latter proved to be higher by an order of magnitude,[58] which was manifested by a reduced thermal stability of the polymer.[59] The results obtained by analytical methods, including isotope analysis,[61] showed that CH_3 end groups predominate in polymerisation with participation of HETBP, whereas in polymerisation involving PPS there is a possibility of the formation of hydroxy-groups at the ends. In the version involving the addition of $\sim CH_2-CF_2-OH$ groups, the latter prove to be unstable and there is a possibility of dehydrofluorination reactions with elimination of HF in accordance with the mechanism $\sim CF_2-OH \rightarrow HF + \sim CF=O$.[59] The thermal stability and the electrophysical characteristics of the polymer are impaired under these conditions. According to the ideas developed,[59] this difference in the macroproperties can be explained precisely by the type of end groups, since other characteristics of the microstructure hardly differed in the two polymers (the number of irregular attachments, the molecular mass of the chain).

The difference between the end groups in PVDF noted above can be manifested also in finer details on the formation of the polymer by crystallisation from the melt. It has been shown[62] that, in the isothermal crystallisation of polymers under identical conditions, the spherulites formed for PVDF with PPS proved more perfect and were larger than for PVDF with HETBP. Under the conditions of nonisothermal crystallisation in PVDF with PPS, only 'normal' spherulites were formed, whereas for the other initiator it was possible to find also 'anomalous' spherulites, differing from the former in the way in which the lamellae were packed along the spherulite radius. Films based on PVDE with HETBP, obtained on rapid nonisothermal crystallisation,may involve the formation of spherulites with a bimodal size distribution, in contrast to the films based on PVDE with PPS. The difference between the end groups and hence between the morphologies of the films affected indirectly also the characteristics of the molecular mobility in the nonordered phase in the vitrification region.[62] Whereas the average relaxation times differed only slightly in the two polymers, this could not be said of either the form of the relaxation time distribution curve or of the magnitude of the total dielectric absorption.

Several investigations touched upon the question of the influence of the polymerisation temperature on the properties of the polymer obtained. Thus, according to the data of Madorskaya et al.,[63] for the copolymerisation of VDF with TEF, an increase in the synthesis temperature from 303 to 373 K gives rise to a tendency towards an increase in the number of 'head to head' defects (from 3.5% to 4.7%)§ for an approximately similar molecular mass of the chain. This leads to a small decrease in the equilibrium melting point and the enthalpy of fusion and to an almost two fold increase in the half-crystallisation time. An increase in polymerisation temperature leads to an increase not only in the number of chemical irregularities in the chain but also in the number of branches in them. For another VDF copolymer (with fluorovinyl ether), an increase in emulsion polymerisation temperature leads to even more striking charges: whereas at low synthesis temperatures the copolymer is characterised by a unimodal molecular mass distribution, at high temperatures it has a bimodal distribution. It is concluded that an increase in the synthesis temperature increases the low-molecular-mass fraction. The study of various factors influencing the microstructure of the VDF homopolymer with the aid of gel-permeation chromatography, electron microscopy, and sedimentation analysis showed that the kinetic parameters of the polymerisation process, the molecular mass distribution, and the dimensions of the latex particles depend primarily on the presence of the emulsifying

‡ In this and all other casts where one is dealing with crystallisation from a solution in hot dimethylformamide of a VDF/TFE copolymer, one should note that the process is accompanied by dehydrofluorination reactions with formation in the chain of new functional group of the type $-CH=CF-$, $CH=CF_2$, $C=O$.

§ Cais and Soane[64] also arrived at the same conclusion in the analysis of the NMR spectra of two types of PVDF with different numbers of chemical irregularities in the chain.

agent in the reaction medium. The polymer synthesised in the presence of the latter is linear, in contrast to the randomly branched polymer formed in a system without an emulsifying agent.[65]

III. The influence of various factors on the polymorphism of poly(vinylidene fluoride) in the isotropic state

For the practical use of PVDF, for example in sensors of different kinds,[3] the choice of crystallisation conditions which would ensure the formation of the required polymorphic modification is important. It was shown above that this can be achieved by selecting a suitable solvent in crystallisation from solution. In the present section, attention is concentrated on the analysis of the characteristics of crystallisation from the melt (at not very high pressures) with emphasis on the discovery of the role of defects in the chemical attachment of units to the chain and on the previous thermal history of the specimen being crystallised.

Doll and Lando devoted several of their studies of the polymorphism in PVDF[36,37,66-70] to the discovery of the influence of 'head to head' type defects (HHTT) on the characteristic features of its crystallisation. The fraction of the above defects was varied by copolymerisation with TFE or TrFE. It was shown that the VDF/TFE 93/7 copolymer is in the polymorphic β modification even in the isotropic state on crystallisation from the melt, whereas the homopolymer always constitutes the α phase under the same crystallisation conditions. Here it is evidently necessary to emphasise the special role of the TFE comonomer, since the VDF/TrFE 91/9 copolymer still crystallises, like the homopolymer, in the form of the α phase. Different workers attribute this to the easier cocrystallisation of the CF_2CF_2 groups with similar groups in PVDF, where the latter also enter into the composition of the usual chemical irregularities of the homopolymer chains. Tables 5 and 6 present the interplanar spacings *d* and the indexing of the reflections for the **b** phases of the homopolymer and the VDF/TFE 93/7 copolymer. The tables show that the spacings *d*, in particular for the intermolecular reflection 200, differ appreciably in these phases.

Table 7 presents the unit cell parameters for PVDF and three of its copolymers. Evidently the introduction of the TFE comonomer into the chain leads to an appreciable loosening of the lattice in the basal plane precisely for the β phase.

The equilibrium packing density in the crystal depends on the number of the defects noted above, so that one may expect also their influence on the kinetic parameters of the crystallisation. This influence has been studied in detail in the crystallisation of the α phase.[71-73] The kinetics of the crystallisation of a large number of PVDF specimens differing both in the number of 'head to head' defects and in the molecular mass have been investigated.[74] The fraction of the former was varied in the range 3.3%–6.1%, while the molecular mass was varied by more than an order of magnitude from 52 000 to 703 000. Differential scanning calorimetric (DSC) data were interpreted in terms of the Hoffman–Weeks relation in the model with nucleation on folded chains. The following relation is valid for this model:

$$T = T_0\left(1 - \frac{2\sigma_e}{\Delta H_f l}\right), \quad (1)$$

where T is the experimentally measured melting point, T_0 the equilibrium melting point for a perfect crystal with an infinite thickness, σ_e the free energy of the 'fold surface' of the nucleus, ΔH_f the heat of fusion per unit volume of the crystal, and l the thickness of the lamella.

One of the tasks in the study by Chen and Frank[74] was to elucidate the question of the location of the 'head to head' defects, namely whether they enter into the composition of the lamella or are displaced on crystallisation into the interlamellar region. Evidently, the former is valid, since the thermodynamic stability of the crystallites decreases with increase in the fraction of the above defects. For a hypothetical defect-free specimen, $T_0 = 481.3$ K is obtained. It has been noted that the linearity of the T–fraction of HHTT relation agrees with the prediction based on Flory's theory[75] and on the Sanchez model[76] if it is assumed that the 'head to head' defect can be regarded as a comonomer unit. The degrees of crystallinity calculated from the heats of fusion on the assumption that $\Delta H_f = 1570$ cal mol^{-1} also decrease linearly with increase in the fraction of the defects. The degrees of crystallinity based on DSC data, corrected by the linear dependence of ΔH_f on the fraction of defects, agree very well with the degrees of crystallinity obtained from density data. The degree of crystallinity of a specimen free of the above defects, found by extrapolation, is 82.5%. The study of PVDF specimens with approximately the same number of irregular junctions but differing in molecular mass has led to the conclusion that the degree of crystallinity may depend also on the molecular mass, other conditions being equal.

The above experimental facts, indicating the influence of the HHTT type defects on the nature of the packing of the chains in

Table 5. Indexing of the reflections and the corresponding interplanar spacings for the PVDF β phase in the form of oriented fibres.[36]

hkl	*d*/Å (experiment)	*hkl*	*d*/Å (experiment)
110	4.24	600	1.41
200	4.24	121	1.36
001	2.56	511	1.36
020	2.45	530	1.36
310	2.45	002	1.28
111	2.19	040	1.24
201	2.19	112	1.24
220	2.13	202	1.24
400	2.13	331	1.24
021	1.77	601	1.24
221	1.64	240	1.18
401	1.64	530	1.18
330	1.41		

Table 6. Indexing of the reflections for the isotropic specimens of the β phase of the VDF/TFE 93/7 copolymer.[36]

hkl	*d*/Å (experiment)	*hkl*	*d*/Å (experiment)
200	4.42	021	1.78
001	2.55	221	1.67
310	2.50	401	1.67
020	2.20	420	1.67
111	2.20	510	1.49
201	2.20	600	1.21
400	2.20	112	1.21
311	1.81	240	1.21
		520	1.21

Table 7. The lattice constants for PVDF and its copolymers.[36]

Composition	Phase	Unit cell parameter /Å		
		a	*b*	*c*
PVDF	α	9.63	5.02	4.62
PVDF/PTrFE 91/9	α	9.59	4.98	4.66
PVDF	β	8.47	4.90	2.56
PVDF/PTFE 93/7	β	8.85	5.00	2.55
PVDF/PTFE 83/17	β	8.84	5.03	2.54

the lattice, initiated the development of studies on the theoretical justification of the above phenomenon. For this purpose, the nature of the variation of the potential energy of both isolated PVDF chains and of block PVDF as the number of defects in the HHTT form or in the form of the TFE comonomer is varied was analysed in detail.[77] For an isolated chain having the $TGT\bar{G}$ conformation, an increase in the number of defects of both types leads to a linear increase in the potential energy. For an isolated chain in the 'planar zigzag' conformation, the potential energy also increases linearly with increase in the number of defects in the form of the TFE comonomer, whereas for the HHTT defects it diminishes. Therefore the potential energy of an isolated PVDF chain with the 'planar zigzag' conformation and a content of HHTT defects in excess of 10% also proves to be lower than for a chain with the *TGTG* conformation (in contrast to defect-free chains). However, the use only of data on intramolecular interactions (isolated chain) can give rise to serious errors in the conclusions concerning the influence of the number of defects on the properties of a real block polymer, since it is obligatory to take into account also the change in the nature of the packing (intermolecular interactions). For PVDF with 5% of type HHTT defects, it has been shown that some increase in the potential energy minimum is observed for both forms of the polymer. More complete data are presented in Table 8.

Evidently the introduction of 5% of HHTT defects into the chain has a more significant influence on the intermolecular component of the energy. Comparison of the nature of the change in the total energy for the β and α phases in the monoclinic system (usually adopted by the majority of investigators) has shown that the changes are greater in the former case. This agrees qualitatively with the conclusion that the loosening of the α phase lattice is less marked compared with the β phase when comonomers are introduced into the PVDF chain (Table 7).

In order to develop their concept, Chen and Frank[74] investigated the influence of the concentration of the HHTT defects on the characteristics of the solid-phase $\alpha \rightarrow \gamma$ transformation. We shall consider the principal features (based on the data of different investigators) of this transformation. Ishida and coworkers and Prest and Luca[78-80] should apparently be regarded as the first to report the possibility of this process, their papers being published at approximately the same time. In the study of the annealing defects in PVDF, it was shown[78] that the γ phase, or more precisely its further two modifications, appear during high-temperature annealing in the α phase of PVDF specimens crystallised from the melt.[79] The above phases were identified from specific absorption bands: these are the 530, 767, 796, and 855 cm^{-1} bands for the α phase and the 510, 779, 809, and 833 cm^{-1} bands for the γ phase (Table 1). In the general case, three melting endotherms were observed on the DSC curves, one of which is presented in Fig. 4. It was shown by spectroscopic methods that the lowest-temperature fusion peak (P_3) is associated with the α phase, and that the two peaks at higher temperatures (P_2 and P_1) are associated with the γ phase. It has been suggested that the fraction of the latter be estimated from the ratio of the optical densities of the 510 and 530 cm^{-1} absorption bands:

$$F(\gamma) = \frac{D_{510}}{0.81D_{530} + D_{510}} . \qquad (2)$$

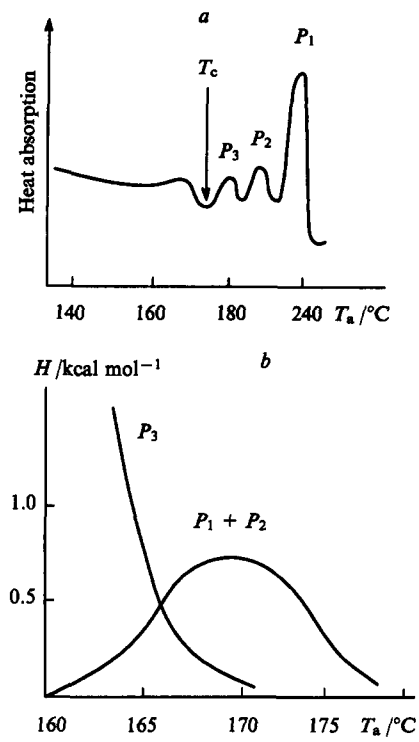


Figure 4. The melting endotherm for PVDF crystallised as the α phase after high-temperature annealing (*a*) and the variation of the ratio of the peaks on the melting endotherm as a function of the annealing temperature (*b*).[79]

Eqn (2) was obtained by interpreting the results of experiments with different film thicknesses. Such experiments made it possible to determine the molar absorption coefficients of the above bands: $K_\alpha = 10 \times 10^3$ and $K_\gamma = 8.1 \times 10^3$ cm^2 mol^{-1}. The variation of the fractions of the α and γ phases as a function of the annealing temperature T_a is illustrated in Fig. 4*b*. Evidently in the range $T_a = 160-170$ °C the fraction of the former phase decreases sharply, whilst that of the second increases appreciably. This has been attributed to the occurrence of the high-temperature solid-state transformation $\alpha \rightarrow \gamma$. The equilibrium melting points of the α and γ phases, found with the aid of the Hoffman–Weeks relations, are 188 and 218 °C respectively. Prest and Luca[80] investigated the high-temperature crystallisation of PVDF, the morphology of the PVDF being studied together with the phase analysis. According to their data,[80] the melting endotherm is also characterised by three fusion peaks, but (in contrast to the paper by Osaki and Ishida[79]) the peak with the intermediate temperature is assigned to the fusion of the β phase. The morphology of the specimen is characterised by the presence of spherulites with negative birefringence (Δ*n*) and a bimodal size distribution. The largest spherulites (with a high Δ*n*) are attributed to the α phase, whilst the small ones (with a low Δ*n*) are attributed to the β phase. The γ phase crystals produce structures which give rise to a specific pattern in crossed polarisers, called by Prest and Luca[80] a 'wagon wheel', and not a Maltese cross.

Table 8. The energies of two polymorphic modifications of PVDF with and without allowance for type HHTT defects.[77]

Modification of PVDF	β Phase			Monoclinic α phase			Triclinic α phase		
	I	II	III	I	II	III	I	II	III
Without HHTT	−16.4	−64.5	−80.9	−21.6	−57.7	−79.3	−21.6	−63.9	−85.5
With 5% of HHTT	−16.6	−58.6	−75.2	−19.5	−56.5	−76	−19.5	−56.3	−76.4

Note. The following designations have been adopted for the energy (kcal mol^{-1}): I — intramolecular; II — intermolecular; III — total.

Somewhat later, the same investigators concluded[81] that the acceleration of the crystallisation process in the $\alpha \rightarrow \gamma$ transformation may be ensured by introducing surface-active additives. The tentative mechanism of their action is believed to be associated with the fact that, on fusion of the α phase, the molecules of the additives retard the diffusion of the chains in the melt and hence increase the probability of the stabilisation of the fluctuation nuclei of the γ phase. These questions were investigated in greatest detail in a series of studies.[82-85] Their authors observed three types of spherulites depending on the crystallisation temperature T_c. For low T_c (< 150 °C), spherulites with the α phase are produced, whilst at higher T_c the so called mixed spherulites are formed where large spherulites of the α phase and small spherulites of the γ phase coexist. The latter have a low Δn owing to the poor regularity of the arrangement of the lamella along the spherulite radius. For still higher T_c, spherulites of the pure phase are formed. As in the study of Prest and Luca,[80] they are characterised by the 'wagon wheel' scattering figure. A general feature has been noted for the two types of PVDF: for low T_c, the α spherulites grow faster than the mixed ones, whereas for higher T_c the mixed spherulites actually increase faster than the α spherulites. It is concluded that the solid-state transformation $\alpha \rightarrow \gamma$ begins in mixed spherulites at the boundaries of coexistence of the α and γ phases. The latter grows in the direction opposite to that of the growth of the α phase spherulite. It was shown that the rate of the transition $\alpha \rightarrow \gamma$ along the spherulite radius is much higher than in the tangential direction.

The questions concerning the possible degradation of the polymer and the high crystallisation temperatures necessary for the $\alpha \rightarrow \gamma$ transition have been examined.[85] Attention was drawn to the fact that the specimens crystallised under the conditions mentioned above (high temperatures and long times) have a yellowish colour. It is believed that thermal degradation reactions may occur under these conditions together with the transformations $\alpha \rightarrow \gamma$. The colouring of the specimens is heterogeneous in character, since the colour centres are mainly located in the regions of the γ phase formed. It has been suggested that the chains in this phase have an increased intramolecular energy. In stressed chains of this kind, the occurrence of dehydrofluorination reactions with formation of $CH=C-CH=CF$ groups, responsible for the appearance of the colour, is more likely at high temperatures.[85] The mechanism of the parallel occurrence of the thermal degradation reactions can apparently be also more complex if account is taken of data on the characteristics of the dynamics in PVDF.

As in the above studies,[80-85] Kochervinskii et al.[62] observed two types of spherulites, which differed in the magnitude of the Δn and in the average size, on high-temperature nonisothermal crystallisation of two types of the homopolymer (with different end groups). On the basis of the results of the analysis of the form of the absorption bands for the symmetrical and antisymmetrical stretching vibrations of the methylene groups, the small spherulites were attributed to the γ phase.[62] Attention was drawn to the fact that the PVDF obtained by suspension polymerisation (PVDF-S) exhibits, under identical crystallisation conditions, a higher degree of the $\alpha \rightarrow \gamma$ transformation and a more intense colour than the PVDF obtained by emulsion polymerisation (PVDF-E). This means that the thermal degradation reactions should occur more vigorously for PVDF-S. The relaxation times of the cooperative forms of motion in the noncrystalline regions, extrapolated to the region of the crystallisation temperatures for PVDF-S, proved to be several orders of magnitude shorter than in PVDF-E. Since the amorphous sections in the crystallising polymers may be 'weak' sites in the thermal degradation reactions, the probability of such processes should be higher precisely in PVDF-S, where the average relaxation time is shorter (the frequency of the reorientations of the segments of the amorphous phase is higher). One may postulate that the higher degree of the $\alpha \rightarrow \gamma$ transformation noted in PVDF-S can be explained precisely by the characteristic features of its dynamics in the nonordered regions of the polymer. Indeed, the packing density of the γ phase lattice is higher than that of the α phase lattice. The polymorphic transformations $\alpha \rightarrow \gamma$ should therefore be accompanied by an increase in the free volume, which is naturally located in the interlamellar regions. Since the relaxation times of the chains of the amorphous phase are inversely proportional to the fraction of the free volume, there should in fact be shorter relaxation times in PVDF-S, which has been confirmed experimentally.[62]

Conclusions similar to those examined above have been obtained also in a study[86] where the crystallisation in the temperature range 151-161 °C was also accompanied by the formation of spherulites of two types. The DSC curves reached in this study are qualitatively similar to those presented by Osaki and Ishida[79] (Fig. 4). Morra and Stein[86] also observed three fusion peaks but only the P_2 and P_1 peaks were attributed to the fusion of the γ and γ' phases respectively. It was postulated that the first phase is formed on crystallisation, whilst the second is produced as a result of the transformation $\alpha \rightarrow \gamma$. It is assumed that the formation of the α phase is kinetically favourable, whilst that of the γ phase is favoured by thermodynamic factors. On the one hand, it is concluded that the γ and γ' modifications are crystallographically identical but differ markedly morphologically. On the other hand, the α and γ' modifications have identical morphologies but are crystallographically completely different.

In experiments with wide variation of the molecular masses of PVDF and the type HHTT defects, an attempt was made[87] to discover the characteristic features of the influence of the latter on the polymorphic transformations $\alpha \rightarrow \gamma$.The dependence of the degree of transformations $\alpha \rightarrow \gamma$ on the content γ of phase spherulites was found from DSC data. According to the authors,[87] the observed linear relation confirms the conclusion that the polymorphic transition $\alpha \rightarrow \gamma$ occurs mainly along the boundaries of the coexisting phases. The influence of the concentration of the HHTT defects both on the fraction of the interlamellar amorphous phase and on the content of γ spherulites was considered for PVDF specimens crystallised at 433 K in the course of 24 h. In the first case, the increase in irregularities increases sharply the fraction of amorphous regions. In the second case, it was concluded that an increase in the fraction of chemical irregularities in the PVDF chain should be reflected in a complex manner in the degree of polymorphic transformations $\alpha \rightarrow \gamma$. This conclusion is due to the fact that the fractions of the amorphous interlamellar phase and of γ spherulites have opposite effects on the degree of the $\alpha \rightarrow \gamma$ transformation.

Thus the experimental data indicate the possibility of the high-temperature polymorphic transformation $\alpha \rightarrow \gamma$. In a series of studies,[88-90] this transition was predicted theoretically — by calculating the free energy of the PVDF chain in various conformations.

A number of studies[91-97] have dealt with questions concerning the detailed specification of the conformational rearrangements in PVDF chains in the transition mentioned above. The authors began with the concept that regions of conformational disorder arise (the presence of kink bonds), a confirmation of which was found in the consistent blurring of the 02 ξ reflections.[92] Fig. 5 presents the detailed pattern of the changes in the chain conformation for α phase crystals in the region of the formation of 'kink' defects, where sections of the chain in the $TG\bar{T}\bar{G}$ conformation alternate with bonds in the 'planar zigzag' conformation, the number of which may be even or odd. Model studies on different versions of the formation of kink bonds led to the conclusion that the formation of kinks with an odd number of monomer units is more probable. The best agreement with experiment occurs if it is assumed that the kink contains one monomer unit (two neighbouring bonds in the TT position). For its formation, it is necessary to postulate the transition $TG\bar{T}\bar{G} \rightarrow \bar{T}\bar{G}TG$, which takes place as a result of a 'flip-flop' type of movement with subsequent transition from G or $\bar{G}$ to T. It is emphasised that the first stage of this transition is decisive.

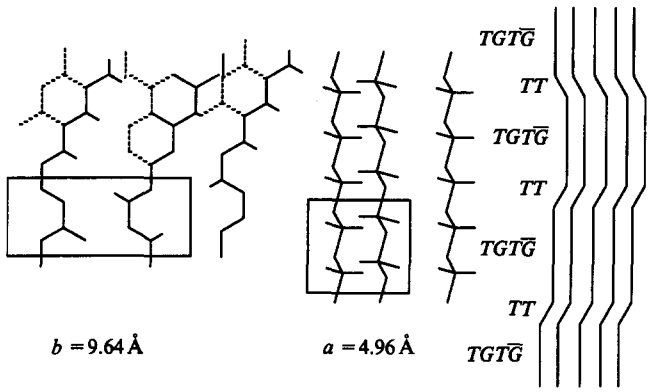


Figure 5. Schematic illustration of the formation of kink bonds in the α modification of PVDF.[97]

Overall, the nature of the transition should be distinguished by its cooperativeness.

According to Lovinger's conclusions,[98] 'flip-flop' movements with participation of three bonds are more favourable than movements involving five–seven bonds. This means that the conformational rearrangement in the transition must proceed via a two-stage mechanism. An intermediate state (with a low potential energy) is formed in the first stage in accordance with the scheme

$$TG\bar{T}GTG\bar{T} \longrightarrow TGTTTTG\bar{T} \longrightarrow TTTGTTTG\bar{T}.$$

The second stage involves the formation of the polar lattice of the γ phase, which should be accompanied by the reorientation of each second chain of the cell, which may occur as a result of the inverse movements of the chain with the altered conformation (Fig. 6 *b*).[97]

We shall now deal with the analysis of a series of results obtained in the study of the formation of the isotropic ferroelectric β phase of the pure VDF homopolymer on crystallisation from the melt in accordance with a definite regime.

The appearance of β crystals on quenching thin (~100 nm) films of the PVDF melt in a medium with liquid nitrogen, melting ice, or even in water at room temperature was reported by Hsu and Geil .[99] It is emphasised that a significant factor in this process is the film thickness. For example, for a film μm thick, β crystals are formed only in the surface, whereas α crystallites are produced in the bulk phase. Later the same workers investigated this phenomenon in greater detail.[100] They varied the temperature of the quenching agent more widely and the results of electron diffraction were supplemented by the results of the study of the morphology of the films formed on quenching. According to data obtained by transmission electron microscopy, the most homogeneous structure is obtained in films quenched in liquid isopentane. At quenching temperatures of 136 and 273 K, inhomogeneous 20–30 nm sections are seen. At a quenching temperature of 288 K, it is possible to see the appearance of individual fibrils with a transverse dimension of 25 nm and a length up to several hundreds of nanometers. An increase in the quenching temperature to 313 K complicated the morphology somewhat, but crystals of the β phase are formed in all cases. The possibility of obtaining the latter at fairly high quenching temperatures has been confirmed also by other workers.[101,102] In these studies the 'planar zigzag' conformations, detected from the 470, 510, 840, and 1280 cm^{-1} absorption bands, were noted for films at a quenching temperature of 303 K. An increase in temperature to 358 K leads to the formation of the α and γ phases together with the β crystals, the size and perfection of the α and γ crystals increasing with increase in the quenching temperature.[100] The morphology of the films becomes more complicated: together with fibrils, structures of incomplete spherulites appear.

Similar results were obtained also in another study, where type KF200 PVDF films 10–15 μm thick were quenched from the melt in melting ice. The appearance of absorption bands at 442, 470, and 510 cm^{-1}, characteristic of the 'planar zigzag', was also noted in the IR spectra of the quenched films. However, it is significant that the conformers obtained apparently serve as nuclei in the subsequent annealing, since the intensity of the above band increases. The results of X-ray studies have shown that the annealing is accompanied by the improvement of the β phase crystals, since the narrowing of the main intermolecular 100, 200 reflection is observed.

Figures 7 and 8 illustrate the scheme which explains the appearance of β crystals on crystallisation under the conditions of rapid quenching. It is postulated that the rate of nucleation is characterised by a distribution curve, the rate maximum for the α phase being displaced towards higher temperatures compared with that for the β phase (Fig. 7). The time taken to traverse the $T_3 - T_4$ (t_α) temperature range depends on the rate of cooling of the melt (Fig. 8). Then the rate of cooling is high, t_α proves to be low and there is insufficient time for the formation of the nuclei of the α phase. Since the maximum in the rate of nucleation for the β phase is displaced towards lower temperatures, the time taken to traverse the temperature range $T_1 - T_2$ is longer and may be sufficient for the formation of β crystals. Estimates[103] have shown that such crystals may be formed at rates > 800 K s^{-1}. The above hypothesis has been confirmed also by the results of thermal analysis.[104,105] An increase in the rate of cooling of the melt of the VDF homopolymer creates a tendency towards a displacement of the main crystallisation peak towards lower temperatures, whilst quenching in liquid nitrogen leads to its shift into the region of temperatures actually below 300 K.

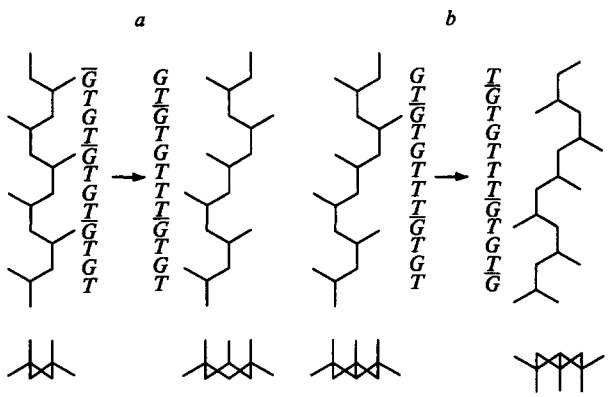


Figure 6. Two modes of molecular motion associated with the solid-state transformation α → γ.
(*a*) Segmental 'flip-flop' motion; (*b*) inverse motion.[97]

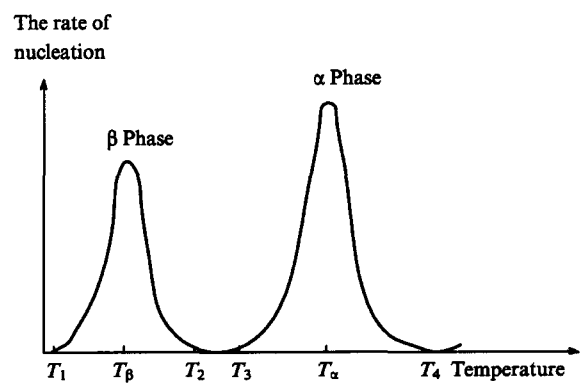


Figure 7. Temperature variation of the rate of nucleation for the α and β phases.[103]

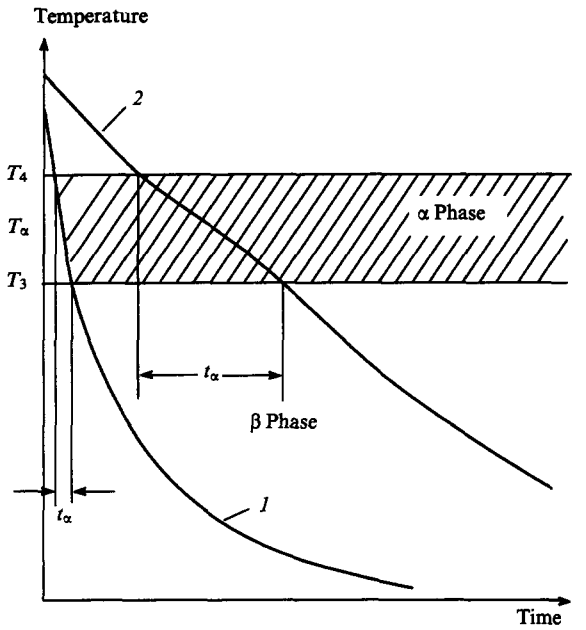


Figure 8. Diagram illustrating the formation of α and β crystallites on rapid (*1*) and slow (*2*) quenching.[103]

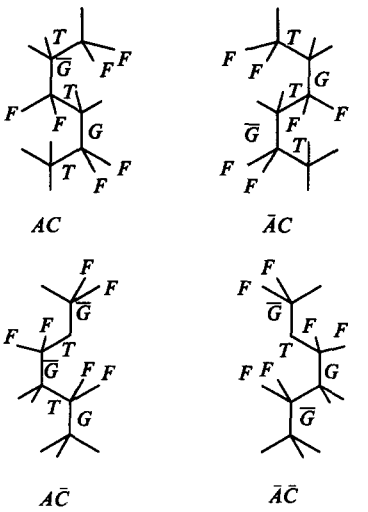


Figure 9. The possible orientations of the chains of the PVDF α phase in the $TGT\bar{G}$ conformation.[105]

Under real experimental conditions (fairly thick specimens and not unduly high rates of cooling), nuclei of both phases are apparently formed, although their fraction in the α modification may in fact be low. This is confirmed by the fact that, together with the bands due to the β phase, there are a further two bands (612 and 765 cm^{-1}) characteristic of the $TGT\bar{G}$ conformations.[103] Analysis of the X-ray diffraction profile indicates that there are few nuclei of the α phase and they do not attain large sizes, since reflections characteristic of the α phase have not been noted. Annealing of the quenched specimens leads to an increase in the number of $TGT\bar{G}$ conformers, since the intensity of the above bands increases. The possible structure of such defective regions of the α phase has been examined on the basis of the results of thermal analysis.[104, 105] It was noted that, on rapid cooling of the melt ($\geqslant$ 10 K min^{-1}) of the VDF homopolymer, an additional endotherm appears on the DSC curves in the range 320–350 K of the kind not observed for specimens obtained at low rates of cooling.[105] The appearance of this endotherm had been attributed to the existence of conformational disorder in the imperfect crystals of the α phase (condis-crystal). In terms of Takahashi's concept,[106] when the PVDF chains have the same $TGT\bar{G}$ conformation, they may assume four possible orientations under the conditions of nonequilibrium crystallisation temperatures (Fig. 9) — *AC*, $\bar{A}C$, $A\bar{C}$, and $\bar{A}\bar{C}$. Evidently the fluorine atoms may be located above ($\bar{C}$) or below (*C*) and to the left ($\bar{A}$) or to the right (*A*) relative to the molecular axis. Since the CF bonds have a high dipole moment, such orientations are characterised by different directions (upwards or downwards) of the axial component of the dipole moment. The transition from the *A* to the $\bar{A}$ orientation is possible as a result of rotation about the *c* axis, while the *C* and $\bar{C}$ states are obtained by the mirror reflection relative to this axis. The transitions between the above orientations, occurring as a result of the movement of the entire chain are impossible because of the very high activation barrier, but they can be achieved as a result of local conformational rearrangements.

The studies, mentioned above, of the influence of the copolymerisation of VDF with TFE and TrFE[67] on the change in the equilibrium polymorphic modification of the homopolymer have greatly developed recently. This was caused by two facts. On the one hand, it was the discovery of ferroelectric properties in PVDF: it was found, in the presence of fairly high contents of the second component, that the ferroelectric–paraelectric transitions in the VDF/TrFE copolymers and fusion proper differ appreciably as regards temperature, which makes it possible to employ this copolymer as a model compound for the study of the mechanism of the appearance of ferroelectric properties in organic polymers. On the other hand, modifications of the materials employed, particularly those with increased piezoelectric constants, were needed for practical purposes. Therefore, when it was shown for a series of VDF/TrFE copolymers[107] that an approximately equimolar component ratio in the copolymer leads to a significant increase in both the electromechanical coupling factor and in the piezoelectric constant *d*, the interest in the study of the structures of the above copolymers increased.

Initially Lovinger et al.[108] demonstrated in relation to the VDF/TrFE 52/48 copolymer that the specimen crystallised from the melt consists of a mixture of two disordered crystalline phases, one of which is characterised by the 'planar zigzag' conformation, whereas the other has the 3/1 helical conformation. The wide variation of the composition of the copolymer made it possible to obtain later more detailed information about its crystal structure.[109] On the basis of the analysis of the results of detailed X-ray diffraction patterns and spectra over a range of temperatures, the authors concluded that the low-temperature phase (LTP), a cooled phase (CP), and a high-temperature phase (HTP) exist in the isotropic state. Comparison of model calculations with experiment showed that the 'planar zigzag' conformation in the LTP should be characterised by a deviation from the plane by an angle 2σ. As for the β phase of the VDF homopolymer,[110, 111] this conclusion follows from the passage of the relative difference between the calculated and observed structure factors (the *R* factor) through a minimum as the angle σ is varied. When such chains are packed in the cell, the following parameters of the low-temperature phase are obtained: monoclinic system, a = 9.12 Å, b = 5.25 Å, c (chain axis) = 2.55 Å, β = 93°, tilt angle (in the 130 plane) = 3°. The scheme of the transitions in the above copolymers[109] shows that the transition from the ordered LTP to the fully disordered HTP proceeds via the formation of the intermediate (cooled) phase CP. The model of the conformational rearrangements in an isolated chain in this transition is illustrated in Fig. 10. An increase in temperature in accompanied by the appearance of 'skew' bonds (*S* and $\bar{S}$ in Fig. 10) for the chain in the 'planar (distorted) zigzag' conformation. A further increase in temperature leads to the appearance of single bonds in the *G* or $\bar{G}$ conformation, which corresponds to the chain conformation in the cooled phase.

The transition from LTP to CP is accompanied by a change in the unit cell parameters (a = 9.16 Å, b = 5.43 Å, c = 2.53 Å, and

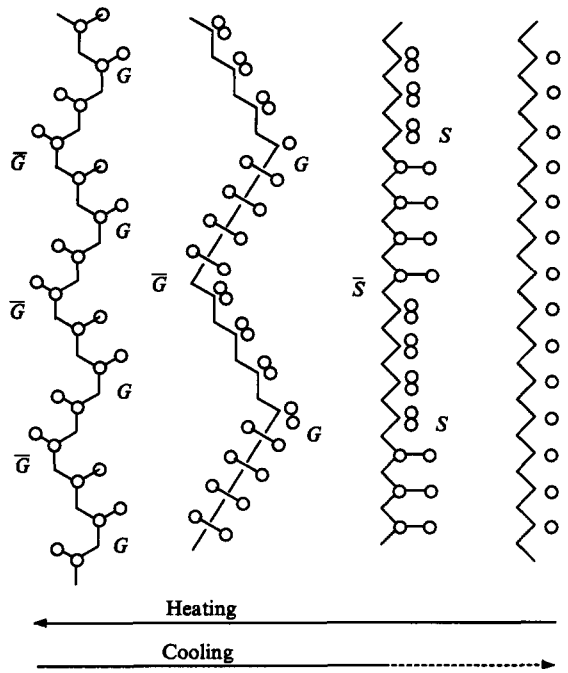


Figure 10. A model of the conformational changes in the single chain of the VDF/TrFE 55/45 copolymer during heating–cooling cycles.[109]

$\beta = 93°$) and an appreciable increase in the tilt angle (in the 130 plane) to 18°. The packing of such chains in the cell of the cooled phase is presented in Fig. 11. This lattice may be considered also in the light of the concept of a crystal with kink bonds. The transition from the cooled phase to the high-temperature phase on further increase in temperature is accompanied by the accumulation of conformational irregularities, which, according to IR spectroscopic data, represent a set of sequences of the type $TG\overline{T}\overline{G}$ and $T_3GT_3\overline{G}$. To a first approximation, the lattice is characterised by hexagonal packing with the parameters $a' = 9.75$ Å and $b' = 5.63$ Å ($a'/b' = \sqrt{3}$). Taking into account these values, the calculated and experimentally observed interplanar spacings d and the structure factors $\sqrt{I}$ for a series of reflections are presented in Table 9.

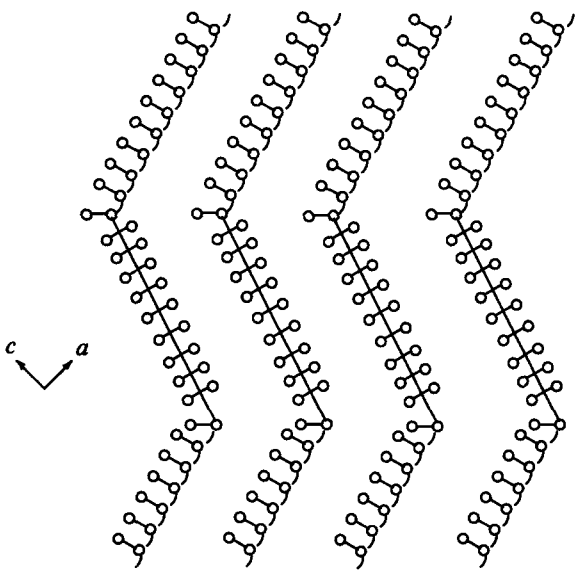


Figure 11. A model of the structure of the crystal of the cooled phase for the VDF/TrFE 55/45 copolymer.[109]

Table 9. Interplanar spacings and structure factors for the reflections due to the high-temperature phase of the VDF/TrFE 55/45 copolymer.[109]

hkl	Calculation		Experiment	
	d/Å	$\sqrt{I}$	d/Å	$\sqrt{I}$
200	4.87	35.4	4.88	38.4
110	4.87			
310	2.81	5.1	2.83	3.2
020	2.81			
400	2.44	3.7	2.44	3.0
220	2.44			
510	1.84	2.2	1.85	1.8
420	1.84			
130	1.84			
600	1.62	(2.2)		
330	1.62			
620	1.41	(0.9)		
040	1.41			

Evidently, there is a satisfactory agreement between the measured and calculated parameters, which confirms the correctness of the chosen lattice. Overall, the lattice is found to be nonpolar and the chains may execute rotational motions with large amplitudes. According to Tashiro et al.,[109] the crystal in this state may resemble one of the varieties of a rotator phase. When the HTP is cooled, the reverse transition of the type HTP → CP takes place and is accompanied by the conformational rearrangements noted above (Fig. 10). The cooling of the CP is not accompanied by the reverse transition to the LTP. In this case, chains with conformations of the type

...*TTTTTTTTTSTTTTTTTTTS̄TTTTTTTTT*...

are found to be frozen.

For the occurrence of the transition from the CP to the LTP, one may deform the specimen or subject it to a strong field.

The attempt to find definite analogies between the formation of the structure on quenching of the above 65/35 copolymer and of the homopolymer yielded a somewhat unusual result.[112] It was found that the ferroelectric–paraelectric transition (according to DSC data) in the quenched copolymer is observed at a higher temperature than in the specimen with slow rate crystallisation. Annealing of the quenched specimen (at 120 and 140 °C) leads to a decrease in the temperature of this transition, although the fraction of the long sequences with the 'planar zigzag' conformation, entering into the composition of the ferroelectric phase, increases under these conditions.

In order to investigate the influence of the polarity of the comonomer in the VDF copolymers on the nature of the crystal structure formed, a study was made of a wide range of VDF copolymers with nonpolar tetrafluoroethene, the fraction of the latter being varied within wide limits (19%–100%).[113] Comparison of the structural data with those for the copolymer of VDF with the polar TrFE comonomer shows that the nature of the phases formed and their interconversions are similar. Admittedly certain nuances were also observed for the 81% VDF content in the VDF/TFE, copolymers. Thus the temperature of the LTP → HTP transition (with a conformational change from *trans*- to *gauche*-) proved to be close to the melting point. In the case of high VDF contents, such transitions become more diffuse and the hysteresis phenomena are weaker than in the VDF/TrFE copolymers.

The crystallisation of the VDF/TFE 94/6 copolymers from the melt (or from solution) always leads to the coexistence of the ferroelectric and paraelectric phases at room temperature. The presence of the former was inferred from the 100, 200 reflection, whilst the presence of the latter was associated with the broadened reflection in the range $2\theta \approx 18°$ (CuK_α radiation).[32] The morphology of the films obtained is characterised by the presence of

spherulites which become small and defective on quenching from the melt [114] or a morphology in the form or aggregates of optically anisotropic rods is established.[48] For crystallisation conditions involving quenching, an unusual phenomenon has been observed — the formation of sections of the α phase, the presence of which was inferred from the appearance of either the weak 021 reflection [114] or of strong intermolecular 020, 110 reflections.[115,116] The latter phase proved to be metastable, since even on heating to 70 °C the above reflections are markedly weakened.[117,118] The crystallisation of the copolymers (predominantly as the polar β phase) is accompanied, according to spectroscopic data,[48,114] by the formation of irregular sequences in the $TGT\bar{G}$ and $T_3GT_3\bar{G}$ conformations, the ratio of which depends on the previous thermal history of the specimen.

The study of Roussel et al.[119] was devoted to the influence of the molecular mass on the kinetics of the crystallisation of PVDF. When the DSC method was employed, the crystallisation kinetics were described in terms of the constants of the Avrami equation. It was noted that the rate of crystallisation was lowest in the case of the PVDF with an intermediate molecular mass. According to the authors, this unusual phenomenon could not be associated with different crystallographic forms, since the specimens were selected taking into account IR spectroscopic data. However, the exponent in the Avrami equation could reach 11. The reason for this is believed to be the fact that the additional type HHTT irregularities in certain specimens may serve as additional nucleation centres. It is believed that the above crystallisation anomalies are bounded on the side of high degrees of supercooling.

The influence of the crystallisation temperature on the possibility of polymorphic transformations in PVDF has been investigated [120] mainly with the aid of a spectroscopic technique. The PVDF produced by the Atochem Company (France) in the form of thin (6 μm) films was crystallised from a concentrated solution in dimethylacetamide. On varying the crystallisation temperature, appreciable changes were observed in the IR spectra, which is explained by crystallisation in the form of different modifications. The presence of the α, β, and γ phases was inferred from the presence in the IR spectrum of the 766, 840, and 510 cm^{-1} bands respectively. The fraction of a particular modification was estimated from their intensities. In particular, it was shown that, on prolonged high-temperature (160–185 °C) crystallisation, predominantly the γ phase is formed. This result agrees qualitatively with earlier data.[78–85] A new feature in the above study [120] is the observation of the influence of the crystallisation temperature on the ratio of the α and β phases in isotropic films. It was shown that a decrease in temperature (from 160 to 50 °C) leads to a significant increase in the fraction of the β phase in its mixture with the α phase for the same (20 min) crystallisation time. This feature is not fortuitous, since a similar relation has been observed also for a solution of PVDF in dimethylformamide. At a fundamental level the observed phenomenon may have a common basis with the α → β transformation in the low-temperature deformation of PVDF.

IV. Characteristics of the solid-state transformations under the conditions of tensile deformations

More than twenty years ago, the ferroelectric properties of PVDF and of its copolymers were unknown, but in the studies of Lando [121] and Gal'perin [122] attention was already drawn to the possibility of the polymorphic transformations α → β on uniaxial stretching of PVDF films. It was shown that a decrease in the temperature of the uniaxial stretching and an increase in the draw ratio promote an increase in the latter. It was noted, in particular, that orientation at low temperatures (< 60 °C) leais to an abrupt α → β trarlsition, which is also accompanied by the formation of microcracks in the matrix. At higher temperatures the transition becomes smoother, i.e. the crystals of the α phase are initially oriented along the draw direction, after which the polymorphic transformation takes place in them. Small angle diffraction has shown that an increase in the draw temperature (T_d) is accompanied, on the one hand, by an increase in the long period, and, on the other, by an increase in the intensity of the small angle reflection. Furthermore, a change has also been noted in the nature of the diffraction patterns: whereas at low T_d the reflection has the form of a vertical line or four points, at high T_d it has the form of two points. Annealing of the oriented PVDF films in the isometric or free state has shown [123] that in the latter case a transition from the fibrillar structure to the lamellar structure, accompanied by a change from the *c*-texture to the *a*-texture, is observed.

For PVDF films with an oriented β phase, the nature of the structural transformations on annealing may depend significantly on the previous history of the specimens. Thus, when an unannealed specimen is heated, shrinkage stresses σ arise in it already at 40 °C, reaching a maximum (~ 1.5 kg mm^{-2}) at 120 °C.[124]

In the specimen (with fixed ends) annealed up to 140 °C, these stresses are insignificant, after which they also increase, although their maximum values are appreciably lower (~0.5 kg mm^{-2}), while the maximum is displaced towards higher temperatures — to ~180 °C. In both cases, the decrease in σ is attributed to the fusion of the β phase crystals, since the intensity of the principal 110, 200 reflections due to the β phase decreases under these conditions (to zero at 189 °C). However, when a specimen with free ends was heated, a sharp fall in the intensity of the above reflection occurred at 166 °C, i.e. for the free state the melting point of the β crystallites is lower by more than 20 °.

An analytical description of the α → β interconversion in PVDF on uniaxial stretching has been formulated in a study [125] the authors of which used the method developed [126] for the estimation of the fraction of the α phase N_2 under the conditions of its coexistence with the β phase. The experimental dependences of N_2 on the draw ratio λ, expressed in semilogarithmic coordinates, are linear, i.e. the following relation holds:

$$N_2 = 1 - \frac{\ln \lambda}{10.8 - 29/RT}, \qquad (3)$$

where 29 kJ mol^{-1} is the potential barrier to the α → β transformation.

Temperature has a significant influence on the effective tensile stress, so that the $N_2 - \sigma$ relation is linear (Fig. 12). Extrapolation of this relation showed that the complete disappearance of the α

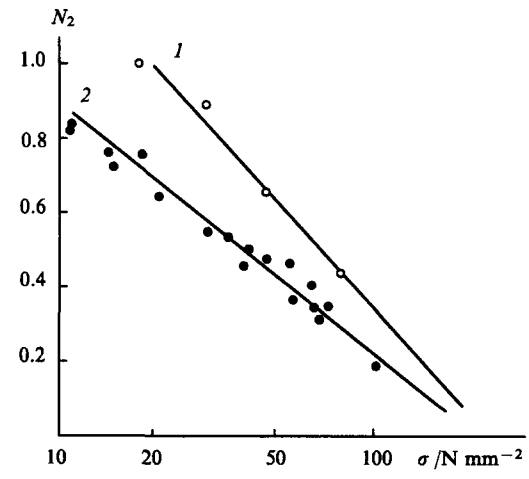


Figure 12. Dependence of the fraction of the α phase (N_2) on the tensile stress in the uniaxial drawing of PVDF before (*1*) and after (*2*) the formation of a neck.[125]

phase requires a stress of 180 N mm^{-1}. Evidently, other conditions being equal, the $\alpha \rightarrow \beta$ transformation takes place more effectively in the region where the material assumes the form of a neck. This conclusion has been confirmed by the data of Matsushige and Takemura,[127] which also showed that the main $\alpha \rightarrow \beta$ transformation on uniaxial stretching begins in the region of deformations where the material assumes the form of a neck. Under the conditions of uniaxial stretching of PVDF, the existence of a critical deformation where intense rotation of the crystals of both modifications begins has been establiahed. For example, the effective rotation in the direction of stretching, for both the newly formed β crystals and for the remaining α crystals, takes place in the range $\lambda = 2-2.5$.[125]

The importance of the role of the tensile stresses in the polymorphic $\alpha \rightarrow \beta$ transformation has been emphasised also in another study.[128] Taking into account the role of temperature as regards the values of σ, the author also showed that the values of σ may be raised by increasing the rate of deformation. For large draw ratios ($\lambda = 7$), the final values of Young's modulus (E) in the PVDF specimens may depend significantly on the previous thermal history of the isotropic specimens crystallised from the melt. Thus it was found that Young's modulus for films with the same value of λ is higher in the case of slow crystallisation of the initial films obtained by quenching. The maximum values of E in the direction of the draw axis are ~4 GPa, whereas along the c axis they are 177 GPa (according to X-ray diffraction data), which is comparable to the theoretical value of 237 GPa for β phase crystals.

It was found with the aid of the dependence of E on λ for films of one kind, obtained at different draw temperatures, that, other conditions being equal, the decrease in T_d leads to an increase in E. This can be explained [in conformity with Eqn (3)] by an increase in the fraction of the β phase, for which E in the direction of the c axis is found to be greater than E for the α phase. However it appears that this is not the only reason. Such doubts arise from the results of studies[129,130] in which uniaxial stretching processes were investigated in specimens of the VDF/TFE 94/6 copolymer. Here it was also found that a decrease in T_d leads to an increase in E (according to the results of acoustic measurements). However, since this copolymer crystallised in isotropic films in the form of the β modification, the polymorphic $\alpha \rightarrow \beta$ transition noted above was absent, as in the homopolymer. For this reason, the increase in E for films with different T_d was attributed to the different microstructures of the noncrystallising regions. In particular, it was shown that in films with a lower T_d the latter are characterised by an increased concentration of chain sections in the 'planar zigzag' conformation, while the packing density in them should be greater, since there is a steady decrease in the intensity of the maximum of the small angle meridional X-ray scattering.

The results of the analysis of the acoustic characteristics indicate that one may expect a high content of stressed chains passing through films with a lower T_d. NMR data for PVDF specimens with different draw ratios agree qualitatively with this conclusion. This can also be inferred from the decrease in the mobility of the 'fast' protons associated with the noncrystallisable chain sections in specimens with larger draw ratios.[131]

The nature of the polymorphic transformation $\alpha \rightarrow \beta$ occurring on uniaxial stretching affects also the morphology being established. Thus the diffraction pattern produced by a laser beam which has passed through a deformed PVDF film, crystallised in the isotropic state with formation of α phase spherulites, has been investigated.[132,133] It was observed that at high T_d there is intense equatorial scattering, which indicates the existence of spherulites deformed in the direction of the draw axis. At low T_d, there exist, together with the latter spherulites also undeformed spherulites with the initial phase, which was inferred from the 'anomalous' eight-lobe dispersion pattern. It is assumed that the mechanism involving the 'retwisting' of the lamellae on deformation plays an important role in spherulites disposed favourably in relation to the direction of action of the external force and that the transition from the α to the β modification may proceed as a result of local fusion and subsequent recrystallisation.[132] As the draw temperature is reduced due to the higher viscosity of the noncrystallising sections, the external stress may be effectively transmitted to the crystallites of the α phase, reaching critical values for the $\alpha \rightarrow \beta$ transition noted above.[133]

For intermediate draw ratios, the 'anomalous' eight-lobe H_v scattering pattern (in crossed polarisers) has been observed also in the polymorphic $\gamma \rightarrow \beta$ transition.[134] An analogy between the $\alpha \rightarrow \beta$ and $\gamma \rightarrow \beta$ transitions was noted, although the required deformation energy for the former is found to be greater than for the latter. Indeed, the complete transformation can be achieved at $T_d = 80$ °C and $\lambda = 4$. On the other hand, in the case of the $\gamma \rightarrow \beta$ polymorphic transition with the same λ, it takes place fully at a draw temperature as high as $T_d = 150$ °C. An unusual feature of the latter transformation is the fact that the appearance of the β phase is noted not immediately after the start of the orientation of the initial crystallite but in the deformation process, where the orientation function reaches 0.25.

In the light of the foregoing, one may conclude that the preparation of PVDF with highly oriented γ phase crystals is by no means a simple task. Indeed, the procedure usually employed, involving the uniaxial stretching of an isotropic film with γ phase crystallites, fails because of the $\gamma \rightarrow \beta$ transformation noted above. In this connection, the results of a study[135] in which a novel method of preparation of such PVDF was proposed are of interest. The scheme reduces to the following features. In the first stage, an isotropic film with α phase crystallites was oriented at 150 °C up to $\lambda = 4-5$ without the polymorphic $\alpha \rightarrow \beta$ transition. In the second stage, the film obtained was polarised in a field with $E = 1$ MV cm^{-1}, after which the crystals of the α phase were converted into the polar α_p form. In the third stage, the film obtained was annealed isometrically at temperatures above 120 °C (it is even better when $T > 170$ °C), after which the formation of the γ phase was observed. The presence of the latter was inferred from the presence of specific absorption bands in the vibrational spectra — at 300, 430, 656, 776, and 813 cm^{-1}.

A method was proposed in the same study for the quantitative estimation of the fraction of the γ phase $\rho(\gamma)$ from the optical densities D of the 410 and 430 cm^{-1} bands. It was found that

$$\rho(\gamma) = \frac{D_{430}}{rD_{410} + D_{430}}, \qquad (4)$$

where $r = K_{430}/K_{410}$, while K_{430} and K_{410} are the molar absorption coefficients for the 430 and 410 cm^{-1} bands respectively, the values of which proved to be similar. The kinetics of the increase in the fraction of the γ phase, calculated by Eqn (4) for different annealing temperatures in the $\alpha_p \rightarrow \gamma$ transition stage, have shown that an increase in the annealing temperature leads not only to an increase in the rate of transformation on the initial section but also increases the equilibrium value of $\rho(\gamma)$.

According to Brillouin scattering data, under the conditions of the uniaxial stretching of PVDF it is possible to estimate the changes in its nonordered regions.[136] Thus a significant increase in the velocity of ultrarsound V_S in the direction of the draw axis with increase in λ has been observed. The ultrasonic wavelength is ~10^3 Å, while the side of the crystallite is ~10 Å, so that the orientation function determined should characterise the rotations of the chains both in the crystal and the amorphous phase. The velocity of ultrasound can be estimate from the following relation:

$$V_S \approx \left(\frac{E}{\rho}\right)^{1/2},$$

where ρ is the density. The increase in V_S with increase in ρ during the drawing process was attributed by the authors to a more significant increase in Young's modulus. Comparison of the values of E for the crystals of the α and β phases shows that an increase in Young's modulus during drawing cannot be attributed

solely to the polymorphic transition $\alpha \rightarrow \beta$ and account must be taken of the possibility of the partial additional crystallisation of the chains in the amorphous phase.

In order to investigate in greater detail the mechanism of the polymorphic transformation $\alpha \rightarrow \beta$ on uniaxial stretching, the changes in a series of physical characteristics were followed in oriented PVDF films where the initial polymers differed both in the number-average molecular mass $M_{\bar{n}}$ and by in polydispersity factor $M_w M_{\bar{n}}$. In particular, it was shown that higher values of Young's modulus (~6 GPa) are more likely to be obtained on uniaxial stretching on a polymer the $M_{\bar{n}}$ value for which is lower and that the isotropic specimen should be prepared by slow crystallisation.[137]

The PVDF films used for practical purposes were treated in a high electric field, so that the orientation of the 'polar' *b* axis of the lattice in relation to the plane of the film is very important. The data of Mizuno et al.[138], who carried out structural studies on PVDF films obtained by the double orientation method, merit attention in this connection. It was shown that, for a film subjected to repeated uniaxial restretching in a direction perpendicular to that of the initial stretching ($T_d \leqslant 100$ °C, the initial specimen was quenched), the *b* axis of the cell is in the plane of the film. It was noted that the rolling of a PVDF film subjected to uniaxial stretching and different heat treatment conditions make it possible to obtain textures in which the *b* axis may form angles of 0, 30, and 60° with the plane of the film.

Detailed studies of the morphology in thin and thick PVDF films by electron microscopy, electron diffraction, and X-ray diffraction (large or small angle diffraction) indicate significant differences between the structures of thick films oriented at low (80–90 °C) and high (130–140 °C) temperatures.[139] Approximately 85% of well oriented but highly defective β phase crystals and ~15% of residual virtually unoriented α crystals were observed for the former films in the region of the macroscopic neck (with 280% deformation). The residues of the unoriented α phase are visible even for deformations of ~350%, whereupon the growing neck can reach the ends of the specimen. The long period (in the direction of stretching) is ~10.5 nm, which is less than for the initial specimen (13.0 nm). The ellipsoidal microcracks arising under these conditions are located between the microfibrils. In hot drawing, the $\alpha \rightarrow \beta$ transition proceeds somewhat differently: initially the α phase is transformed into microfibrils and then, after the attainment of critical stresses, the polymorphic transition begins. At both high and low temperatures, the deformation occurred heterogeneously, since the regions of the initial α phase remain even for an elongation of 500%.

For polar polymers with fairly high dielectric losses, it is of interest to employ nontraditional heating sources for the specimen during the drawing process. For example, microwave heating may be employed for this purpose. Drawing with this method of heating in polyoxymethylene specimens leads to appreciable improvements in the elastic characteristics.[140–142] or PVDF, this heating method is of interest for a number of reasons. On the one hand, the increased dielectric losses at high frequencies (at room temperature) provide a basis for effective uniform heating throughout the bulk of the specimen by the energy of the UHF field. On the other hand, the similarity of the frequencies of the electromagnetic field to the average reorientation frequencies of the polar segments in the nonordered phase makes it possible to 'pump' the internal energy precisely into the amorphous regions of the PVDF, which play an important role in the processes involving the deformation of a partly crystalline polymer. The data of a study[143] where a magnetron with a power of 1.2 kW and a working frequency of 2.45 GHz was used for heating of the kind described above merit attention in this connection.

Comparison of the limiting PVDF draw ratios and of the acoustic modulus for traditional and UHF heating of the specimen showed that the use of the latter method does not afford a significant increase in the elastic characteristics compared with the traditional heating of the specimen from an external source. According to the authors, the reason for this is that, in contrast to polyoxymethylene, in PVDF the range of temperatures most favourable for maximum stretching is close to the melting point (Fig. 13). In the range of stretch temperatures 150–160 °C (appreciably below the melting point), UHF heating yields a higher maximum draw ratio and hence the highest acoustic modulus. This feature may be a consequence of the local heating of the amorphous regions of PVDF noted above. We may note that Nakagawa and Amano[143] obtained PVDF specimens with the highest draw ratio (8.6) and acoustic modulus (7.5 GPa).

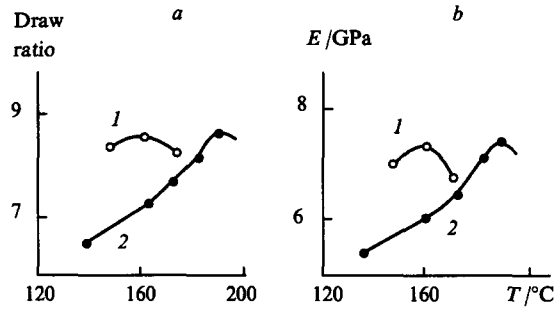


Figure 13. Dependence of the maximum draw ratio (*a*) and the acoustic modulus (*b*) in PVDF specimens on the drawing temperature for HF (*1*) and traditional (*2*) heating.[143]

The influence of the state of the melt on the characteristics of the orientation crystallisation of PVDF has been studied.[144] The initial specimen was subjected to preliminary radiation-induced cross-linking, after which it was melted. Next the specimen was stretched to different values of λ and recrystallised isothermally. The task formulated was to trace the influence of the initial function of the orientation of the chains in the melt and of the density of the cross links in it on the values of the orientation function for the crystallites and the amorphous phase after recrystallisation. On the basis of data obtained by X-ray diffraction and birefringence, it was concluded that in this type of process the *c* axis in the crystal of the α phase formed is disposed along the direction of stretching of the melt, while the chains of the amorphous phase are perpendicular to this direction. It was found that the orientation state of both phases after recrystallisation depends both on the density of the cross links and on the chain orientation function in the amorphous melt, the role of the latter factor being decisive. Here it is also useful to quote the values of the intrinsic birefringence obtained from optical measurements. Thus the intrinsic birefrigence is $\Delta^0_{c,\alpha} = 0.145 \pm 0.002$ for the crystal of the α modification, whereas for the amorphous phase we have $\Delta^0_{\alpha} = 0.098 \pm 0.017$.

The method involving the solid-phase extrusion of polymers, which in many instances yields high orientation characteristics, occupies a definite place in film technology. In this connection, one should mention a series of studies[145–147] in which this technique was used to obtain oriented PVDF films. The extrusion conditions selected by Mead et al.[146] corresponded to a pressure of 0.23 GPa in the extruder and a temperature of 160 °C. The change in melting point corresponding to a pressure change of 1 Pa is 3.3 degree. The pressures employed yield an increase in melting point by 76 °C. For this reason, deformations under conditions such that the temperature was much lower than the melting point of PVDF at the normal pressure corresponded to the chosen deformation regimes. It was shown that an increase in draw ratio is accompanied by an increase in the degree of crystallinity and in the magnitude of the birefringence. The phase composition in the film is characterised by a mixture of the α and β crystals, while the morphology is represented predominantly by the folded-chain form of the crystals with a large period of 20 nm. Contradictory results were obtained. according to X-ray data, the fraction of the

crystals of the α phase is greater than that of the β phase, while IR spectroscopy shows that the crystals of the β phase predominate. The discrepancies may be avoided by postulating that the chosen extrusion regime ensures more intense conformational transformations of the type $TGT\bar{G} \rightarrow (TT)_n$ in the nonordered regions than in the crystal. By selecting the extrusion regimes it is possible to achieve the optimum conditions for the α → β transformation. Indeed, it has been reported [147] that extruded films predominantly in the β modification have been obtained by this method; at the same time, one should expect a high correlation with the arrangement of the chains of the amorphous phase, since the measured birefringence indicated for the extruded films is $\Delta n = 67 \times 10^{-3}$, which had never been noted previously in the literature.

The mechanical characteristics of the PVDF films are improved also when nontraditional orientation methods are used for polymers, for example, rolltruding.[148] At rolling temperatures of 140–160 °C, there is a twofold increase (for the main rolling direction) in Young's modulus and a 12-fold increase in the ultimate strength.

In uniaxial or biaxial mechanical stretching of PVDF films, there is a possibility of the appearance of all kinds of long defects (of the type of voids). It therefore seems promising to develop methods effecting orientation crystallisation without mechanical influences. Lovinger and Wang[149] carried out the zone crystallisation of PVDF at zone migration velocities of 0.6–20 μm min^{-1} and a zone temperature of 153 °C. Analysis of the results obtained by polarisation microscopy, X-ray diffraction, and IR spectroscopy demonstrated that crystallisation in the form of the α phase predominates. Weakly developed β phase spherulites serve mainly as nuclei of α spherulites deformed in the direction of migration of the zone. Analysis of the nature of the diffractometer traces and of the dichroism of a series of IR absorption bands with a known value of the transition moment vector permitted the conclusion that the *b* axis of the lattice is oriented along the direction of migration of the zone. We may note that, in the textured specimens obtained by mechanical stretching, the cell *c* axis is aligned along this direction. A version of the zone stretching of PVDF films at high rates or zone migration has been described.[150] Having selected the stretching conditions, specimens with well oriented crystals and preferential crystallisation in the form of both α and β phases were obtained.

The problem of the formation of voids in PVDF films on uniaxial stretching may be of applied importance since, the formation of microcracks in the bulk of the film is accompanied by a decrease in its relative permittivity. Under certain conditions, this may lead to an increase in the piezoelectric constant *g* for the polarised films, which affects the output characteristics of the energy converters based on these materials. Specialists of the Thorn-EMI Company (England) and of Leeds University have been most actively concerned with this problem. In particular, they developed a method for the preparation of PVDF films with voids resulting from cold drawing (T_d = 80 °C) at high rates.[151] The nature of the morphology arising under these conditions has been studied in detail by electron microscopy.[152,153] It was shown that the voids have the form of an ellipsoid with transverse spans, i.e. they may be regarded as a form of crazing. The voids were disposed between fibrils and were characterised by a fairly wide size distribution. In one case, the average size of the voids in the longitudinal direction was 1.5 μm,[152] whilst in another it was ~5 μm,[153] although in both cases their volume fraction was estimated as 17%.

In a study of the mechanical shear anisotropy in oriented PVDF films, it was shown that the presence of voids in the bulk phase promotes an increase in virtually all the components of the elastic pliability tensor.[154]

Certain details of the formation of the voids in the cold drawing (T_d = 80 °C) of PVDF have been investigated by Kochervinskii et al.[47] Attention was drawn to the fact that the probability of the formation of voids under identical cold drawing conditions may depend significantly on the nature of the initial supermolecular structure. Two PVDF films, obtained by quenching from the melt and by slow crystallisation, were investigated. Spherulites differing significantly in size and degree of defectiveness were detected in them by the method involving small angle scattering of polarised light. The spherulites in the quenched films were an order of magnitude smaller, while the internal arrangement of some of them was characterised by the disposition of the lamella at an angle of 45° relative to the radius of the spherulite (the so called 'anomalous' spherulites). The morphology of the two films was different after cold drawing. For the quenched film, the H_v-diffractometer trace had the form of an eight-lobe figure, arising, as noted above,[132,133] from the presence of deformed and undeformed spherulites. A stronger equatorial scattering in crossed polarisers and a decrease in density and transparency caused by the formation of ellipsoidal voids are characteristic of the stretched film with large spherulites.

A similar result was also obtained on cold drawing (T_d = 20 °C) of films of the VDF/TFE 94/6 copolymer.[48] The formation of voids in the bulk phase (according to small-angle X-ray scattering data) is also observed in the film where the presence of β phase spherulites was noted in the initial state. The formation of voids is apparently accompanied by local releases of the stress, which should affect the conformational characteristics of the crazed films. In the case of the homopolymer, this is accompanied by a decrease in the fraction of the β phase in the oriented state,[33] while for the VDF/TFE 94/6 copolymer crystallised as the β phase this is accompanied by the appearance in the oriented state of sections of the chains in the $TGT\bar{G}$ conformation, which is not characteristic of the given polymorphic modification.[155,156] The fraction and nature of the microstructure of the voids formed may be regulated by isometric annealing processes and under certain conditions it is possible to achieve a decrease in, on the one hand, the concentration of the voids and, on the other, in the concentration of 'defective' conformations of the $TGT\bar{G}$ and $T_3GT_3\bar{G}$ types.[155–157]

The detection by the spectroscopic method of these conformations in the VDF/TFE, copolymer,[114,129,130] which crystallises as the polar β phase with the 'planar zigzag' conformation, most probably confirms the concept that conformational defects of the kink bonds are present in the PVDF crystals.[91–97] The above defects may play a significant role in polymorphic transformations during uniaxial drawing. This has been confirmed, for example, by data[158] according to which the high-temperature drawing of PVDF is accompanied by the formation of an oriented α phase. Electron diffraction patterns reveal certain 'anomalies'. Thus the 110 reflection due to the α phase has the form not of a point but of a strip which coincides with the direction of the *c* axis. Diffuse halo blurring (from the *hk*0 direction) is characteristic of the 002 reflection. The authors also attributed the observed 'anomalies' to the appearance of kink bonds. Instead of the $TGT\bar{G}TGT\bar{G}TGT\bar{G}$ sequence, one should expect in this case the $TGT\bar{G}TTTGT\bar{G}$ combination, where the conformational defects arise due to cooperative segmental 'flip-flop' motions between the $T\bar{G}TG$ and $TGTG$ conformations. Defects of this kind for the oriented α form of PVDF arise also during prolonged isometric annealing.[92]

It follows from the overall analysis of the data that the kink bonds noted above tend to aggregate into chains, which are disposed in the 001 plane.[158] The observed diffuse halo near the 200, 110 reflection, due to the oriented polar β phase,[159] is also caused by the appearance of bent kink bonds. In this case, this is attributed to the insertion of type GT_nG or $TGT\bar{G}$ sections of the chain into the chain with the 'planar zigzag' conformation. The authors of the concept developed believe that the solid-state transformation α → β has a two-step mechanism: the γ → β transition takes place initially and is followed by the γ → β stage.[94] It is postulated that the kink bonds in the initial α phase constitute an intermediate phase between the α and γ modifications and can therefore facilitate significantly the occurrence of the first stage of the transformation.

The presence of chain sections in the $TGT\bar{G}$ and $T_3GT_3\bar{G}$ conformations in the VDF/TFE 94/6 copolymer, which crystallises from the melt or from solution immediately as the polar β phase,[130] can be regarded as evidence for the presence of kink bonds. Their role in the uniaxial stretching processes involving isotropic films of the above copolymer, unaccompanied by a polymorphic transformation, is also extremely significant. Thus it has been shown that identical stretching conditions for the two films are characterised by a greater deformation energy density in the case of the specimen with a lower content of conformational defects in the initial state.[130] The structure of the oriented film arising under these conditions is characterised by a higher Young's modulus and a higher deformation-induced acoustic response.[129] The higher residual polarisations[160] and piezoelectric responses[129] in such films after treatment in an electric field show that the role of the kink bonds must be taken into account also in the technological development of methods for the preparation of films designed for practical purposes.

The stabilities of various polymorphic modifications of PVDF under the conditions of the operation of uniaxially stretching stresses σ have been justified theoretically and predicted.[88] Calculation of the free energy taking into account the interchain and intrachain interactions leads to the conclusion that at least five different phases may exist in PVDF: α, β, γ, σ, (α_p) and m (melt). Analysis of the phase diagram for PVDF in a state of mechanical stress has demonstrated the possibility of the existence of a large number of metastable states.[88] At room temperatures under the conditions of the operation of uniaxially stretching stresses, the α phase may exist only in a metastable state owing to the increased free energy, which agrees well with the characteristics of the α → β transformation described above.

It has been shown[161,162] that the above transition under the conditions of uniaxial stretching proceeds in the neck formation stage in the specimen so that the structural studies devoted to the necking phenomenon in PVDF may extend the ideas concerning the mechanism of the polymorphic transformations α → β. The conclusions of certain investigators on this question are of interest in this connection. Thus according to Kochervinskii,[163] the variation of the short- and long-range order parameters as a function of T_d led the authors to the conclusion that crystallisation processes should occur in the region of the formation of a neck in PVDF and should be preceded by the passage of the system through a strongly disordered or even fused state. However, in the study of the Raman spectra in the course of the deformation of PVDF it was observed[162] that not only does the α → β transformation occur in the region of the neck but there a marked increase in the degree of crystallinity (Fig. 14 *a*). At the same time, as can be seen from the figure, the medium is heated intensely in the region of the neck, such heating depending on the rate of deformation. This factor is apparently decisive for the 'anomalous' decrease in the velocity of ultrasound on formation of a neck in the VDF/TFE 94/6 copolymers.[114,163] The decrease in the velocity of sound under these conditions may reach 15% and the intensity of the transition of the material to the disordered state may depend significantly on its previous thermal history.

Specimen 2, for which the isothermal crystallisation time was five times longer than for specimen 1, has a lower concentration of defective conformers ($TGT\bar{G}$ and $T_3GT_3\bar{G}$), a larger size of the spherulite R_c, a higher density ρ, and an increased fraction of the basic 'planar zigzag' conformations (Table 10).

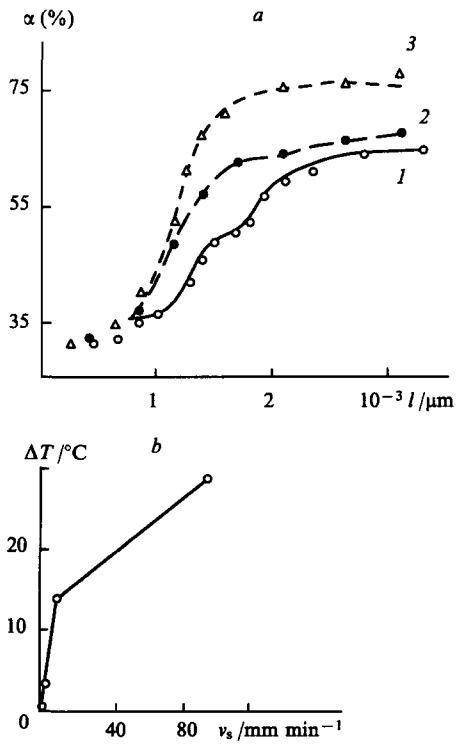


Figure 14. Dependence of the degree of crystallinity (α) on the distance (l) to the neck formation boundary at different rates of deformation (v_s) (*a*) and variation of the temperature in the region of the formation of a neck on uniaxial drawing of PVDF (*b*).[162]
v_s (mm min^{-1}): (*1*) 0.1; (*2*) 10; (*3*) 100.

Table 10. Spectroscopic and morphological characteristics of isotropic films of the VDF/TFE 94/6 copolymer obtained by crystallisation from the melt.[114]

Frequency /cm^{-1}	D/d for specimen 1[a]	D/d for specimen 2[b]
$(TT)_n$ conformation		
442	60	122
70	54	86
$T_3GT_3\bar{G}$ conformation		
431	47	106
300	9	15
90	34	163
$TGT\bar{G}$ conformation		
411	48	45
287	16	4
214	18	6

[a] For specimen 1, ρ = 1.8031 g cm^{-3} and R_c = 3.4 μm.
[b] For specimen 2, ρ = 1.807 g cm^{-3} and R_c = 4.6 μm.

It may be inferred from the values of $\rho(\gamma)$ calculated by Eqn (4) that an increase in the crystallisation time is accompanied by a redistribution of the relative amounts of the conformational defects, i.e. chain sections are enriched in the isomers with the $T_3GT_3\bar{G}$ conformation as a result of their transition from the $TGT\bar{G}$ conformation.

Specimen	ρ(γ)	$\frac{D_{287}}{D_{300}}$	$\frac{D_{411}}{D_{442}}$	$\frac{D_{214}}{D_{442}}$	$\frac{D_{100}}{D_{70}}$
1	0.49	1.8	0.8	0.29	0.67
2	0.70	0.88	0.37	0.04	0.46

An increase in the number of chains in the 'planar zigzag' and T_3GT_3G (which are closer to a planar zigzag than $TGTG$) conformations is in fact apparently the cause of the weaker disordering in the transitional region involving the formation of the oriented β phase (Fig. 15).

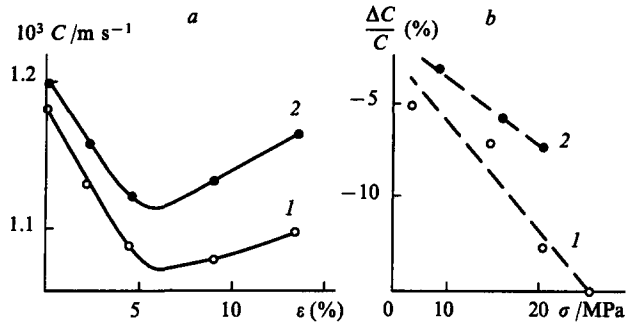


Figure 15. Dependence of the longitudinal velocity of sound on the deformation (*a*) and the relative change in the velocity of sound as a function of the stress in the region of the formation of a neck in two specimens of the VDF/TFE 94/6 copolymer (*b*).[114] Specimen: (*1*) 1; (*2*) 2.

The structure and morphology of the latter for films obtained at different T_d may differ significantly.[129] This follows also from the consistent changes in the long period L and in the intensity of the small angle meridional maximum on the X-ray diffraction curves (Fig. 16). An increase in T_d is accompanied by an increase in L and in the intensity, as mentioned above, the latter being probably due to the increase in the difference between the densities of the crystalline and amorphous regions along the direction of stretching. As can be seen from the same figure, this is accompanied by consistent changes in the response recorded by acoustic (from the velocity of sound) or optical (from the magnitude of the birefringence) methods. In particular, for the specimen with the highest draw temperature, the optical anisotropy in the film for small deformations hardly changes, while the velocity of sound actually diminishes somewhat. The increased concentration of 'defective' isomers noted for oriented films with a high T_d [129] shows that the microstructure of the noncrystallising sections in such systems may determine also the response to external influences (mechanical [129] or electrical [160]). This may prove useful in its turn for the understanding of the mechanism of the piezoelectric response in such systems.

V. Characteristics of the crystallisation of poly(vinylidene fluoride) under the conditions of uniaxial compression and high pressures

The uniaxial stretching effects influence significantly the phase equilibrium in the crystalline PVDF phase and one may therefore expect that the conditions in the uniaxial or all-sided compression also lead to an alteration in the nature of the polymorphic transformations. This hypothesis was confirmed more than 25 years ago in the pioneer studies by Doll and Lando.[164-166] It was shown that isothermal crystallisation from the PVDF melt, which is usually accompanied by the formation of the α modification, leads to the crystallisation of the γ phase (or its mixture with the α phase) on raising the pressure to 2000–5000 atm, the probability of this increasing with decrease in the degree of supercooling.[165] For the VDF/TFE 93/7 copolymer, which usually crystallises as the low-melting β phase (melting point 139 °C), an increase in pressure to 5000 atm leads to the formation of the same modification but with a melting point higher by 20 °C.[166] The same rule holds also for isotropic specimens textured as a result of uniaxial stretching and crystallised at normal and elevated pressures.[166] The results of differential thermal analysis have shown that an increase in pressure at the crystallisation of isotropic specimens is only one of the conditions for the formation of the β phase, the other condition being the maintenance of a low degree of supercooling. It has been shown by electron microscopy that crystallisation under pressure is accompanied by a significant increase in the long period (to 68 nm compared with the usual values of 10–15 nm).[167] An increase in pressure to 3000 atm increases linearly the melting point both of the VDF homopolymer and of its copolymer with TFE, the entropy of fusion diminishing under these conditions.

Similar results have been obtained also in a study whose authors observed the polymorphic transition α → β in the high-temperature annealing of specimens with the α phase under a pressure of 4000 atm. It was noted (as in the above studies [165-167]) that a decrease in the annealing temperature lowers the effectiveness of this transition. It was demonstrated later [110] that, by making the conditions for the annealing of the isotropic PVDF specimens more severe (a pressure of 4500 atm and a temperature of 292 °C), it is possible to ensure also the α → β transformation. The extent of such transformations can be increased by optimising the PVDF crystallisation conditions under high pressure.[169] For this purpose, changes were made both in the temperature (from

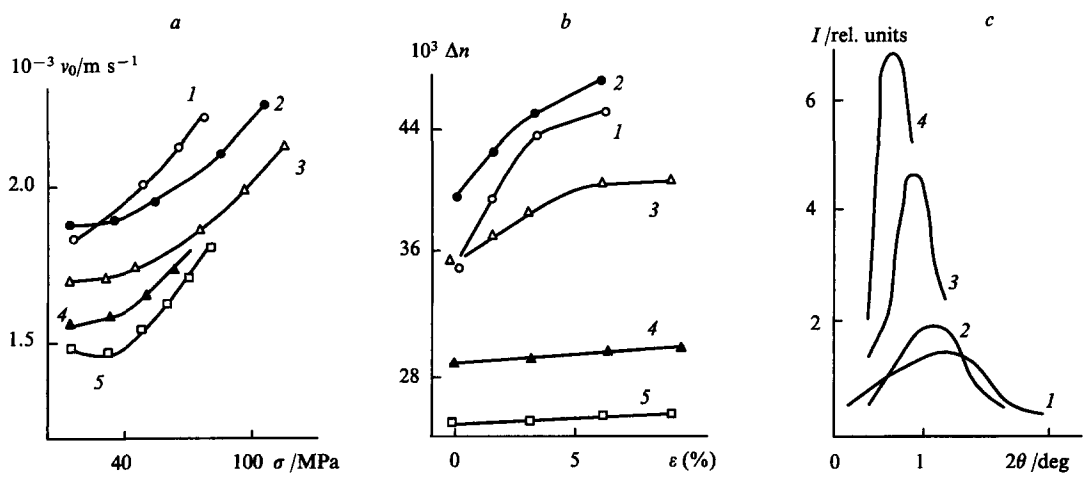


Figure 16. Variation of the longitudinal velocity of sound (*a*) and birefrigence (*b*) as well as small angle X-ray diffraction curves (*c*) for oriented films of the VDF/TFE copolymer obtained at different temperatures (°C): (*1*) 60; (*2*) 80; (*3*) 100; (*4*) 120; (*5*) 140.[129]

Table 11. Characteristics of the crystallisation conditions and the parameters of the PVDF structure during formation under increased pressure.[169]

P_i /kbar	P_f /kbar	T_i /°C	T_f /°C	Fraction of β phase (%)	α (%)	$\Delta T/\Delta P$ /K kbar^{-1}
0.93	6.25	213.1	254.4	4	51	7.76
1.15	6.38	217.3	255.6	12	50	7.32
1.45	6.21	225.8	257.3	19	52	6.62
1.80	6.4	231.9	261.0	95	60	6.33

the initial T_i to the final T_f and in the temperature (from the initial T_i to the final T_f) and in the pressure (from the initial P_i to the final P_f) of this process as a result of which it is possible to vary appreciably both the fraction of the β phase and the degree of its crystallinity. This is illustrated by the data in Table 11.

The nature of the changes in the parameters of the unit cells in the PVDF crystals formed under pressure has been investigated.[170] For this purpose, the changes in the interplanar spacings were followed in specimens of the α and β phases under pressure. In the α modification of PVDF, they proved lower in the 110 plane than in polyethylene (PE), whereas along the axis of the macromolecule the opposite was true. The variation of the unit cell parameter of the α phase along the *b* axis was found to be greater than along the *a* axis, whereas for the β modification the changes in the interplanar spacings along the normals to the 110, 200, 020, and 310 planes are similar. It has also been shown that the compressibility of the lattice decreases in the direction PE → $PVDF_\alpha$ → $PVDF_\beta$. The study of the volume compressibility β_v with the aid of physicomechanical characteristics in block PVDF specimens crystallised as the β modification evidently makes it possible to obtain definite information about the structure of the nonordered regions.[171] Thus, it has been shown that, under the conditions of the crystallisation of PVDF in the form of one modification, β_v for the oriented specimens proved to be always lower than for the isotropic ones. On the assumption that the degree of crystallinity is constant, this can be accounted for solely by the denser packing of the chains of the amorphous phase in the former. The large fraction of the latter phase in PVDF (> 50%) is believed to be the main cause of the abrupt change in Young's modulus with increase in pressure, where the vitrification of the nonordered regions is postulated.[171] The role of the latter is manifested also by the dependence of the linear expansion coefficient *L* of the specimens with a nonoriented phase on the pressure *P* described by the polynomial

$$L = A + BP + CP^2 + DP^3 , \quad (5)$$

where $A = 2.540$, $B = -1.733 \times 10^{-2}$, $C = -1.605 \times 10^{-3}$, and $D = -1.386 \times 10^{-4}$.

The two bends in the temperature variations of the linear expansion coefficient (at −50 and 22 °C) are attributed to transitions in the amorphous phase and the crystal respectively.

In a series of studies Matsushige and coworkers [127, 171-175] also indicated the possibility of the α → β transformation on crystallisation (or annealing) under high pressure. The presence of three endothermic fusion peaks for the PVDF specimens crystallised in this way is attributed to the fusion of the residues of the α phase and of the regions of the β phase, which results in the formation of folded-chain crystals and extended chain crystals (ECC).[171-175] It was noted that such crystals have significantly different morphologies: a spherulite structure was observed for the folded-chain crystals, whereas for the ECC lens-like formations with dimensions of ~10 μm were noted. The corresponding melting points (at the normal pressure) are respectively 190 and 207 °C, both increasing linearly with pressure. As the PVDF specimens with the β phase crystallised under a high pressure are heated under normal conditions, the reflections characteristic of the β phase remain unchanged up to 189 °C (which is not the case in the oriented specimens with the β phase). This indicates the high stability of the above modification and the absence of the reverse transition β → α up to the temperature indicated.[174] The results of the study of the high-temperature annealing of specimens of the PVDF phase under a pressure of 4000 kg cm^{-2} have shown that the virtually complete transition α → β takes place over a period of 165 min at 278 °C (the melting point of the α phase is 286 °C). A decrease in the annealing temperature lowers the rate of the transformation. The activation energy for the above transition (calculated from kinetic data for the initial stage of the process) has been estimated as 30 kcal mol^{-1}.[173]

When pressure was applied to an oriented PVDF specimen containing a small amount of the residual α phase, a uniaxial deformation arose, which led to the complete disappearance of the α phase.[176] In addition, X-ray photographs at different angles relative to the initial *c* texture have shown that the *h*00 planes of the β phase crystal lattice are located in the plane of the film, the 001 direction again coinciding with the direction of the initial extension, so that the *h*00 planar texture is produced. It is believed that the 100 and 110 planes in PVDF (as in polyethylene) are the closest packing planes with the maximum interplanar spacing. Slip should occur along the above planes in most cases. The formation of fault bands and twinning are characteristic of the structure formed under these conditions.

In the case of the uniaxial compression of isotropic films with the α phase, it was found that the shape of the pistons may play a significant role in the α → β transformation.[175,177] The rectangular shape is preferable for the chosen conditions (5000 kgf cm^{-2} and 125 °C). In this case, the X-ray diffraction pattern proved to be similar to those for the extended specimens, the degree of orientation of the β crystallites reaching 95%.[175] The results of the study of the compression process at variable temperatures have shown that the most complete α → β transformation takes place at 125 °C. On the other hand, on extension an increase in temperature (under the conditions of constant deformation) leads to a decrease in the extent of the above transformation. It is therefore concluded that the mechanisms of the α → β transitions on compression and extension are different. With increase in pressure, there is also a change in the mechanism of the transformation on extension. At a temperature above 130 °C, uniaxial stretching proves ineffective for the α → β transition. However, if it is carried out under a pressure of 4000 kgf cm^{-2}, then the transition occurs up to draw temperatures in the range 250–265 °C.[127] The changes in the nonordered phase in high-temperature annealing processes under a high pressure have been investigated in a study[127] of the α → β transitions in relation to single crystals of the α phase. In particular, the above transformation goes to completion in such crystals over a period of 15 min at 533 K and a pressure of 400 MPa. Presumably the nonordered phase gives rise to definite hindrance to the α → β transition, since the annealing at the same pressure of a PVDF specimen with a lower degree of crystallinity requires 165 min and a temperature of 551 K for the 100% yield of the β phase.[173]

The structural transformations for different versions of the uniaxial and all-sided compression should be reflected also in the electromechanical characteristics of the polarised PVDF films.

Table 12 shows that, during annealing at a high pressure, the piezoelectric constants of uniaxially extended films increase by a factor of 3.5–4. Drawing under a high pressure requires the optimisation of the process with respect to temperature. For the variant involving uniaxial compression, the piezoelectric moduli may be increased appreciably by combining the film deformation and polarisation processes.

Table 12. Piezoelectric properties of PVDF specimens obtained by different methods.[127]

Preparation conditions	Piezoelectric stress constant $10^2 l_{31}$ /C m^{-2}	Elastic modulus /GPa	Piezoelectric strain constant d_{31} /pC N^{-1}
1 kgf cm^{-2} drawing and 75 °C	1.0	1.5	6.7
Drawing (annealing) under 4000 kgf cm^{-2} pressure and 278 °C for 30 min	3.5	1.3	27
Drawing under 4000 kgf cm^{-2} pressure at different temperatures /°C			
165	2.7	1.4	20
200	3.0	1.4	21
250	4.1	1.6	26
265	1.7	1.3	13
Uniaxial compression at 5000 kgf cm^{-2} and 125 °C			
Poling after compression	1.5	1.5	8.0
Poling during compression	2.8	1.5	19

For the VDF homopolymer with crystals of the β phase, an increase in pressure to 4.5 kbar increases its melting point by more than 100 °C.[170] For the VDF/TrFE 70/30 copolymer, in which the melting point and the temperature of the ferroelectric–paraelectric transition are different, an increase in pressure is accompanied by an increase (albeit in accordance with different laws) in the regions of both transitions. The nature of the above phenomenon has been investigated in detail in studies[179–181] of the structural changes under the influence of high pressure in ferroelectric VDF/TrFE copolymers having different compositions. In particular, it has been shown for PVDF/TrFE 54/46 that under normal conditions (room temperature, normal pressure) the crystal structure is characterised by the coexistence of the paraelectric and ferroelectric phases, to which correspond different angular positions of the main intermolecular reflection.[179] An increase in pressure to 450 GPa is accompanied, together with the general shift of the reflections towards larger angles, also by a significant weakening of the paraelectric component, the above changes being reversible.[179] An increase in pressure in the copolymers indicated is accompanied, according to X-ray and electrophysical measurements, by an appreciable shift of the region of the ferroelectric–paraelectric transition towards higher temperatures.[180]

A combined study of the structural and electrophysical properties of films of the VDF/TrFE 94/6 copolymer resorting to X-ray diffraction, scanning electron microscopy, and thermal analysis data has shown that crystallisation at high pressures is accompanied by the formation of lamellar crystals of the β phase with hexagonal packing and a thickness of 100–200 nm, which retain their stability at very high temperatures. By generalising these data, the authors[181] were able to put forward a phase diagram for the VDF/TrFE 94/6 copolymer (Fig. 17). It follows from the latter, in particular, that the melting point and the Curie point (T_c) increase with pressure according to different laws and that the hexagonal phase may be present only at high pressures. As a result of the analysis of the morphology of the supermolecular structures formed, it was later concluded that the ECC regions are formed when crystallisation from the melt gives rise to a metastable hexagonal phase, which may be subsequently converted into a stable orthorhombic phase.[182, 183]

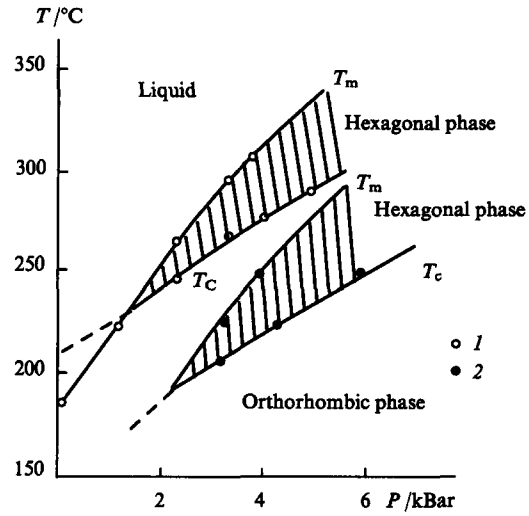


Figure 17. The $P-T$ phase diagram for the PDF/TrFE 94/6 copolymer.[181]
(*1*) curves obtained in the heating regime; (*2*) curves for the cooling regime; hexagonal phase — paraelectric; orthorhombic phase — ferroelectric.

VI. The polymorphism of the poly(vinylidene fluoride) induced by strong electric fields

The dipole moment of the monomer unit of the PVDF chain in the 'planar zigzag' conformation is 7×10^{-30} C m,[184] so that it is natural to expect a high sensitivity of this polymer to strong fields. Indeed, numerous experimental data have confirmed this. High fields may affect the crystal lattice, altering the nature of the supermolecular formations in the PVDF and the isomeric composition of its chain. The above changes are usually observed by large- and small-angle X-ray diffraction methods, the method based on the small angle scattering of polarised light, and IR and Raman spectroscopy. Examination of the polymorphic transformations in PVDF under the influence of high fields can be usefully begun with a simpler case where a PVDF specimen crystallised as the β phase, in which a polymorphic should not be expected, is subjected to the action of the field. Such a case has been described in a study[184] where the β phase was obtained as a result of low-temperature drawing and subsequent annealing. The nature of the change in the profile of the principal β phase reflection 200, 110 after poling (in a 60 MV m^{-1} field) showed that the polar cell uncoils under the influence of the field.

Another variant of the behaviour of PVDF in a high field has been examined in studies,[185, 186] where crystallisation led to the formation of a mixture of the α and β modifications. Fig. 18 presents X-ray diffraction curves for the initial (biaxially oriented) film and the film treated in a corona discharge. Evidently, poling in the corona discharge even at a potential of 5 kV leads to the disappearance of the 100 and 020 reflections of the α phase and to an increase in the principal 200, 110 reflection of the β phase. The intensity of the latter increases significantly with the simultaneous decrease in yet another reflection (110) of the α phase with increase in the potential to 10 kV, which has been attributed to the polymorphic α → β transition. Certain details of the structural changes occuring under these conditions may be noted by analysing the data in Table 13. In particular, it is seen that, after the treatment of the film in the field, the principal reflections of both the α and β phases shift towards small angles and are broadened at the same time. The former fact, indicating some 'loosening' of the transverse dimensions of the crystallites, has been attributed to the deformation of the bond angles in the main chain as a result of the interaction of the field with the polar CF_2 bonds. On the other hand, the broadening of the β reflection after

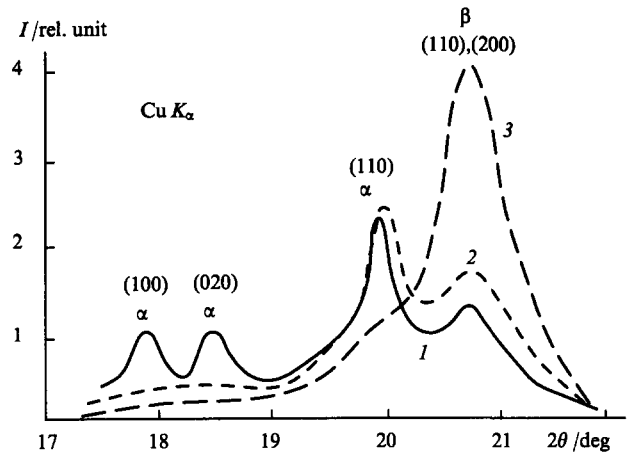


Figure 18. Diffraction curves for the initial PVDF film (*1*) and the film charged in a corona discharge (*2*, *3*).[185]
Potential in the corona discharge (kV): (*2*) 5; (*3*) 10.

charging the film is due to the decrease in the size of the crystallites or an increase in their defectiveness.

For oriented PVDF films containing only 5% of the β phase, the effect of the 1.5 MV cm^{-1} field did not lead to the appearance of any new reflections, but a number of those arising from the initial film changed significantly.[187] A similar phenomenon in low fields was noted also in other investigations.[188, 189] A significant change in the concentration of the groups in the $TGT\bar{G}$ conformation was not then found [187] and it was therefore postulated that a new crystallographic modification α_p (δ−) is formed under these conditions.

The $\alpha \rightarrow \alpha_p$ transition leads to the formation of a new cell in which the dipole moments of two chains are parallel (Fig. 2). This transition requires the rotation of one chain by 180° (as a result of the energy of the external field and temperature) with a translational displacement along the axis of the macromolecule over a distance $c/2$. The identity periods of the new lattice are then found to be the same as in the α phase, but the structure factors for a series of the reflections may differ appreciably (Table 14).

The appearance of the new 110, 200 reflection of the β phase in higher fields [188, 189] indicates that two stages in the structural rearrangement should be expected for the α phase: in accordance with the scheme $\alpha \rightarrow \alpha_p \rightarrow \beta$. In low fields, the $\alpha \rightarrow \alpha_p$ transition takes place without changes in the chain conformation and in the geometry of the lattice, the unit cell becoming polar under these conditions. The last factor is apparently the reason why certain reflections from the α_p phase undergo a change in intensity or are altogether extinguished (Table 14). However, this transition is not

Table 14. The structure factors for the reflections due to the α and α_p modifications of PVDF.[188]

hkl	2θ /deg	Structure factor /rel. units	
		α phase	α_p phase
100	17.88	60	0
020	18.41	86	86
110	20.13	137	165
120	25.77	92	0
021	26.73	119	119
111	27.97	79	85
121	32.35	65	0
130	33.20	75	93
200	36.2	69	106
210	37.44	81	0
040	37.41	14	14
002	38.99	78	78

accompanied by any significant changes in the initial morphology.[190] In higher fields, conformational rearrangements of the type $TGT\bar{G} \rightarrow (TT)_n$ begin, which entail a change in the type of the unit cell. The structural rearrangements noted above are accompanied by the rotation of the dipoles relative to the direction of the field and by a change in the relative intensities of a series of characteristic bands in the IR spectrum.[191] It is postulated that the rotations of the dipoles for the chain sections in the $(TT)_n$ conformation proceed with greater difficulty than for the chain sections in the $TGT\bar{G}$ conformation.[192] Analysis of the kinetics of the variation of the intensity of the 512 cm^{-1} band (characteristic of segments with the 'planar zigzag' conformation) after the application of a rectangular electric field pulse permitted the conclusion that there are fast and slow stages in the orientation of the dipoles.[193] The former is attributed to the rotation of small crystals and the latter to the slow rotation of the chains in the crystal. It is postulated that the slow stage of the orientation process should not reduce solely to 'flip-flop' motions with 180° rotation of the chain, which are inactive in the IR region.[193]

For the cyclic variation of the strength of the field and of its polarity, the orientation processes are in the nature of hysteresis. This can be inferred from Fig. 19, in which the intensity curves for two absorption bands sensitive to the 'planar zigzag' conformation are presented. If *A* and *B* are initial points, then the antiparallel nature of the curves is due to the difference between the directions of the transition moment vector for the two bands: for the 512 cm^{-1} band, it is parallel to the dipole moment of the CF_2 group, while for the 446 cm^{-1} band it is perpendicular.[193] The retention of a definite orientation of the dipoles after the removal of the high field is apparently one of the factors needed for the establishment of a residual poling in PVDF films.

Table 13. X-Ray diffraction data for the initial (biaxially oriented) PVDF film and PVDF film treated in a corona discharge.

Thickness of specimen /μm	Data from Refs 110 and 111			Data from Ref. 186					
				before treatment in discharge			after treatment in discharge		
	2Φ /deg	phase	plane	I	II	III	I	II	III
16	17.9	α	100	17.7	11.2	–	17.7	1	–
	18.4	α	020	18.4	3.4	–	18.4	1	–
	20.1	α	110	20.0	54.52	0.00614	19.4	3.3	–
	20.85	β	110	20.7	45.16	0.00636	20.16	63.25	0.00883
			200						
25	20.1	α	110	20.15	76.5	0.00448	19.9	11.2	–
	20.85	β	110	20.9	93.5	0.00537	20.6	109.6	0.00846
			200						

Note. The following designations have been adopted: I — Bragg angle 2Φ /deg; II — area /arbitrary units; III — integral width /rad.

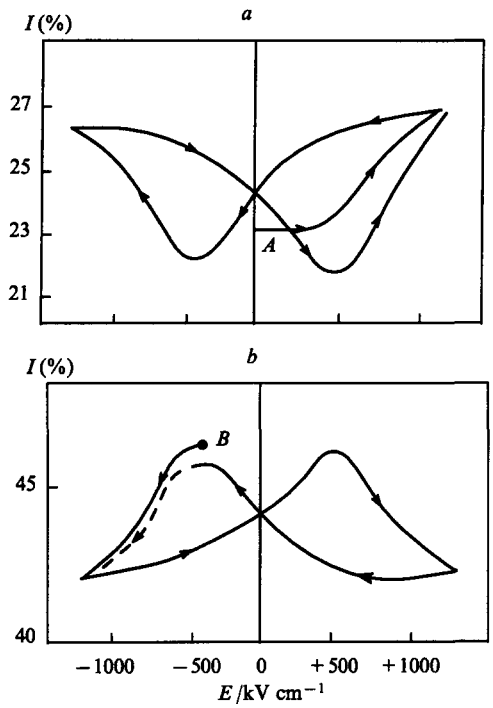


Figure 19. The hysteresis character of the 512 cm^{-1} (*a*) and 446 cm^{-1} (*b*) band intensity curves for a variable field in a PVDF film. *A* and *B* — initial points.[192]

The above hypothesis that the $\alpha \rightarrow \alpha_p$ transition is not accompanied by a change in the nature of the H_v dispersion pattern[190] was refined to some extent data by the data of Broussoux et al.[194] They observed an increase in the intensity at the centre of the pattern when a PVDF film in the α_p modification was placed in a high field. Since the crystals of the α_p phase are polar, the forces acting on them alter the form of the orientation function $N(\alpha)$ for the crystallites in the spherulite. This should disturb the order in which the crystallites are arranged along the spherulite radius and should increase the scattering intensities at the centre of the pattern. During the repolarisation of the PVDF films in an 800 kV cm^{-1} field, the above changes in intensity occur over several minutes.[194] In high fields, this can be explained only by the influence of the space charge.

In a later study[195] by the same workers, the role of plastic deformation in the $\alpha \rightarrow \alpha_p \rightarrow \beta$ polymorphic transformations on poling of PVDF films was investigated. The change in the nature of the orientation of the β phase crystals under the influence of a high field was estimated (from the 201, 111 reflection) for this purpose. In one case, the poling was carried out after rolling the film and in another both processes were combined. Furthermore, by employing together with the X-ray method yet another variant of the IR spectroscopic distorted total internal reflection method, they estimated the nature of the orientation both in bulk and on the surface. The results demonstrate appreciable differences for the two poling methods. When the rolling and poling are carried out separately, the orientation in bulk proved to be less marked than on the surface and for the latter it is significantly more pronounced on the side of the positive electrode. This difference is attributed to the change in the local field as a result of the injection of carriers from the electrode. On the other hand, when the rolling and poling processes are combined, the difference between the orientations on the surface and in bulk are insignificant, as for different signs of the potential on the surface of the poling film. Owing to the high mobility of the chains, the plastic deformation processes promote an effective 'dissipation' of the space charge of the injected carriers and thereby smoothe out the inhomogeneity of the poling along the film cross-section.

The experimental critical fields for the $\alpha \rightarrow \alpha_p$ (100–150 MV m^{-1}) and $\alpha \rightarrow \beta$ (500 MV m^{-1}) transitions[188] have been confirmed, as regards order of magnitude, by calculations of the local free energy in terms of the average field approximation.[196] A decrease in the fields with increase in the poling temperature has also been predicted, in agreement with experimental data.[197] On raising the temperature from 20 to 65 °C, coercive fields decrease by a factor of 2 as a consequence of the initiation of thermal defects, which should facilitate the above transitions. It is significant that this concerns only conformational defects, since irregularities in the 'head to head' attachment of groups actually increase the intramolecular potential barrier to the transition under consideration.[198] If it is postulated that the conformational defect is produced in the form of a kink of the kind mentioned above, the $\alpha \rightarrow \alpha_p$ transition can be modelled by the motion of a defect along a chain.[199] According to this model, the rate of migration of the kink depends on the field strength. At 373 K and for a field strength of 100 MV m^{-1}, the rate is ~10 m s^{-1}. This means that the kink migrates over a lamella 10 nm thick over a period of ~1 ns.

Estimates have shown that the proposed ,mechanism of the $\alpha \rightarrow \alpha_p$ transition requires ~1 ms for the 180° rotation of the chain. For a quantitative justification of the proposed model, it was postulated[200] that the motion of the kink along the chain in the form of soliton waves is the basis of the mechanism for the polarisation of the longitudinal component of the dipole moment, observed in PVDF films. Calculations based on the proposed hypothesis yield an activation energy for the migration process of ~10 kcal mol^{-1} in the case of an ideal chain. This is an order of magnitude higher than the value obtained in dielectric relaxation experiments. It is assumed that the difference may be smaller if account is taken of the 'head to head' defects which actually exist in the chairs and of the stressed bonds which may arise in the crystal or at its boundary with the nonordered phase. Another mechanism of the growth of the domain disposed most favourably relative to the polarising field has been proposed.[201] The mechanism is based on the idea of the twisting of the boundaries.[202] It has been shown that the additional energy per chain for 180° rotation in the conformation with minimum energy is 42 kJ mol^{-1}. The energy barrier which is overcome during the migration of the boundary along the chain is not less than 7.5 kJ mol^{-1} per repeat unit. This is comparable with the energy gain of 1.45 kJ mol^{-1} on transpolarisation of PVDF in a 2 MV cm^{-1} field.

The above structural transformation occurs only for high field strengths. Indeed, in the crystallisation of PVDF from solution in dimethyliormamide in a 100 kV cm^{-1} field, neither the formation of a new phase nor a change in the form of the spherulite were observed.[203] However, even at 115 °C appreciable changes in the intensity of the 616 cm^{-1} band are observed only for field strengths in excess of 100 MV m^{-1}.[204,205] In the temperature range 50–70 °C, the increase in the intensity of the conformational rearrangements occurring in the field (350 MV m^{-1}) agrees qualitatively with the data of Lu et al.[197] The regions of mobility in the PVDF crystal phase observed in this range by the dielectric method necessitate the assumption that above motions should play an important role in structural rearrangement processes under the influence of a field. This has been confirmed by data[205] showing that, under the conditions of an identical field, an increase in the poling temperature from 20 to 100 °C leads to an increase in the fraction of the β phase formed from 60% to 95%. Data obtained in studies on depolarisation processes in such specimens indicate that the temperature range 50–70 °C is important also for the deorientation processes involving some of the dipoles in polarised PVDF specimens and the β phase formed under these conditions remains stable up to high temperatures.[205] The deorientation processes affect also the relaxation of the modulus in PVDF films in the early stages of stress relaxation.[206] It must be noted that the mobility in these experiments (mentioned above) may also have a positive effect on the elastic properties,

since after longer times the inverse increase in the modulus is observed, which is most probably attributable to additional crystallisation.

Kepler et al.[207] investigated the possibility of the theoretical estimation of the changes in the degree of crystallinity α in PVDF films with the β phase under the influence of an electric field. Estimates have shown that an increase in α with increase in field strength should be linear with a coefficient of 2.8×10^{-11} V m^{-1}. The experimental coefficient was found to be somewhat higher, namely $(1.8 \pm 0.2) \times 10^{-11}$ V m^{-1}. One of the causes of the difference between the coefficients is, according to the authors, the difference between the relative permittivities of the amorphous and crystalline phases, giving rise to an inhomogeneity in the effect of the field on them. Yet another cause of the above difference may be the irreversible changes in the intermolecular packing of the PVDF chains under the influence of high fields. This can be inferred from the appreciable frequency shift of the characteristic bands in the IR spectra of PVDF on exposure to a strong electric field, which is reflected in Table 15.

Table 15. Variation of the band frequencies in the IR spectrum of PVDF during poling and after poling.[208]

Bond /cm^{-1}	Type of vibration	Frequency /cm^{-1}		
		before poling	during poling	after poling
976	$t(CH_2)$	975.9	974.8	975.8
796	$\gamma(CH_2)$	796.4	796.3	796.3
765	$\sigma(CF_2)+\sigma(CCC)$	765.1	764.3	764.0
614	$\sigma(CF_2)+\sigma'(CCC)$	614.7	614.0	614.3
530	$\sigma(CF_2)$	532.3	533.5	532.7
845	$\gamma(CH_2)+\nu_a(CF_2)$	843.5	846.0	844
510	$\sigma(CF_2)$	510.1	510.9	510.4

The same tendency towards a displacement of a series of β phase bands after the poling process towards higher frequencies has been noted also for the VDF/TFE 75/25 copolymer.[209] The state of the more ideal packing of the chains after polarisation can be judged from the narrowing of the above bands and from the simultaneous increase in the density from 1.875 to 1.895 g cm^{-3}.[209] As in the study of Kepler et al.,[207] the polarisation of the VDF homopolymer is accompanied by an increase in α, but this occurs without change in the size of the crystallites. This finding indicates the formation of additional ordered regions from the amorphous phase.[210]

The changes in the intensity of the 510 cm^{-1} band during the cyclic variation of the field applied to a biaxially oriented PVDF film[211] agree qualitatively with the changes in the intensity of this band found by Naegele and Yoon.[193] Comparison of the coercive fields obtained from spectroscopic data and from the field dependences of the electric shift showed that in the latter case they are appreciably greater. The 510 cm^{-1} band is characteristic of both the β and γ phases (Table 1). For this reason, Guy and Unsworth[211] believe that one of the causes of the difference between the coercive fields is the presence together with the β phase of small amounts of the γ phase, which may have high coercive fields. Another cause is most probably the fact that the 510 cm^{-1} band is sensitive to the presence of 'planar zigzag' conformations not only in the crystal but also in the amorphous phase. The hysteresis phenomena for the latter should undoubtedly be characterised by lower coercive fields than the domain switching processes in the crystal, which are in fact responsible for the characteristics of the hysteresis in electrophysical experiments.

The influence of the poling temperature on the nature and kinetics of the structural transformations in PVDF in the range 20–100 °C has been investigated.[212] For films with three different thicknesses, the changes in the intensities of the 510 and 530 cm^{-1} bands, which characterise the 'planar zigzag' and $TGT\bar{G}$ conformations respectively, were analysed mainly. Fig. 20*a* presents the dependence of the relative change in the intensity of the 530 cm^{-1} band as a function of the polarising field strength. Evidently an increase in the poling temperature leads to an approximately linear displacement of the structural rearrangement region towards lower fields (Fig. 20*b*). The kinetics of the variation of the intensity of the 530 cm^{-1} band when a high field (2.1 MV cm^{-1}) acts on a PVDF film shows that the equilibrium value of ΔI_{530} is attained after 40–60 min. The domain switching times in such fields should be less than 10^{-3} s.[127] The considerable differences between the domain switching and structural rearrangement times make it possible to put forward certain considerations about the details of the latter. When a field is applied to a specimen, the reorientation of crystallites takes place initially in the first stage. In the new position, the latter generate an internal field, which promotes the occurrence of orientation processes in the amorphous phase itself and at its boundaries with crystallites. The slowest stage in this process is the diffusion-controlled generation of a space charge both from the free carriers present in the initial state (before the application of the field) and as a consequence of the injection of charges from the electrodes.

A confirmation of the hypothesis of the occurrence of structural rearrangement processes in the amorphous phase may be found in the results of the study of Hsu et al.,[212] although the authors did not draw attention to this fact. Indeed, during the poling process the 490 and 470 cm^{-1} absorption band intensities are redistributed, a decrease in that of the former and an increase in that of the latter being noted. These bands are attributed to the amorphous regions and their changes imply that poling leads to a

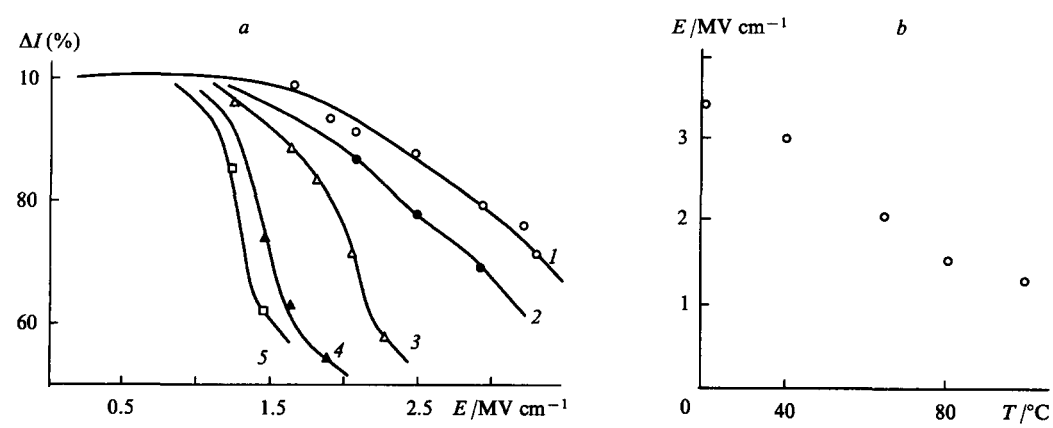


Figure 20. Field dependences of the relative change in the intensity of the 530 cm^{-1} absorption band at different poling temperatures (*a*) and temperature dependence of the critical fields in the structural rearrangement (*b*).[212] T (°C): (*1*) 20; (*2*) 40; (*3*) 65; (*4*) 80; (*5*) 100.

decrease in the fraction of the *gauche*-conformation as a result to the transition to the *trans*-conformation.

Yet another rather unpredicted phenomenon was later observed.[213] In previous sections, it was shown that the $\alpha \rightarrow \gamma$ transition initiated by prolonged high-temperature annealing of films with crystals of the α phase or by the crystallisation of PVDF from the melt with slight supercooling. The crystallisation of PVDF from the melt with high degrees of supercooling has been investigated in a 0.07 MV cm^{-1} electric field.[213] An experiment involving crystallisation with the same degree of supercooling but in the absence of an electric field was carried out as a control. It was observed that in the latter case PVDF always crystallised as the α phase. On the other hand, IR spectroscopic data showed that crystallisation in a weak field is accompanied by the appearance of an appreciable amount of the γ phase. This was inferred from the appearance of the 815, 776, 510, and 430 cm^{-1} bands characteristic of the $T_3GT_3\bar{G}$ conformation. It is significant that the fraction of the γ phase increases with decrease in the degree of supercooling and reaches 70% in the best cases. This phenomenon may be not only of academic interest but may also find a practical application.

The characteristics of the structural transformations under the influence of strong electric fields have been observed also for the VGF/TrFE 75/25 copolymer, which crystallises immediately as the ferroelectric β phase in the absence of the field.[214] It was observed by IR spectroscopy that the number of long sections of the chains in the 'planar zigzag' conformation (the 850 and 1290 cm^{-1} bands) changes in different ways following the application of a strong field depending on the temperature. Thus the application of a field at room temperature, which differs markedly from the Curie temperature, leads to a decrease in the concentration of the above sections (this is not observed for the VDF homopolymer), whereas at temperatures close to the Curie point the opposite behaviour is noted. It is believed that the improvement of order occurs only if it has been disturbed in the initial state (in the absence of a field) owing to large thermal fluctuations.

Transitions under the influence of a field on PVDF films obtained by different methods have been observed by X-ray diffraction, IR spectroscopy, and DSC.[215] Variation of the method of preparation showed that the threshold fields for the structural transformations of the α phase may be 0.6 and 1.6 MV cm^{-1}.

In a series of studies designed to estimate the possible structural changes in PVDF after and during the treatment by operation of strong electric fields, NMR spectroscopy was employed.[216-210] Significant changes were noted in the direction of the *b* axis of the lattice in a field of 1 MV cm^{-1} even at room temperature.[216] Variation of the field strength demonstrated an appreciable decrease in the fraction of mobile protons in fields of 1.5–1.6 MV cm^{-1},[217] whilst analysis of the second moment of the absorption line indicates the presence, together with the crystalline phase, of highly oriented chains of the nonordered phase, the fraction of which may reach 0.14.[218]

The distribution function for the *b* and *c* axes of the lattice in PVDF films after their poling has been analysed.[219] Comparison of the intensities of the 111 and 001 reflections for the PVDF β phase before and after poling shows that a high field affects not only the distribution functions for the polar axes of the lattice (*b*) but also the distribution functions for the axes of the macromolecules (*c*). At the same time, it was noted that, despite the high fields the distribution of the *b* axes relatively to the normal to the film surface remains fairly wide. According to the authors[219], this creates potential possibilities for increasing the residual poling P_r in the ferroelectric PVDF by a factor of at least 2.[219] In the case of uniaxially extended PVDF films, P_r can be partly increased by selecting the conditions for preliminary isometric annealing. Thus it has been shown that such annealing at high temperatures (160–180 °C) is accompanied by an appreciable increase in P_r (from 51.4 to 65.2 mC m^{-2}).[220] This is attributed to a considerable increase (from 45% to 68%) in the degree of crystallinity under such annealing conditions. Somewhat later, Takase et al.[221] showed that such annealing is accompanied by an increase in the chain packing density in the lattice of the β crystallites and by an increase in their perfection. At the same time, these structural changes decrease appreciably (from 67.0 to 41.3 μs) the domain switching times for a 2 MV cm^{-1} field in the ferroelectric phase.[221]

The structural transformations in oriented PVDF films, crystallised as a mixture of the α and β phases, have also been investigated by the method of X-ray pole figures.[222] Analysis of the data shows that the distribution of the orientations of the dipoles along the direction of polarisation begins to charge appreciably already in fields of 80 MV m^{-1}, although the nature of the distribution is restored after the removal of the field. Such low threshold fields may be associated with the high draw ratio ($\lambda = 6$) of the initial film. A field-induced increase in crystallinity has been observed,[222] which corresponds qualitatively to the data of Kepler and Anderson.[184] The dependence of the additional increment in the degree of crystallinity in PVDF films on the polarising field strength (Fig. 21) indicates nevertheless also certain differences with the above study. Whereas in the latter a monotonic linear dependence was noted in the entire range of fields, it can be seen from the figure that in the range 160–100 MV m^{-1} an 'anomalous' decrease in the degree of crystallinity takes place. The cause of such decrease is probably the competitive effect of two processes. In low fields, the structures of the crystallites, the polar axis of which assumes a favourable disposition relative to the external field, are built up (using the chains of the amorphous phase). In a higher field, the energy of the latter is sufficient to initiate the rotation of single chains in crystals with an unfavourable disposition. Such rotations may disrupt the crystals, which in fact leads to a decrease in the degree of crystallinity. One should also note that, after the field has been switched off, the degree of crystallinity falls significantly. This finding most probably indicates that the reversible component or the increase in the degree of crystallinity is effected via a transition to an ordered state of some of the chains of the amorphous phase (or of its boundaries with the crystal). After the removal of the electric field, these regions again pass to the disordered state.

The contributions of the dipoles of the crystalline and amorphous phases to the field-induced orientation processes have been divided on the basis of a modified scheme for IR spectroscopic analysis,which provides for the possibility of altering the angle at which the beam enters the textured PVDF films.[223] Use was made of a uniaxially extended film in which the fraction of the residual α phase was less than 5%, i.e. the polymorphic transformation under the influence of the field could be neglected

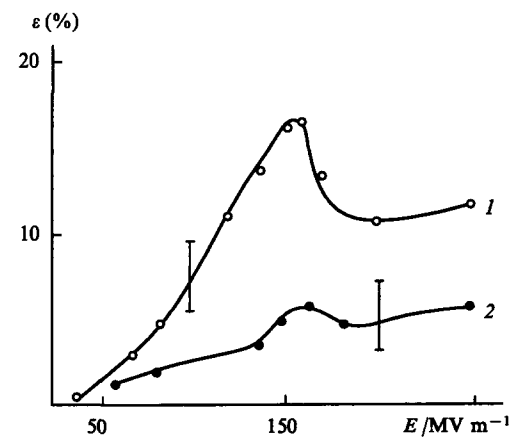


Figure 21. Dependence of the additional increment in the degree of crystallinity in PVDF films on the poling field strength.[222]
(*1*) With the field applied; (*2*) after the removal of the field.

and the changes in the IR spectra could be unambiguously attributed solely to the change in the orientation of the dipoles. Two vibrational bands (at 510 and 445 cm^{-1}), characterising the 'planar zigzag' conformations were selected. The former corresponds to the CF_2 groups in both phases, while the latter corresponds only to the dipoles in the crystallites. Analysis of these data showed that, whereas in the initial state the dipoles form an angle of 42–44° relative to the normal to the film, after the application of a 2.4 MV cm^{-1} field the angle is 27° for the 510 cm^{-1} band and 18° for the 44 cm^{-1} band. The significant difference between these values demonstrates unambiguously that, for the same field, the dipoles are better oriented in the crystal than in the amorphous phase.

A general thermodynamic approach to the quantitative description of the influence of the field on the crystallisation of PVDF (in the α or γ phases) has been developed.[224] The authors of this study began with the concept of homogeneous primary nucleation. The free energy of formation (in the absence of a field) of N cylindrical particles with a length L and an area A may be found from the relation

$$\Delta F_0 = -NLA\Delta f + 2NA\sigma_e + 2L\sqrt{NA\pi\sigma}\,, \qquad (6)$$

where Δf is the free energy of fusion of a crystal with a unit volume and σ_e and σ are the end-face and lateral surface free energies of the nucleus respectively. In order to take into account the contribution of an electric field with a strength E_0, a modified Guggenheim approximation was used. The free energy function $F(T, V, E_0)$ assumes the following form for the formation of a crystalline nucleus with a volume V_c and a permanent polarisation P_0:

$$\mathrm{F}(T, V, E_0) = \mathrm{F}_0(T, V) - V_c P_0 E_0 - \frac{V_c \varepsilon_0 \varepsilon E_0^2}{2}\,. \qquad (7)$$

where ε is the relative permittivity of the system. Experiments designed to investigate the Kerr effect in PVDF demonstrated a weak orientation of the chains in an electric field. On this basis, it was assumed that the induced polarisation is much smaller than the permanent polarisation. Taking this into account, the authors[224] concluded that there is a large difference between the nucleation processes in an electric field for particles with polar and nonpolar phases. The overall free energy equation for crystallisation in nonpolar (α) and polar (γ) phases subjected to a field is

$$\Delta F = -NAL(\Delta f + PE_0) + 2NA\sigma_e + 2L\sqrt{NA\pi\sigma}. \qquad (8)$$

For the α phase, in which the permanent polarisation is zero, P has the significance of the induced polarisation P_i:

$$P = P_i = \varepsilon_0 \varepsilon_a \frac{(\varepsilon_c - \varepsilon_a)}{(\varepsilon_a + \varepsilon_c)} E_0\,. \qquad (9)$$

For the polar γ phase, one should consider, for the reason stated above, only the permanent polarisation P_p, which is linked to the polarisation of the crystal P_c and the relative permittivities of the crystal (ε_c) and the melt (ε_a) by the relation

$$P = P_p = \frac{2\varepsilon_a}{\varepsilon_a + \varepsilon_c} P_c\,. \qquad (10)$$

By differentiating Eqn (10), it is possible to find the values of the critical parameters: the concentration N_e^*, the size L_e^* and the free energy of formation ΔF_e^* of a nucleus with the critical size in an electric field. For temperatures which are not far below the equilibrium melting point T_m^0 the expression for ΔF_e^* is

$$\Delta F_e^* = \frac{\Delta h \Delta T}{T_m^0}\,,$$

where Δh is the enthalpy of fusion and $\Delta T = T_m^0 - T$ is the degree of supercooling.

Taking into account all the above considerations, the rate of nucleation J_e may be found from the equation

$$J_e = K' \exp\frac{-U_0}{k(T - T_\infty)} \exp\frac{-\Delta F_e^*}{kT}\,, \qquad (11)$$

where K' is a constant, U_0 is the activation energy for the transfer of the species comprising the nucleus (1.5 kcal mol^{-1}), and $T_\infty = T_g - 30$ K.

For analysis, it is more convenient to use the relative change in the rate of nucleation in a field (J_e) and in its absence (J_0) rather than Eqn (11). Such relations (in terms of semilogarithmic coordinates) as a function of field strength for different degrees of supercooling ΔT are presented in Fig. 22. In particular, it is seen that the effects of the field on the crystallisation of the polar and nonpolar modifications of PVDF are different. Whereas the field intensifies nucleation in the γ phase, and to a more significant extent for lower degrees of supercooling, the opposite effect is observed for the α phase (with a nonpolar cell). The theory developed has been confirmed qualitatively by the results of experiments[203,212] and investigation[225]. According to the data obtained in the last study, the application of a 0.1 MV cm^{-1} field during crystallisation does indeed accelerate significantly (for the same crystallisation temperatures) the rate of formation of the γ phase, 100% conversion being achieved already at temperatures of ~165 °C. The field alters significantly also the form of the dependence of the total degree of crystallinity (taking into account the α and γ phases) on the crystallisation temperature.

However, the theoretical ideas which have been developed do not account for a series of new experimental relations. Thus it has been observed[225] that the morphology arising in PVDF specimens crystallised in high fields and at high temperatures is not homogeneous along the film area. Indeed, the spherulites which have appeared during crystallisation at different depths differed both in size and birefrigence, on the one hand, and in concentration, on the other. We may note that the sign of the potential on the electrode is an important factor for the formation of crystallites. For example, near the positive electrode the nucleation density is always greater than in the vicinity of the negative electrode. in the light of the theory developed, the latter factor should be most probably attributed to the fact that the permanent polarisation in the vicinity of the positive electrode is always greater than near the negative one.[226] Direct observations of the crystallisation process have shown[225] that the role of the field does not reduce to the direct inhibition of the rate of formation of the α phase, as predicted by the theory.[224] The decrease in the number and

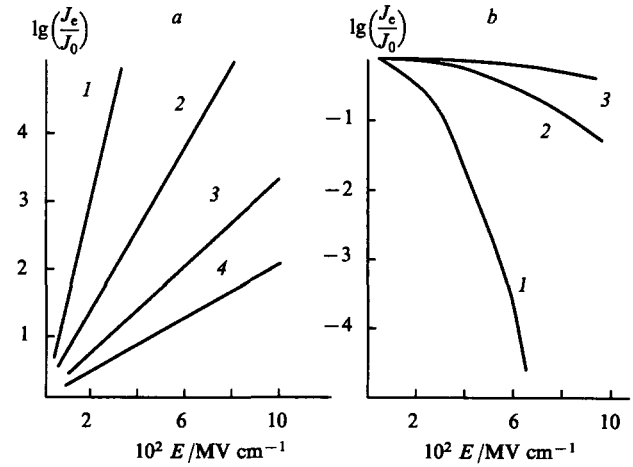


Figure 22. Dependence of the relative change in the rate of nucleation with and without the application of the field with different degrees of supercooling for the γ phase (*a*) and the α phase (*b*).[224]
ΔT (°C): *a*: (*1*) 30; (*2*) 40; (*3*) 50; (*4*) 60; *b*: (*1*) 5; (*2*) 10; (*3*) 15.

average size of the α spherulites occur as a result of the acceleration of the processes involving the crystallisation of the γ phase spherulites. It has also been noted that, whereas in the absence of the field γ spherulites of approximately equal size are obtained, crystallisation in a field lowers the above homogeneity. The intensity of the depolarisation in the scatterred light pattern is also reduced, which has been attributed to the disturbance of the radial disorder of the *b* axes of the γ phase crystallites in the spherulite under the influence of the field. The fact that disc-shaped spherulites in which the radial direction is in the plane of the film arise near the negative electrode indicates that the field affects not only the processes involving the formation and growth of the nuclei but also the secondary crystallisation processes accompanied by the formation of a supermolecular structure.

This conclusion agrees with the results of a study[227] which confirms, in particular, the theoretical conclusion[224] that the field has an inhibiting effect on the crystallisation of the α phase. However, results which cannot be predicted by the theory have been obtained for γ phase crystals. For example, it has been observed that the nature of the morphology generated may depend significantly on the configuration of the electrodes. An increase in the rate of growth of γ spherulites under the influence of the field has been observed only for direct contact between the specimen and both electrodes. In contrast to the results of Marand et al.,[224] disc-shaped γ spherulites were formed near the positive electrode. Experiments on crystallisation, where one or both electrodes were blocked, showed that such conditions affect appreciably the nature of the morphology produced. Apparently, this can be most reasonably explained by the appearance of local electric fields, arising due to the injection of carriers from the metal into the polymer and captured by traps in the latter.

The VDF/TrFE copolymer exhibits ferroelectric properties most distinctly. The structural transformations in an electric field as a function of the number of triangular pulses applied to the specimen have been investigated for this polymer.[228] The amplitude value of the field strength was 160 MV m^{-1} and the pulse frequency was 0.001 Hz. For an isotropic specimen crystallised as a mixture of the α, β, and possibly γ phases, a virtually complete $\alpha \rightarrow \beta$ transition was observed after only 6–8 pulses and the residual polarisation and the coercive field also attained the equilibrium values. Comparison of the temperature variations of the principal reflections from two polarised specimens in the same investigation made it possible to reach an important conclusion concerning the role of the morphology in the stability of the structure formed under the influence of the field. Isotropic and uniaxially extended specimens were compared, the nature of the X-ray diffraction by both being identical. The former crystallised with formation of thick lamellar crystals with a thickness of ~0.1 μm, while in the latter a typical fibrillar morphology with the usual (~100Å) longitudinal dimensions of the crystals was observed. For isotropic specimens, the principal 200, 110 reflection of the β phase remains constant up to ~150 °C, while for the oriented specimen its intensity begins to change appreciably above 70–80 °C. The above differences have also been confirmed indirectly: the higher piezoelectric constant *d* of the oriented specimen shows that the nature of the structural changes following the application of mechanical loads differs significantly for the isotropic and textured polarised films.

The nature and dynamics of the domain structure were elucidated for the same copolymer (with the composition 65/35) by determining on the real time scale the changes in the structural characteristics during the ferroelectric switching of the specimen.[229] The influence of the poling field strength, primarily on the size of the β phase crystallites and on their perfection, has been tested in relation to the oriented specimen. For this purpose, the integral widths (*B*) of the 110, 220 and 330 reflections, i.e.

$$B = \frac{1}{L_{110}} + \frac{(my)^2 m^2}{d_{110}}, \qquad (12)$$

were estimated for three specimens obtained by polarisation in 60, 90, and 200 MV m^{-1} fields. Here L_{110} is the transverse dimension of the crystallite in the direction of the normal to the 110 plane, *m* is the diffraction order, $y = <d_{110}>/d_{110}$ the degree of defectiveness of the second kind in the crystal, and d_{110} the interplanar spacing.

The analysis showed primarily that the main contribution to *B* comes from the size of the crystallite, which increases from 19 to 39 nm in the field change indicated above. The defectiveness of the crystal was within the limits of 3% and tended to decrease somewhat on poling. Data on the dynamics of the structural changes in the transpoling of a nonoriented specimen, obtained on the real time scale, are valuable and unique. The increase in the electric displacement on switching the poling is accompanied by characteristic changes in the parameters of the 110 reflection of the polar β phase (Fig. 23). The intensity of the reflection at the maximum as well as its integral intensity at the characteristic time pass through a minimum, while the integral width passes through a maximum. Evidently, the parameters of the above reflection vary within the limits of several per cent and in a number of

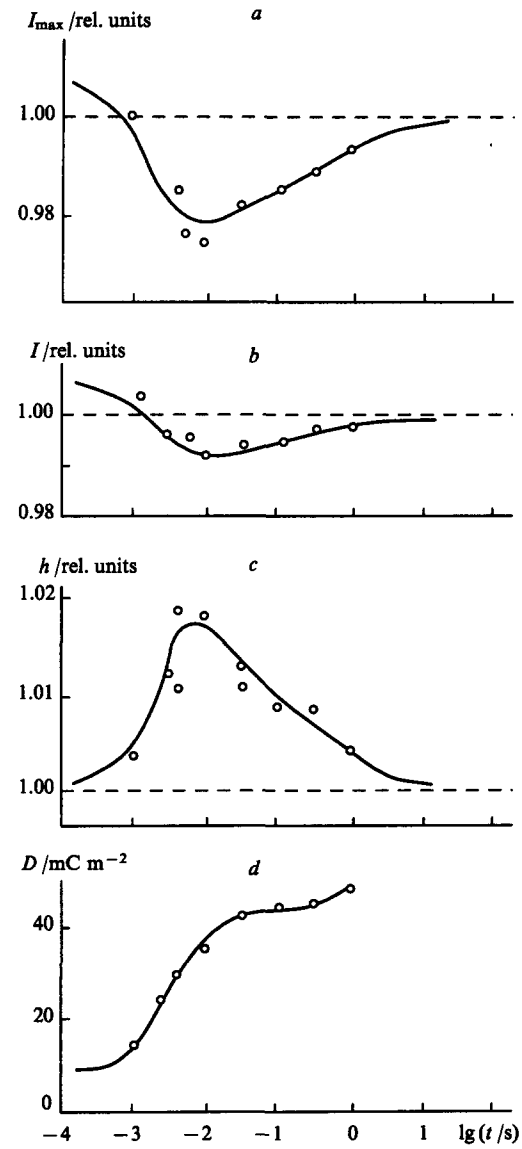


Figure 23. Time variations of the intensity of the maximum (*a*), the integral intensity (*b*), the width (*c*), and the electric displacement (*d*) of the 110 reflection during the switching of the poling of the VDF/TrFE copolymer.[229]

instances their monotonic variation may be observed. The latter presupposes a large contribution to processes responsible for the characteristic features of the supermolecular structure. The nature of the change of the integral intensity indicates the 180° rotation of the chains on transpoling of the specimen, in contrast to the 60° model which is frequently employed.

The new reflections observed by Servet and Rault [230] and later also by Newman and Scheinbeim [231] and Weinhold et al.[232], which could not be indexed in terms of the lattices of any of the known polymorphic transformations, are important for the understanding of the details of the mechanism of the structural transformations in PVDF under the influence of strong electric fields. more detailed study showed [233] that the reflections of the new superlattice in a specimen with the polar α phase are located in the vicinity of the reflections characteristic of the β form: 110, 200, 001, and 111, 201.

We discussed above a series of results indicating the existence in the α phase of kink bonds, which are detected from the characteristic features of the scattering in the vicinity of the reflections mentioned above. Taking this into account, the hypothesis was put forward that the reflections from the superlattice are reflections from ordered regions formed by aggregates of the kink bonds. Thus the new form is intermediate between the polar modification of the α phase and the β phase in the course of the field-induced type $\alpha \rightarrow \alpha_p \rightarrow \beta$ transformation. Calculations showed that the probability of intramolecular rearrangements on formation of the new form may depend significantly on the parity of the number of bonds n passing to the 'planar zigzag' conformation when the conformational defects noted above are formed. As an example, one may consider two schemes of transformations for even and odd values of n:[233]

...$TG\overline{T}G\overline{T}G\overline{T}G\overline{T}G\overline{T}G\overline{T}G$...
...$TTTG\overline{T}G\overline{T}TTG\overline{T}G\overline{T}TTG$...
1

...$TG\overline{T}G\overline{T}G\overline{T}G\overline{T}G\overline{T}G\overline{T}G\overline{T}G$...
...$TTTTTG\overline{T}G\overline{T}TTTTG\overline{T}G\overline{T}TTT$...
2

It may be said that the transformation in accordance with Scheme 2 should take place preferentially compared with Scheme 1. Indeed, whereas the rearrangements in the second scheme are effected as a result of transitions of G or $\overline{G}$ bonds to T bonds, in Scheme 1 there are in addition the transitions $G \rightarrow \overline{G}$ and $\overline{G} \rightarrow G$, which require the cooperative motion of the entire chain. Fig. 24 presents two variants of the chain conformations (with an odd number of bonds in the repeat unit) for the new form. The presence of chain sections with the $GT\overline{G}$ conformation between the bonds in the 'planar zigzag' conformation makes it possible to regard the polar β phase and the new modification as conformationally incommensurable. Fig. 24 shows that two features are characteristic of the above superlattice. Firstly, the identity period along the axis of the macromolecule is found to be greater than for the β phase with the 'planar zigzag' conformation. Furthermore, the appearance of a definite tilt angle for the axes of the macromolecules forming the triclinic lattice is characteristic of this superlattice.

Partly crystalline polymers, including PVDF, are known to have a heterogeneous structure. The presence of a large volume fraction of a nonordered phase complicates the molecular mechanism of the structural rearrangements in PVDF under the influence of strong electric fields. The elucidation of the role of the amorphous phase and of its microstructure in the above phenomena should be the subject of separate investigations. A series of experimental results indicating the nontrivial role of the microstructure in the changes occurring under the influence of a field are presented below. The paper of Sen et al.[234], who described a study of the influence of added plasticiser (tricresyl phosphate) on the nature of the field-induced structural transformations, should probably be regarded as the first communication of this kind. Despite the fact that the plasticiser molecules should be

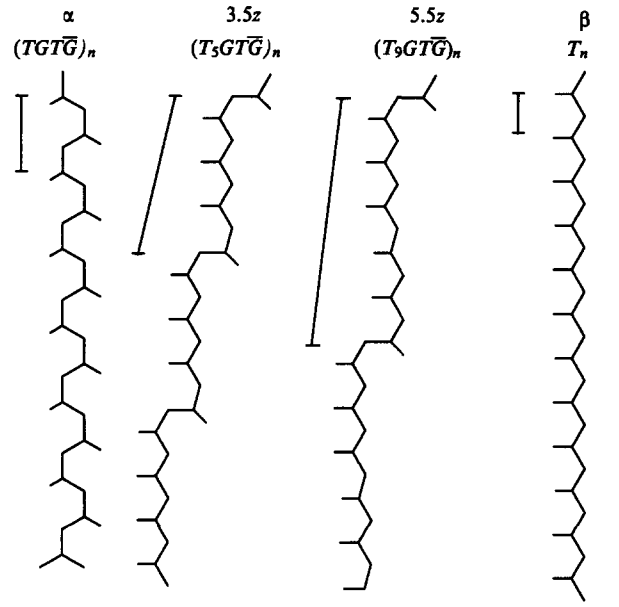


Figure 24. Molecular models for the conformations of the chains in the PVDF superlattice.[233]

located predominantly in regions with an increased free volume, i.e. in the amorphous phase, it was found that the plasticiser influences significantly the characteristics of the polymorphic transition which occurs particularly in the crystalline regions. In plasticised PVDF, the $\alpha \rightarrow \alpha_p \rightarrow \beta$ transitions occur in the presence of appreciably lower fields than in the nonplasticised polymer. As a result of this, the fraction of the β phase formed in the plasticised PVDF is found to be higher almost by a factor of 2 under the same polarisation conditions. The accompanying increase in macroscopic characteristics such as the residual polarisation and the relative permittivity leads also to higher values of the piezoelectric constants d_{31} and e_{31}. A qualitatively similar result has been obtained also in a study [235] where the plasticiser for PVDF was poly(ethylene glycol).

Direct evidence for the important role of the nonordered phase in the strong field-induced structural transformations has been obtained in a study [160] where uniaxially extended VDF/TFE 94/6 copolymer films were investigated. It was shown that, in the presence of high fields, hysteresis-type electric displacement and switching current curves arise for the films. These characteristics for two films with draw temperatures of 60 and 140 °C (for the same draw ratio $\lambda = 4$) may be compared in Fig. 25. Evidently, the remanent electric displacements (as well as their maximum values) differ appreciably. The current hysteresis curves also differ significantly. Structural studies have shown that the above copolymer forms the β modification with the 'planar zigzag' conformation under the usual crystallisation conditions.[32, 160] However, taking into account the increased concentration of bonds in the $TG\overline{T}G$ and $T_3GT_3\overline{G}$ conformations of films oriented at high draw temperatures,[160] one may assume that the difference between the current hysteresis curves is caused by the characteristic features of the microstructure of the amorphous regions. This confirms the small angle X-ray diffraction curves (in the meridional direction) for the same films (Fig. 16). The higher intensity of the maximum for films with an increased draw temperature is most probably due to the greater difference between the densities in the amorphous and crystalline regions. If the β modification is produced in all the films, then the foregoing finding must be attributed to the less dense packing of the amorphous regions along the direction of stretching. The characteristics of the microstructure of the amorphous region affect the remanent and maximum electrical displacement for field strengths in excess of the critical values, where a remanent poling appears (Fig. 25). The

Table 16. Physical characteristics of the VDF/TFE 94/6 copolymer films uniaxially oriented up to the draw ratio $\lambda = 4$ at different temperatures.[160]

T_d /°C	R at different frequencies /cm^{-1}				L /Å	l /Å	n/N
	470	490	508	600			
60	17	1.8	3.4	3.0	88	78	
80	15	1.7	3.3	2.9	120	84	0.102
100	14	1.6	3.1	3.1	189	98	0.082
120	7	1.2	2.3	2.6	221	113	0.049
140	6.7	0.8	2.1	1.4	189	102	0.049

Note. The following notation has been adopted: R — dichroic ratios for a series of specific IR bands; L — long period of the crystal; l — longitudinal dimension of the crystal; n — number of chains per unit area in the amorphous phase; N — ditto in the crystal.

increased response to the external field depends significantly on the degree of orientation of the chain in the amorphous regions (Table 16).

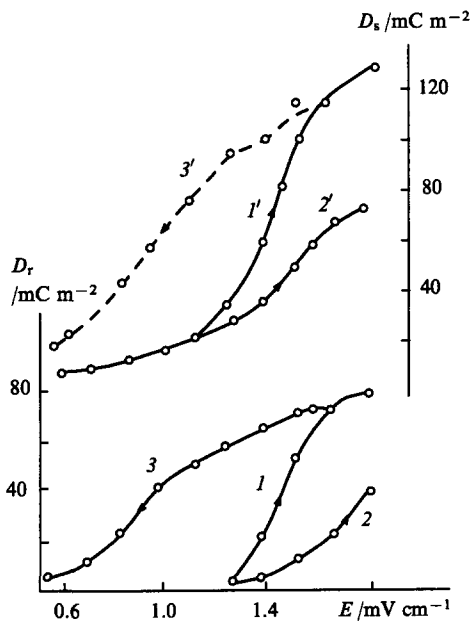


Figure 25. The field dependences of the remanent ($1-3$) and maximum ($1'-3'$) electric displacements for films of the VDF/TFE 94/6 copolymer uniaxially oriented at 60 °C ($1, 3, 1', 3'$) and 140 °C ($2, 2'$).[163]

The dichroic ratios at frequencies of 470, 490, and 600 cm^{-1} are attributed only to the amorphous phase, whereas at a frequency of 508 cm^{-1} they are believed to be due to the 'planar zigzag' conformers in both phases. Evidently the increase in T_d leads to a decrease in R for all the frequencies specified. At the same time, this is accompanied by an increase in the size of the amorphous gaps obtained in the form of the difference between the long period and the longitudinal size of the crystal.

The decrease in size between neighbouring crystallites is accompanied by an increase in the number of stressed chains passing through them [tie-tough-chains (TTC)], which is indicated by acoustic relaxation data.[129] At the polarisation temperature (in our case, this is 20 °C), the amorphous regions are in the rubber state, i.e. their compliance is an order of magnitude higher than in the crystalline phase. This means that the polar chains of the amorphous phase should respond in the first place to the increase in the external field strength. The presence of 'planar zigzag' conformers, for which the transverse component of the dipole moment is greater than for the $TG\overline{T}G$ and $T_3GT_3\overline{G}$ conformations because the field strength vector is perpendicular to the surface of the film, is of great importance in this connection. The TTC regions may play a very important role in these phenomena, since the same chain may enter into both regions mentioned above and into the β phase crystal itself. As a result of this, the rotations in the TTC chains arising under the influence of the field should be transmitted also to the chains of the crystal, leading ultimately to their reorientation as a whole.

Thus the response in textured films of PVDF and its copolymers may be intensified by bringing them closer to the texture of the 'ideal single crystal'. As has been seen, this requires a decrease in the conformational heterogeneity along the chain, an increase in the size of the noncrystalline regions, and an increase in the fraction of the TTC within them.

Special attention must be given to the role of the texture in the materials investigated. The creation of a definite texture in films of the VDF/TFE 94/6[236] and VDF/TFE 71/29[237] copolymers, which can be characterised by the average orientation, promotes a decrease in the coercive fields and an increase in the residual polarisation. The reason is probably that, when a texture is formed, there is a tendency for the arrangement of the axes of the macromolecules in the plane, which facilitates the interaction of the field with the transverse component of the dipole moment, rigidly linked to the main chain.

The role of the amorphous phase in ferroelectric response phenomena can also be seen in relation to isotopic films. A common feature has been observed in the copolymers having the above compositions. For films with a lower degree of crystallinity (this was inferred from the densities and relative permittivities) lower coercive fields and hence greater remanent pollings were noted.[160,237] This was attributed to the greater compliance of the amorphous phase chains and to the initiation of the intrinsic ferroelectric polarisation in the neighbouring β phase crystals.

VII. The influence of irradiation on the structure of poly(vinylidene fluoride) and its copolymers

The structural-chemical transformations in PVDF have been investigated by spectroscopic methods.[238] It was shown that an increase in the radiation dose promotes the accumulation of both vinyl $-CH=CF_2$ (1715 cm^{-1}) and vinylidene $>C=CF_2$ (1750 cm^{-1}) groups. Radiation-chemical processes occur more often on irregularities than on ideal chains. Branches and 'head to head' defects are included among the former. The fraction of irregularities was estimated from high-resolution NMR spectroscopic data. At least two types of radicals, detected in the oriented PVDF specimens, may correspond to the α and β modifications present in such specimens. The appearance of intermediate species (carbonium ions), which are manifested in the form of luminescence peak on the temperature curves of radiothermoluminescence has also been detected.

According to empirical rules, chain rupture reactions should predominate on irradiation in polymers with a structure of the type $(-CH_2CR_1R_2-)$; on the other hand, mainly cross-linking has been noted in PVDF chains. The ratio of the probabilities of scission and cross-linking steps on γ-irradiation has been esti-

mated as 0.35, which leads to an increase in the gel fraction to 0.7 rupture for a dose of 10 Mrad.[239] The hypothesis[238] that the dissociation and cross-linking reactions are linked, which should be associated with the migration of a radical centre (charge) along the chain to the location of the irregularity, has also been confirmed by a study[240] of the irradiation of PVDF by accelerated electrons. The sequences of another comonomer can also serve as irregularities of this kind. Therefore, an increase in the gel fraction in the copolymer of VDF and hexafluoropropene compared with the homopolymer confirms qualitatively the above hypothesis. Additives promoting the formation of a three-dimensional network also play a significant role in cross-linking processes on irradiation. This can be inferred from the increase (other conditions being equal) in the gel fraction following the introduction of a sensitiser into the irradiated PVDF.[240,241]

The form of the energy-carrying species is important for the processes occurring on irradiation. For example, comparison of data concerning the influence of irradiation by electrons and protons on the strength characteristics of PVDF indicates a significant difference between them. It was observed that, in order to reduce the relative elongation at break by a factor of 2, a proton flux smaller by a factor of ~ 20 than the electron flux is needed.[242] These results are related to the data obtained in a study[239] where it was shown that irradiation of PVDF with γ-rays and α-particles leads to a significant difference between the initial free radicals formed. The kinetics of the recombination of such radicals also differ significantly: in the case of γ-rays, the radicals begin to recombine already above 77 K, whereas under the conditions of α-irradiation, the radicals are stable up to 240 K. The dependence of the concentrations of the above radicals on the irradiation dose shows that fast recombinations takes place immediately in the region of the tracks formed along the paths traversed by the particles.

The nature of the radiation damage in the case of helium ions may depend significantly on the energy of the incident particles (for the range 0.4–4.5 MeV).[243] For an energy of 0.4 MeV, the helium ions, which have a path length of only 27 μm, are responsible for an 86% decrease in crystallinity relative to the initial value, while the solubility of the irradiated specimen is reduced by 76%. Such changes in characteristics have been attributed to the probability of the formation of a hydrogen atom, which may rapidly diffuse in space.

By following the dielectric relaxation process associated with micro-Brownian motion in the amorphous regions of PVDF, it is possible to refine the nature of the radiation-chemical transformations and their location. Thus a decrease in the intensity of the above process for irradiation doses of 30–40 Mrad suggests that cross-linking occurs in the amorphous regions, which results in the creation of a definite steric hindrance to the reorientation of a chain segment.[244,245] The possible appearance of polyene chains may give rise to an increase in the intensity of the process under consideration for lower irradiation doses.[245] It is believed that the cross-links appearing on irradiation may be located not only in particularly nonordered regions but also on the surfaces of lamellae, since an increase in the irradiation dose lowers the intensity of the α-process associated with motion in crystalline regions.[245] The observations of irreversible changes in dielectric losses are of interest. After the cessation of irradiation, the latter return to the initial values.[244] This phenomenon may be associated with the accumulation of carriers, which may than fall into deep traps.

Studies on the structural changes occurring in PVDF and its copolymers on irradiation began as early as the beginning of the 1980s but developed to a greater extent only in the last 15 years. One may name a large number of studies in which it has been shown that the degrees of crystallinity α of a series of polymers increase for low irradiation doses.[246–253] This behaviour is common to crystallising polymers, including PVDF.[254,255] The nature of the above phenomenon has not been discussed by the authors of the studies mentioned, so that analysis of the conformational changes in the chains of PVDF during its irradiation may 'throw light' on this effect.[256,257] On γ-irradiation in air of uniaxially and biaxially extended films of the PVDF homopolymer, a weakening of the intensities of the bands associated with the $TGT\bar{G}$ conformations and, conversely, the intensification of a series of bands corresponding to the 'planar zigzag' conformation were observed.[256,257] This occurred predominantly in the range of irradiation doses up to 50 Mrad, i.e. in the region where an increase in the degree of crystallinity has also been noted. The radiation-induced conformational rearrangements in PVDF chains were most probably located predominantly in amorphous regions of the polymer, since the intensities of the bands attributed to the nonordered phase changed most significantly. This follows from the fact that, after irradiation at a dose of 30 Mrad, the intensity of the 470 cm^{-1} band increased appreciably at the expense of the weakening of the 490 cm^{-1} band. These bands are attributed to the 'planar zigzag' and $TGT\bar{G}$ conformations of the PVDF chains in the nonordered regions.[257] The above finding therefore indicates the possibility of conformational rearrangements on irradiation. For a biaxially oriented film, this effect is due to the most marked.[256] The intensity of the 600 and 740 cm^{-1} bands, due to the particular amorphous regions in PVDF, decreased after irradiation, which agrees with DSC data.[256,257]

The above results are to some extent correlated with the conclusions reached in studies[258,259] in which structural changes in irradiated PVDF specimens were recorded by the X-ray method. The authors of these investigations observed a series of interesting effects due to the influence of large irradiation doses. For example, it was shown that powders are more resistant to irradiation than the film prepared from them, which was accounted for by the role of oxygen. For specimens in various polymorphic forms, an increase in the irradiation dose was accompanied by a decrease in the order characteristics. However the stability of the β modification proved greater than that of the α modification. Whereas the initial specimens crystallised as the α form, at doses of 500–600 Mrad the $\alpha \rightarrow \beta$ polymorphic transition took place.

The significant differences between the irradiation doses inducing structural changes found by Kosmynin and Gal'perin,[258,259] on the one hand, and a number of other workers,[254–257] on the other, can be explained by the fact that in the latter the changes concern predominantly the nonordered regions (or regions adjoining the crystal), whereas in the former the crystals proper were considered.

In the case of VDF copolymers with small amounts of added TFE, the trend in the structural changes on irradiation becomes similar to that for the homopolymer. This is confirmed by the nature of the changes in the diffractometer traces for isotropic specimens of the VDF/TFE 94/6 copolymer after irradiation with doses up to 10 Mrad.[115,116] After irradiation,the intensity of the 001 and 210, 111 reflections increases, since the order in the above directions is 'improved'. The broadened reflection at $2\theta = 18°$ is due to the presence of highly disordered paraelectric phase in the initial specimen. Therefore the decrease in the intensity of the above reflection after irradiation can be explained by the partial paraelectric–ferroelectric transition. More significant changes in the structures of the above copolymers have been observed in uniaxially extended specimens for which X-ray photographs were taken in the meridional direction. The intensity of the amorphous halo, adjoining the 001 reflection, decreased significantly after irradiation under these conditions. These results are qualitatively correlated with DSC and IR spectroscopic data.[254–257]

The initial copolymer specimens may be crystallised in a definite metastable state where the crystalline phase consists mainly of the paraelectric α phase[117,118] characterised by the 020, 110, and 021 reflections. The structural changes in the copolymer with increase in the irradiation dose are shown in Fig. 26. For the initial specimen, the intensity of the 110, 200 reflection due to the ferroelectric β phase present was found to be appreciably lower than that of the 110 reflection due to the α

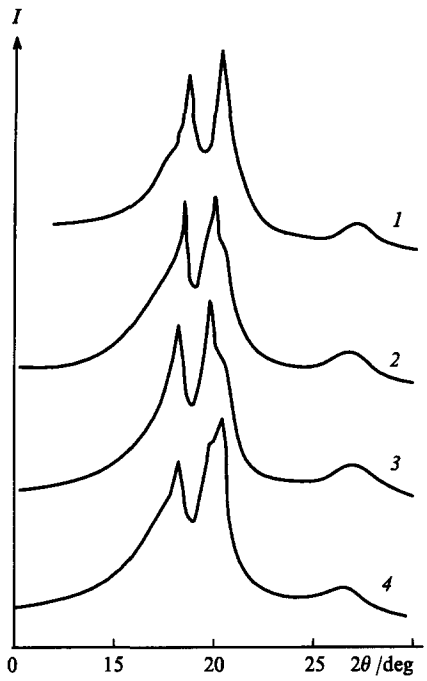


Figure 26. Dynamics of the variation of the diffractometer traces for *isotropic metastable films of the VDF/TrFE 94/6 copolymer after* γ-irradiation.[115,116]
Irradiation dose (Mrad): (*1*) 0; (*2*) 1; (*3*) 10; (*4*) 48.

phase, where former is manifested by the presence of a shoulder (on the side of larger angles) for the latter reflection. With increase in the irradiation dose, the intensity of the β phase reflection rises and for a dose of 10 Mrad, the reflection is fairly well resolved as a consequence of the decrease in the half-width. On the other hand, the increase in the dose to 40 Mrad leads to the equalisation of the intensities of the above reflections due to the α and β phases, which is manifested by some broadening of the resolved doublet. At high irradiation doses, changes were noted also in the region of the 020 reflection ($2\theta = 18.4°$) due to the α phase, where together with the latter a broadened halo arises, indicating the appearance of perturbations in the paraelectric phase. In conformity with the foregoing and also in view of the increase in the intensity of the intramolecular 201, 111 reflection due to the ferroelectric β phase, one may infer the radiation-induced $\alpha \rightarrow \beta$ transition.[115,116]

The mechanism of the above structural transformations in PVDF and its copolymers with TFE is most probably determined by the ferroelectric nature of these polymers. The nature of the changes in the 470 and 490 cm^{-1} absorption bands for the uniaxially extended PVDF after irradiation agrees with those for the film after treatment in a corona discharge.[257] In the latter case, the above conformational changes of the type $TGT\overline{G} \rightarrow (TT)_n$ occur under the influence of the field, including the field generated by the surface layer of the injected charges and charges captured by deep traps. The irradiation of PVDF is accompanied by an appreciable increase in the dielectric loss factor, which can be accounted for, with a high degree of probability, by the appearance of additional free carriers.[244] Bearing in mind the high penetrating capacity of γ-radiation, their concentration is on average the same throughout the volume, in contrast to the charges in the corona polarisation of PVDF, which are located predominantly on the surface of the film. The decrease in the conductivity of the PVDF films after the cessation of irradiation may be associated with carrier recombination processes. However, bearing in mind their low mobility, capture by deep craps must be regarded as a more likely cause. In the case of the strongly polar ferroelectric β phase crystal, the carriers may be located on charged planes.

Thus local internal fields, sufficiently strong to induce the above conformational transformations, may be generated at these sites. If one begins with this mechanism, then the location planes (in isotropic specimens) are 201, 111, since the intensity of the reflection from them changes most significantly.

The structural transformations under discussion may occur via an epitaxial crystallisation mechanism where sequencies of the chain in the $TGT\overline{G}$ conformation, undergoing a transition to the 'planar zigzag' conformation, may undergo additional crystallisation, producing neighbouring regions of the ferroelectric β phase. This mechanism is supported by spectroscopic data, according to which the above conformational transformations are manifested most distinctly in films containing the crystals of the α and β phases.[256,257] Naturally, in structural modification processes account must be taken also of the role of the chemical changes in the PVDF chains on irradiation.

As mentioned above, the advantages of the cross-linking processes occurring in the amorphous regions have been confirmed both by the nature of the decrease in the intensity of the dielectric absorption for the micro-Brownian motion in the amorphous regions[245,260] and by the decrease in the coefficient of thermal expansion of the lattice in the *a* and *b* directions in the cell.[261] However, the nature of the morphology, which is extremely variable in such systems, may affect the ratio of the yields of the scission and cross-linking reactions. Analysis of the changes in the mechanical characteristics in PVDF and in its copolymers with TFE on irradiation shows that in the oriented state there is an increase in the fraction of tie-tough-chains in the amorphous phase, in which degradation reactions should predominate although the polymer as a whole may remain in the cross-linked state.[262] The above significant change in the ratio of the intensities of the amorphous halo and of the 001 reflection after irradiation of a uniaxially extended specimen of the PVDF copolymer also confirms the hypothesis put forward. Indeed, the scission processes on the TTC should facilitate the thermal motion processes in the remaining fragments, as a result of which they may be incorporated in the neighbouring crystals of the β phase, increasing their size and perfection in the direction of the 001 plane.

Copolymers of VDF with TFE in which the fraction of the latter comonomer is low and its chemical structure is similar to that of PVDF were considered in the studies quoted above. This may explain the similarity of the behaviour on irradiation of the above copolymers and PVDF.

Another object for which radiation-induced physicochemical changes have been studied in detail is the copolymer of VDF with trifluoroethene. In contrast to TFE, the latter has a structure differing appreciably from that in the homopolymer. It may be that this factor is one of the reasons why these copolymers behave differently from the homopolymer and the VDF/TFE copolymer.

On γ-irradiation of the VDF/TrFE 65/35 copolymer, it was observed that an increase in the dose is accompanied by the impairment of the structural characteristics.[263] Thus irradiation with a dose of 120 Mrad at room temperature of a specimen consisting of the ferroelectric phase leads to its transition to the paraelectric state, which may be inferred from the shift of the main intermolecular reflection towards lower angles (Fig. 27). If the crystal is in the paraelectric state, irradiation of the specimen is accompanied by significant changes in the initial structure. The ferroelectric–paraelectric transition becomes in this case more diffuse and shifts towards lower temperatures. The latter has been noted also on irradiation of these copolymers by accelerated electrons.[264]

The results of experiments[265–268] for the same copolymer but with the composition 70/30 indicate a qualitatively similar conclusion. Irradiation of thin films (7 μm) with a beam of electrons having an energy of 100 keV leads to a smooth displacement of the Curie point with increase in the irradiation dose towards lower temperatures, which, however, are always found to be higher than the glass transition temperature.[265] The

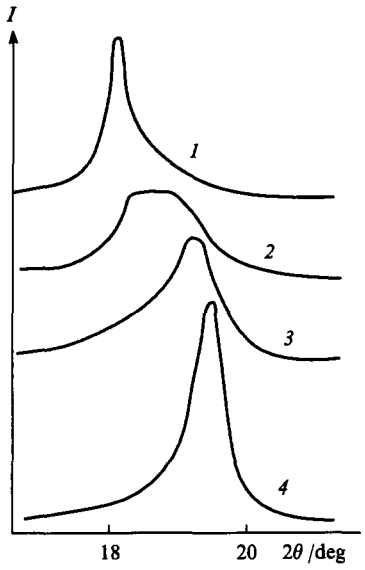


Figure 27. The nature of the variation of the profile of the 200, 110 reflection due to the ferroelectric phase on γ-irradiation of the VDF/TrFE 65/35 copolymer.[263]
Irradiation dose (Mrad): (*1*) 120; (*2*) and (*3*) 60; (*4*) 0; (*1*), (*3*) and (*4*) irradiation at room temperature; (*2*) irradiation at 120 °C.

experiments failed to confirm the conclusion [263] that more intense processes, leading to the impairment of order, take place when the crystal is in the paraelectric phase. According to the temperature dependence of the internal friction, accelerated electrons convert the copolymer into the amorphous form and lead to the accumulation of defects in the crystallites.[267]

The last conclusion has been confirmed also by X-ray diffraction data, which showed that an increase in the irradiation dose induces a decrease in the packing density in both the paraelectric and ferroelectric phases of the copolymer.[266] At the same time, it was established that, for the same irradiation dose, more significant changes are noted for the paraelectric phase. A new phenomenon has been observed: an increase in the energy of electrons (from 100 keV to 3 meV) leads, under the conditions of the same irradiation dose, to less significant decrements in the melting and Curie points. It is believed that electrons with a higher energy cause the preferential conversion of the copolymer into an amorphous form, whereas particles with a lower energy are mainly responsible for specific defects within the crystals. The decrease in the average size of the crystallite, noted in such processes, is not the main cause of the decrease in the melting and Curie points.[268] The process involving a decrease in the energy of the dipole interactions as a result of the increase in the concentration of the double bonds and carbonyl and other new groups arising on irradiation is believed to be more important. The decrease in the melting and Curie points with increase in the irradiation dose is fairly well described by a model taking into account the decrease in the internal pressure.[268,269]

Thus one may see a significant difference between the radiation-induced structural changes in the VDF homopolymer and in the VDF/TrFE copolymer, on the one hand, and in the VDF/TrFE copolymers, on the other. One of the reasons for this may be associated with the chemical structure of the TrFE unit (CH_2CFH), which, in contrast to the TFE unit (CF_2CF_2), is 'chemically incommensurate' with the VDF repeat unit (CF_2CH_2). The fact that the glass transition temperatures in PVDF and TrFE (in contrast to PVDF and TFE) differ markedly may be regarded as confirmation of this postulate.

Other causes of the significant differences in behaviour on irradiation of the VDF/TrFE and VDF/TFE copolymers may be associated with the fact that in the former the fraction of TrFE is fairly large (30–35 mol %). A decrease in the latter (to 20 mol %) does not alter the situation fundamentally, since radiation-induced conformational rearrangements of the type $(TT)_n \rightarrow TGT\bar{G}$ and $(TT)_n \rightarrow T_3GT_3\bar{G}$ have been noted in such copolymers on irradiation with γ-rays at doses as low as 1–10 Mrad. In the homopolymer, the opposite rearrangements take place.[256,257] Yet another cause of the differences may be that all the VDF/TrFE copolymers were investigated in the isotropic state, whereas the 'anomalous' behaviour on irradiation of the homopolymer and VDF/TFE copolymer was noted in uniaxially or biaxially oriented states. Copolymers in the latter states are known to be metastable systems in which the role of internal stresses may be manifested to a greater extent. It is noteworthy that a more detailed study of the behaviour of the VDF/TrFE copolymers at low irradiation doses is needed.

VIII. Characteristics of the dynamics of the chains in the block state of isotropic and anisotropic poly(vinylidene fluoride) specimens

For the practical employment of PVDF films as the material of the active element in energy transducers, it is necessary to know their stable electrophysical parameters.[3] This requirement cannot be met without the knowledge of the characteristics of the molecular mobility and of the mechanism of the relaxation phenomena in films. Taking into account the high degree of heterogeneity of the test materials, it is possible to obtain from the characteristics of the molecular mobility information about the structural features of the nonordered phase, which frequently cannot be achieved by classical structural methods. In this section, attention is concentrated on the analysis of studies predominantly on the dielectric relaxation of the test materials, since this method has recently undergone a new development and proved very informative in the analysis of the microstructures of PVDF-based blends.

As early as the beginning of the 1970s, when the valuable properties of PVDF for practical purposes were not known, a series of studies of the molecular mobility in PVDF copolymers by the dielectric relaxation method appeared.[270–272] This polymer has a high dipole moment per monomer unit (7×10^{-30} C m) and is superior to others as regards the glass transition temperature. This in fact explains the great early interest in it and the high information content afforded by the dielectric relaxation method. The ferroelectric properties of these polymers, discovered subsequently, led to additional possibilities for the above method.[270] The majority of investigators observed three or four types of molecular motion in these compounds. In the α modification of PVDF crystals, these are always four different forms of motion. The forms of molecular mobility are usually designated as δ, γ, $\beta(\alpha_a)$, and $\alpha_c(\alpha)$.¶

An example of the temperature variations of the real (ε') and imaginary (ε'') components of the complex relative permittivity in PVDF for different electric field frequencies is presented in Fig. 28. The two separate dispersion regions in order of increasing temperature are attributed to $\beta(\alpha_a)$ and $\alpha(\alpha_c)$ relaxations. The lower-temperature regions of the δ and γ mobilities are not seen, but the nature of the variation of ε' and ε'' in them is the same. The generalisation of ideas about the mechanisms of the above types of mobility can be more conveniently begun by the analysis of the mobilities in the low-temperature regions (at temperatures below the glass transition region of PVDF).

According to Sasabe et al.,[274] the γ mobility is described by the Arrhenius equation with an activation energy of 2.1 kcal mol^{-1} and is determined by localised kinetic units. There are two contradictory views concerning the location of such units. Thus, according to Yano,[273] they should be located in the amorphous phase. However, in a later study [275] the contrary claim was made

¶ Here and henceforth double designations for relaxation are given, since in the literature these processes are designated in different ways.

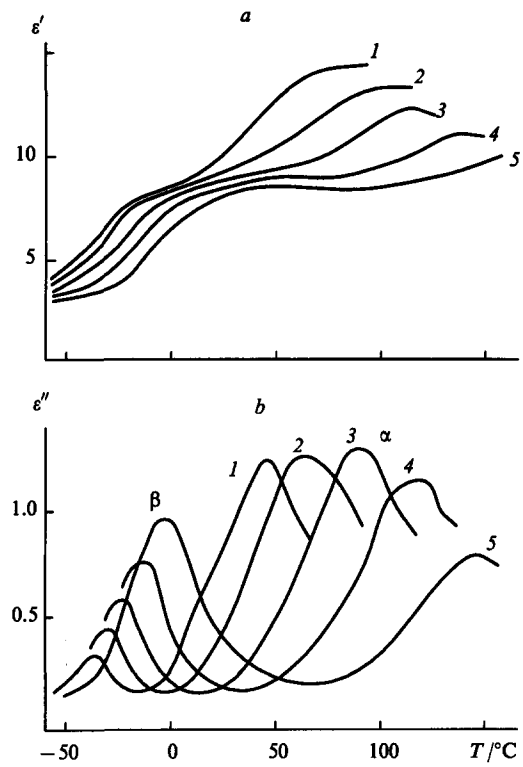


Figure 28. Temperature dependence of the components of the complex relative permittivities ε' (*a*) and ε'' (*b*) in the region of the β and α dispersions of PVDF.[273]
Frequency (Hz): (*1*) 10; (*2*) 100; (*3*) 1000; (*4*) 10 000; (*5*) 100 000.

that they should constitute crystalline regions. This was based on the observation of a single low-temperature γ-relaxation process on VDF specimens in the α modification. The region of the δ mobility is located near 50 K.[276] A detailed study[277] has shown that the δ mobility is due to the defects in the α phase lattice. This conclusion was confirmed by the decrease in the intensity of the δ mobility with increase in the degree of crystallinity as the crystallisation conditions were varied. It is significant that this mobility is generated precisely by the defects in the α phase. In specimens of the VDF/TrFE copolymer, which crystallises as the β modification, the above mobility was not observed.[277]

A similar conclusion was reached in a study[276] where there was no δ process in the PVDF specimens with the β phase obtained as a result of uniaxial stretching. At the same time it was noted that a region of ε relaxation is present in such specimens, occurring at still lower temperatures (~20 K). The activation energy for this process is ~1.9 kJ mol^{-1}, whilst that for the δ process is 12.6 kJ mol^{-1}. It has been shown that poling decreases the intensity of the ε process severalfold. This finding indicates that the ε process is associated with defects in the β phase lattice. The activation parameters for the δ and ε relaxation and the temperature ranges where they are manifested differ significantly, so that the defects in the lattices of the α and β modifications responsible for the mobility under discussion are different.[276]

The curves for the temperature and frequency dependences of ε' and ε'' for one of the VDF/TFE copolymers have been discussed.[278] A characteristic feature of the β relaxation is the increase in the loss factor to a maximum with increase in temperature. The characteristics of this process in the above copolymer are common also to PVDF (Fig. 28) and one may therefore consider them in greater detail.

Analysis of the shape of the above curves shows that they are described satisfactorily by the Williams–Watts equations.[279] The experimental frequency dependences of ε'' correspond to those calculated from the relation

$$\varepsilon' - \varepsilon_\infty - i\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty)\sum_{n=1}^{\infty}(-1)^{n-1}\frac{\Gamma(n\beta+1)}{\Gamma(n+1)}(i\beta\tau)^{-n\beta}, \quad (13)$$

where i is an imaginary number, ε_0 and ε_∞ are the limiting relative permittivities at low and high frequencies, β is the parameter of the distribution of the relaxation times ($1 \geqslant \beta > 0$), $\Gamma(n+1)$ is the gamma function, and τ is the relaxation time. The temperature dependences (in terms of the Arrhenius coordinates) of the frequencies corresponding to the ε'' maxima are not linear and it has been shown[278] that they can be described by a modified Williams–Lundell–Ferry (WLF) equation in the form proposed by Brereton:[280]

$$\lg f_{max} = A + \frac{C_1(T-T_g)}{C_2+(T-T_g)} + \lg\left(1-\frac{T_g}{T}\right), \quad (14)$$

where A, C_1, C_2, and T_g are numerical constants.

The above form of the curve is characteristic of processes occurring in the glass transition of polymer. The dispersion region under discussion should therefore be associated with the micro-Brownian motion of the chains in the nonordered regions. A series of experimental facts may be regarded as confirmation of this conclusion. For example, the intensity of the above process decreases steadily with increase in the degree of crystallinity of PVDF and its copolymers.[273,274,281] The constant T_g in Eqn (14) agrees with the point corresponding to the characteristic break on the temperature dependences of the coefficient of thermal expansion[278] or the specific volume.[281] The significant decrease in the intensity of the micro-Brownian motion of the chains after irradiation[282] may also serve as confirmation of the validity of the assignment of the above process.

Indeed, as shown above, irradiation is accompanied by cross-linking predominantly in the nonordered regions, which should lead to an increase in the steric hindrance to the reorientation of the segments. The enthalpies ΔH and entropies ΔS of relaxation are usually determined from the temperature variations of the relaxation times. For the given process in PVDF with the α phase, ΔH varies from 22 to 41 kcal mol^{-1} while ΔS varies from 50 to 120 e.u. in the temperature range from 3 to −30 °C.[273] Taking into account these values as well as the enthalpy of vaporisation for a monomer unit, equal to 3.8 kcal mol^{-1}, it has been found[273] that the number of repeat units in the kinetic segment is 23.

The presence of crystalline regions in the bulk of PVDF may give rise to a difference in the relaxation behaviour in the vicinity of T_g compared with that in purely amorphous polymers. The significant difference (by almost 30 °C) between the experimental T_g (−38 °C) and its value calculated by the WLF equation (−67 °C), whilst in the amorphous polymers the difference is 5–6 °C, may be regarded as confirmation of this finding. The reason for the appearance of this difference may be that, as the amorphous polymers approach the equilibrium glass transition temperature, the size of the cooperatively rearranged region should approach a microscopic size, whereas in the crystallising polymers it should be restricted to the size of the nonordered region between crystallites. The same anomalies in the glass transition have been explained[280] by the influence of the local field effects (allowance for the correlated motion of dipoles).

In order to discover the reasons for the observed increase in ε''_{max} with temperature in the region of the $\beta(\alpha_a)$ dispersion, Nakagawa and Ishida[283] modelled this type of mobility. It was found that the increase in ε''_{max} mentioned above is associated with the increase in the absorption $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$. It was shown in relation to two specimens (quenched and annealed) that $\Delta\varepsilon$ passes through a diffuse maximum in the temperature range 30–80 °C. General relations yield

$$\Delta\varepsilon = \frac{4\pi N\bar{\mu}^2\xi}{3kT}, \tag{15}$$

where N is the number of repeat units, $\bar{\mu}^2$ the mean square of the effective dipole moment per monomer unit, ξ the local field factor, k the Boltzmann constant, and T the absolute temperature.

Calculation of $\bar{\mu}^2$ on the assumption of an Onsager internal field showed that all its values are higher than μ_0^2 (μ_0 = 1.93 D is the dipole moment of difluoromethane). The quantity μ^2 was expressed in the form $\bar{\mu}^2 = (\bar{\mu}_s^2/n_s)g_n$, where μ_s is the dipole moment of the 'segment' containing n_s repeat units and g_n is the correlation factor. For $g_n > 1$, the correlated motion of neighbouring dipoles takes place in the nonordered regions and in fact may be responsible for the characteristics of the relaxation behaviour in the vicinity of the glass transition region.[280] The passage of $\Delta\varepsilon$ for the β relaxation considered through a maximum is known to be characteristic of order–disorder transitions, in particular of the ferroelectric–paraelectric transformation in the test systems. The latter occurs in the crystalline phase of PVDF and its copolymers. However, the observation of the above dielectric anomalies, for example in highly polar vinylidene cyanide/vinyl acetate copolymers, shows[284] that in the amorphous phase of such systems there may be regions with an intermediate form of order analogous to that observed in polymeric liquid crystals. If it is assumed that a definite proportion of the amorphous phase of PVDF is in the nematic phase, the local nematic–isotropic liquid transition will be accompanied by the dielectric anomalies noted above.

A reasonable interpretation of a large number of new experimental data for crystallising polymers nevertheless requires ideas concerning the existence of regions with an intermediate order. It may be that the detection of the isotropic and anisotropic components of the amorphous phase in the VDF/TFE 94/6 copolymers constitutes a confirmation of the above hypothesis.[115] The above change in the average interplanar spacing in the sections of the anisotropic phase noted above most probably indicates the occurrence of the postulated nematic–isotropic liquid transition.[117] The similar postulated transition in the amorphous component of the PVDF with the α phase is significantly more diffuse and is displaced towards lower temperatures compared with the transition in the VDF/TFE copolymer.[283] This can be explained by the higher fraction in the latter of segments in the 'planar zigzag' conformation than in the VDF homopolymer.

Indeed the modelling of the dynamics of the chains in the amorphous phase of PVDF shows that the best agreement between the calculated and experimental temperature variations of μ^2 is observed only if the neighbouring segments in contact are in the GG or $G\bar{G}$ conformations.[283] If the dipole interactions are decisive in the establishment of the above order, it is possible to find an explanation of the lower transition temperature in the homopolymer[283] compared with the VDF/TFE copolymer.[117,118] When neighbouring segments are in contact, the transverse component of the dipole moment relative to the axis of the macromolecule is limiting. The transverse component of the dipole moment of the segments with the GG and $G\bar{G}$ conformations is known to be smaller than that for the segments with the predominant 'planar zigzag' conformation (as in the VDF/TFE copolymer). Accordingly, the lower energy of the interaction in the former does actually lead to a displacement of the transition under consideration in the homopolymer towards lower temperatures.

Since the packing of the chains in the amorphous phase is less dense than in the crystal, the presence of a free volume in this phase is postulated. The role of the latter for β-mobility processes may be traced, for example, from the significant increase in the relaxation times in the VDF/TrFE 73/27 copolymer with increase in pressure.[285,286] The free volume causes the displacement of the end groups into the amorphous phase and various kinds of chemical perturbations in the .chain (branches, etc.) on crystallisation of PVDF. This can explain the changes in the width of the relaxation times spectrum and in the effective dipole moment per monomer unit in PVDF obtained by the emulsion and suspension polymerisation methods.[62]

As the glass transition temperature is approached, the frequency dependences of ε'' are greatly broadened. The role of the free volume effects in such broadening has been investigated in a series of studies.[287–291] It was postulated that the relaxation time τ obeys the Dolittle equation:

$$\ln\tau = \ln\tau_0 + \frac{1}{f}. \tag{16}$$

Here f is the fraction of the free volume:

$$f = f_0 + \alpha_f(T - T_0), \tag{17}$$

where α_f is the temperature coefficient of the increase in the free volume. Under these conditions, the frequency dependence of ε'' can be described by the function

$$\varepsilon''(\omega) = \int_0^1 \varepsilon_f''[\omega, \tau(f)]\mathrm{F}(f)\mathrm{d}f, \tag{18}$$

where $\varepsilon_f[\omega, \tau(f)]$ is the loss factor corresponding to the segments with the free volume fraction f and $\mathrm{F}(f)$ is the normalised free volume distribution function. The latter was specified in the form

$$\mathrm{F}(f) = \frac{(f - f_1)\exp[-(f - f_1)/\lambda]}{\lambda}, \tag{19}$$

where f_1 is the minimum volume and λ the parameter of the width of the distribution.

Comparison of the calculated and experimental relations $\varepsilon''(\omega)$ shows that, at temperatures approaching the glass transition temperature, the significant broadening of the curves is determined in the first place by the free volume distribution effects whereas at higher temperatures account must also be taken of the distribution of the relaxation times.

Textured PVDF films are usually employed in practice. From the analysis of the influence of, for example, uniaxial stretching on the nature of the micro-Brownian motion in the nonordered regions, one may formulate general relations.[272,281,292] In all cases the uniaxial stretching process did not lead to an appreciable alteration of the relaxation times, but the total absorption $\Delta\varepsilon$ increased steadily. This implies [in conformity with Eqn (15)] an increase in the effective dipole moment per monomer unit. There may be several causes of the increase. In a textured film, the chains in the amorphous phase assume a definite preferred orientation, which can be inferred, for example, from the appearance of the IR dichroism of the 600 cm^{-1} absorption band, which is sensitive to the presence of the amorphous phase.[129] In this case the quantity $3kT$ in Eqn (15) for the isotropic film should be reduced when account is taken of the anisotropy in the disposition of the chains in the amorphous phase. Another cause, apparently decisive, is that the conformation of the sequencies of the chain in the amorphous gaps may change in the oriented state. The probability that chain sections entering into the region of higher local mechanical stresses will pass to the 'planar zigzag' conformation increases. The sequencies of the TTC mentioned above apparently constitute the 'limiting case' for the scheme mentioned above, since increased mechanical stresses cause their transition to the 'planar zigzag' conformation.[160]

For an anisotropic film, one may speak of three components of the relative permittivity. Under the usual conditions of the measurement (electrodes deposited on the surface of the film), one should be dealing with the component ε_{33} if the direction 3 coincides with the normal to the surface. If the chain of a textured amorphous phase is located predominantly in the plane of the film, then the values of ε_{33} depends significantly on the transverse component of the dipole moment. As mentioned above, this component for the chain sequencies in the 'planar zigzag' conformation is greater than for the sequencies with the $TG\bar{T}\bar{G}$

conformation. For this reason, the increase in $\Delta\varepsilon$ in the textured films agrees with the increase within the plane of the films in the number of chain sections of the amorphous phase in the 'planar zigzag' conformation. Evidently data concerning the anisotropy of the dielectric desorption in the regions of the β dispersion for specimens of uniaxially extended PVDF may serve as confirmation of this correspondence.[293] After drawing, the specimens were cut out in a way such that in one case the electrodes were located perpendicular and in another parallel to the draw axis. It was found ε''_{max} in the region of β relaxation is almost three times greater in the second case than in the first.

The high-temperature $\alpha(\alpha_c)$ relaxation process is unambiguously associated with motions in the PVDF crystalline phase. This has been confirmed by the observation of the $\alpha(\alpha_c)$ mobility in crystalline mats[275] and also by the increase in the intensity of the above process with increase in the degree of crystallinity.[274] The majority of investigators assume that this mobility occurs predominantly in the α modification of PVDF crystals. This is based on numerous data showing that, in specimens where the α and β phases coexist, an appreciable decrease in the intensity of the $\alpha(\alpha_c)$ relaxation is observed.[273,281,292] Furthermore, there is evidence that this process is altogether absent from PVDF specimens obtained in the γ phase,[294] while in the PVDF copolymers, where the α phase is usually not formed, it is extremely weak.[278] There exists also a communication,[295] which unfortunately has been confirmed by only one other investigation,[296] stating that in specimens with coexisting α and β phases two $\alpha(\alpha_c)$ relaxation regions are observed. The low-temperature region is attributed to the motion of the chains in the crystals of the α phase, while the high-temperature region is attributed to relaxation in β phase crystals.

Analysis of the above studies shows that in all cases the relaxation times are described by Arrhenius equations and the activation parameters are characterised by the quantities $\Delta H = 24$ kcal mol^{-1} and $\Delta S = 23-26$ e.u.[273,281] Detailed analysis of the characteristics of this process shows that they may reflect fine details of the microstructure. For example, it has been observed that the increase in the fraction of 'head to head' defects in PVDF chains reduces the intensity of the α relaxation.[273] The thickness of the lamellae in the above process affects the mobility parameters: an increase in thickness is accompanied by an increase in mobility.[273,283] Annealing, which usually leads to the thickening of the lamellae, is also accompanied by an appreciable increase in the average α relaxation times.[283] One of the characteristic features of the process is that it exhibits anisotropy. The results of three different studies[293,297,298] indicate unambiguously that, when the field vector $\bar{E}$ is arranged perpendicular to the draw axis, the intensity of the process is higher than in the case where these directions coincide.

The mechanism of the processes in the above dispersion region has been discussed in greatest detail by Nakagawa and Ishida[283] and Myjamoto et al.[298] In the first study, the discussion began with the postulate that motions of two types are possible in folded-chain crystals: the motion in the surface itself (loops and other defects) and rotation of the chain (or of its section) in the bulk phase with a small longitudinal displacement. The number of monomer units in the fold (n_f) was estimated from the thickness of the lamella using electron microscope data. It was found that, for the range $n_f = 50-130$, the reorientation frequencies of the moving segments varied linearly. It was therefore concluded that the rigid rod approximation used in the study is correct for the kinetic unit. Comparison of the calculated and experimental relations shows that the enthalpy of activation for the above transition is determined mainly by the fold in the chain. Analysis of the experimental $\Delta\varepsilon(T)$ relations enabled the authors[298] to conclude that the rotations of sections of the lamellae within the crystal make the dominant contribution to α relaxation, but with the stipulation that motion within the folds cannot be fully excluded under these conditions. The chains in the folds are more mobile than within the crystal, but the contribution of the latter to the process is decisive because of the high resultant dipole moment.

The above studies[293,297,298] confirm the conclusion that the chains in the internal regions of the crystal make the main contribution to the α-relaxation process. Indeed, after orientation, the normal to the surface of the folds coincides with the draw axis. Under these conditions, the inner chains of the lamellae are arranged at right angles to the direction of orientation. Taking into account the fact that the perpendicular component of the dipole moment of the PVDF chain in the $TGT\bar{G}$ conformation is greater than the parallel component, the absorption when the field is applied perpendicular to the draw axis should be more intense, which has in fact been observed.[293,297,298]

The mechanism of the α relaxation has also been considered by Myjamoto et al.[298] with the aid of the same two positions model. Using the dependence of $\Delta\varepsilon$ on the angle between the field vector and the stretch direction and having assumed that the longitudinal component of the dipole moment μ_{11} varies, the authors obtained a reasonable explanation of the relations noted above. Conformational analysis shows that such a case may occur, for example, in the $TGT\bar{G} \rightarrow GT\bar{G}T$ transition within a section of the lamella. This transition is possible, since even when account is taken of the activated state (in the form of the 'planar zigzag' conformation), which requires a 10% deformation along the axis of the macromolecule, the change in the conformation is then local and significant translational migrations of the chain as a whole are not required. Despite the fact that the fluorine atoms should move in such conformational transition along the c axis, the packing of the chains along the a and b axes changes little. The mechanism of the $TGT\bar{G} \rightarrow GT\bar{G}T$ conformational change presupposes the existence between chain sequences with different conformations of a defect (of the 'head to head' or conformational type), which may migrate along the chain as a result of thermal excitation and may induce a change in the dipole moment component μ_{11}.

According to another model, the position of the defect within the chain is fixed and the initiation of the above conformational transformation begins on the surface of the lamella as a result of a 'wormlike' excitation and is then transferred to another surface. In both models, account is taken of the important role of chemical defects, although the importance of conformational defects is not denied. It is assumed that with the aid of the latter one can explain a series of 'anomalous' effects in the characteristics of the α relaxation. Thus, when the relaxation times of the above process were compared for two specimens (isotropic and oriented), it was observed that, although in the former case the long period (and tentatively also the thickness of the lamella) is greater than in the latter (150 and 135 Å respectively), the relaxation time in it is an order of magnitude shorter than in the latter. It is assumed that, owing to the uniaxially stretching, the concentration of conformational defects changes in the second specimen and these in fact influence the rate of the relaxation processes. The proposed two positions model begins with a single relaxation time, whereas experiments yield a distribution of times. This discrepancy may vanish if account is taken of the distribution of the lamellae with respect to thickness and also of the distortions in the form of the potential energy function as a result of the presence of defects.

When α relaxation was observed in the region of high temperatures, usually at low frequencies of the electric field, anomalously high values of the ε' and ε'' components were noted. This has been attributed to the influence of impurities causing high losses due to dc conductivity. It was observed that they can be significantly reduced by maintaining the PVDF specimens at elevated temperatures in an electric field, where electrolytic processes take place.[299] An increase in the electric field strength accelerates the decrease in the above conductivity during the electrolytic process. The imposition of a $\sim 20-30$ kV cm^{-1} electric field lowers the values of ε' at high temperatures, this being manifested to the greatest extent at low frequencies.[299] After the field has been switched off, the increased conductivity is partly

restored. Nevertheless, it has been shown that, in cases where the α process was masked by losses due to dc conductivity, annealing of the specimens subjected to the field made it possible to observe the above process distinctly. Experiments with mercury electrodes showed that calcium ions make a large contribution to the ionogenic impurity conductivity.[299]

For theoretical justification of the above experimental facts, it has been suggested[300] that the experimental ε' and ε'' each have two components:

$$\varepsilon' = \varepsilon'_i + \varepsilon'_p, \tag{20}$$

$$\varepsilon'' = \varepsilon''_i + \varepsilon''_p, \tag{21}$$

where the components with subscripts i and p denote the contributions of the ionic impurities and the polymer itself respectively. Taking into account the fact that only some of the impurities dissociate, their contributions to the components of the complex relative permittivity are defined by the relations[300]

$$\varepsilon'_i = \frac{2v_0q^2}{lkT\pi^{0.5}}\left(\frac{D_0}{f}\right)^{3/2}\exp\left[-\left(\frac{3E_d}{2}+\frac{W}{2\varepsilon_0}\right)/kT\right], \tag{22}$$

$$\varepsilon''_i = \frac{2v_0q^2}{kT}\left(\frac{D_0}{f}\right)^{3/2}\exp\left[-\left(E_d+\frac{W}{2\varepsilon_0}\right)/kT\right], \tag{23}$$

where v_0 is the concentration of mobile ions, l the thickness of the specimen, q the ionic charge, D_0 the diffusion coefficient of the ion, f the field frequency, E_d the activation energy for the diffusion of the ion, and W the ion dissociation energy.

Taking into account the relations obtained, a series of quantitative characteristics were found for the ionogenic impurities in PVDF. Thus at 160 °C the diffusion coefficient proved to be $D_0 = 4.36 \times 10^{-7}$ cm^2 s^{-1}, which (on the assumption that the ions are univalent) corresponds to their mobility $\mu = 1.2 \times 10^{-5}$ cm^2 V^{-1} s^{-1} ($\mu = qD_0/kT$) and the concentration $v_0 = 6.8 \times 10^{14}$ cm^{-3} (at a concentration of monomer units of 1.7×10^{22} cm^{-3}). The activation energies for the dissociation of ions and their diffusion have been estimated as 342 and 34 kcal mol^{-1} respectively. An interesting fact was noted: prolonged (10 days) annealing at 160 °C of PVDF specimens leads to an appreciable decrease in the contribution of the ionic impurities to the low-frequency dielectric characteristics.

The anomalously high values of ε' and ε'' at low frequencies in the region of fusion of the PVDF α phase crystals have also been noted by Yano et al.[301] It was shown that there is a sharp fall of ε' and an increase in ε'' in the range 153–155 °C (according to DSC data the melting point is 157 °C). Analysis of the conductivity in this system before and after fusion indicates significant differences. In particular, the independence of the conductivity of the electric field frequency was noted for the melt. It was proposed that the melt be regarded as a homogeneous medium and that the nature of the conductivity in it is similar to that in an electrolyte solution. In this case, the dielectric parameters depend on the characteristics of the electrical double layer at the electrolyte–electrode boundary and Eqns (22) and (23) should be valid. According to the equations, the conductivity should be frequency-independent and the relations between ε'_i and lg$f$ should be characterised by a coefficient of 3/2. Interpretation of the experimental data confirmed the validity of the chosen model: the conductivity indeed proved to be frequency-independent and the above coefficient was close to the predicted value, namely 1.67–1.79. At temperatures below the melting point, the homogeneous medium model was not confirmed. This may be inferred if only from the fact that the conductivity proved to be a function of the field frequency. The correct interpretation of experimental data can be achieved if account is taken of the differences between the values of ε' and of the conductivities of the crystalline and amorphous regions.

Similar anomalies in the behaviour of ε' and ε'' in the fusion region have been observed also on VDF/TFE copolymers.[278] The loss factors in this region vary in accordance with the law

$$\varepsilon'' = A\omega^{-m}, \tag{24}$$

where A is an empirical constant and m is a constant which varied in the range 0.3–0.5 as a function of temperature and the conductivity of the specimen. Eqn (24) is characteristic of the polarisation of the space charge of ionogenic impurities[302] and it too confirms the necessity to take into account the heterogeneity (in terms of the electrical characteristics) in systems based on PVDF at elevated temperatures.

The Maxwell–Wagner polarisation process under discussion has also been detected in uniaxially extended PVDF films[303] and its characteristics (mainly the loss factor at the maximum) proved to be extremely sensitive both to the phase ratio in PVDF and to the state of orientation of the chains in its nonordered regions. It is noteworthy that the characteristics of the electrical heterogeneity for the ordered and nonordered regions have been found to be sensitive to the polarisation process in the corona discharge, since under these conditions the intensity of the interlayer polarisation process diminishes significantly.[303]

This process has been investigated in greater detail in a study[304] where the high-temperature transition α → γ was considered. If the crystals are obtained in the γ modification, the low-frequency dependences of ε' are found to differ significantly from those for the care where PVDF crystallises as the α phase (Fig. 29). Indeed, in the former case the values of ε' at low

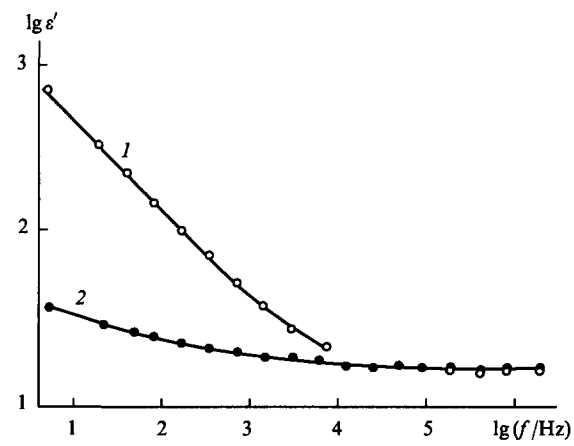


Figure 29. Frequency dependences of the high-temperature relative permittivity for PVDF films crystallised as the γ modification (*1*) and the α modification (*2*) at 160 °C.[304]

frequencies are significantly higher and do not obey the law ε' ($f^{-3/2}$), as happens in the case of α PVDF. As already mentioned above, this law is characteristic of electrode polarisation and this mechanism is therefore inapplicable to crystals of the PVDF γ phase. This conclusion is confirmed also by the dependence of ε' for PVDF films in both modifications on the thickness of the specimen (Fig. 30). Evidently, in the case of crystals of the α modification an explicit dependence of ε' on thickness is observed (which is characteristic of electrode polarisation, whereas for films with the γ modification ε' remains approximately constant. The interlayer (Maxwell–Wagner) polarisation mentioned above may serve as another possible explanation of the observed relaxation process with an activation energy of 627 kJ mol^{-1}. For spherical crystals with a conductivity σ_2 and a relative permittivity ε_2, immersed in an amorphous matrix with the corresponding values of σ_1 and ε_1, the frequency f of the loss maximum can be found from the equation[305]

$$f = \frac{2(2\sigma_1 + \sigma_2)}{2\varepsilon_1 + \varepsilon_2}. \tag{25}$$

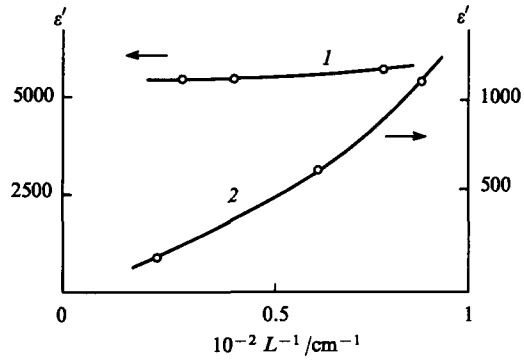


Figure 30. Dependence of the high-temperature relative permittivity on the thickness of PVDF films crystallised as the γ modification (*1*) and the α modification (*2*) at 165 °C.[304]
Frequency (Hz): (*1*) 0.2; (*2*) 0.1.

Since the γ phase crystals have an uncompensated dipole moment per unit cell, $\sigma_1 \gg \sigma_2$ and $\varepsilon_2 \gg \varepsilon_1$ and Eqn (25) may be replaced by

$$f = \frac{4\sigma_1}{\varepsilon_2}. \qquad (26)$$

The equilibrium value $1.5 \times 10^{-10}\,\Omega^{-1}\,cm^{-1}$, obtained after 15-h maintenance of the specimen at 185 °C in a 400 V cm^{-1} field, was used as σ_1. The frequency f calculated by Eqn (26) is 0.6 Hz, which differs by more than two orders of magnitude from the experimental value.

The possibility of orientational motions of the γ crystals as a whole was considered as an alternative mechanism of the high-temperature relaxation process mentioned above. This is based on the linear dependence of ε''_{max} for the process on the heat of fusion of the γ phase crystals (DSC data), which indicates that the magnitude of the absorption is determined mainly by the volume fraction of the γ phase crystals. The possibility of the motion of the crystals as a whole in this process does not lack justification. Indeed, with increase in the long period (linked directly to the size of the crystalline lamella), the maximum of the mechanical loss modulus shifts towards higher temperatures. Finally, yet another argument in support of the hypothesis that the crystal moves as a whole follows from estimates Δε by Eqn (15) using the experimental numbers of monomer units per kinetic unit. It proved to be 6×10^3 repeat units. This number exceeds by more than an order of magnitude the number of monomer units in a lamella of the usual size ($\sim 10^2$ units). Osaki at al.[304] does not discuss the reason for this discrepancy but the latter may indicate the involvement in the given transition of motions accompanying a ferroelectric–paraelectric transition in which cooperative effects should prevail.

Indeed the above relaxation region is in the vicinity of the melting point, where a ferroelectric–paraelectric transition has been postulated for the VDF homopolymer in a polar form (as in the given instance). The relation between the mobility in the crystalline phase and the motions in a ferroelectric transition may be inferred from the nature of the temperature variation of the dielectric parameters in the VDF/TrFE copolymer, which is known to be ferroelectric[306] and for which the temperature of the above transition differs from the melting point. Here too one observes a high-temperature mobility in the crystalline phase, which is characterised by high values of Δε. Analysis of the temperature variation of the latter shows that its increase with increasing temperature represents the onset of the anomalous rise in Δε in the region of the ferroelectric transition.[306]

Mention should be made of the results of a study[307] of the mechanism of the high-temperature relaxation in PVDF. The low-frequency dielectric characteristics of PVDF films with α-phase crystals were investigated. Here attention was concentrated on the role of the material of the electrodes. Aluminium and gold, for which different temperature variations of the components of the complex conductivity had been found, were employed. The authors explained the highly intense tan δ maximum (amounting to 12–25!) at low frequencies by the manifestation of the space charge at the material–electrode interface. However, in contrast to other investigators, they believe that the majority carriers are the F^- and H^+ ions. This presupposes the presence in the bulk of the film of a finite number of HF molecules which should be partly dissociated. This hypothesis is confirmed by a whole series of facts. For example, one of them is that the presence of excess fluorine has been observed in the bulk of PVDF by the method of reverse Rutherford scattering.[307] A finite number of the (–CH=CF–) groups have been found in the initial state of different PVDF films from the characteristic IR absorption bands. Such groups may be formed by the reaction

$$(-CH_2-CF_2-) \longrightarrow HF + (-CH=CF-),$$

initiated by thermal energy or irradiation.[300] A sufficient amount of HF may be formed by this reaction already at ~60 °C.[309] Thus taking into account the presence of the H^+ and F^- ions in the bulk phase, the low-frequency tan δ maximum should be attributed to the behaviour of these ions in a variable electric field.[307] It is believed that the mobility of the hydrogen cations is significantly greater than that of the fluoride ions, so that the former accumulate near the negative electrode at ultralow frequencies, creating a space charge, which is in fact responsible for the relaxation process under discussion.

The less mobile fluoride ions are captured by traps, but their role may vary significantly for different electrode materials. If the electrode material is aluminium, then, under the influence of the combined action of a high temperature and a weak variable field, the fluoride ions, having reached the electrode, may diffuse into the latter. This is confirmed by the detection of fluoride ions in the surface of the electrode after the application of the combined influence mentioned above.[307] X-Ray photoelectron spectroscopic data demonstrate that the fluoride ions which have migrated into the electrode can react with the aluminium atoms to form new compounds.[310,311]

Thus analysis of data on the high-temperature relaxation shows that the mechanism of the above processes may be fairly complex. A number of workers have noted the dependence of its characteristics on experimental parameters such as the magnitude and duration of the effect of the field.[312]

Information about the relaxation process can be obtained by the method of thermostimulated depolarisation currents, with the aid of which processes involving local and segmental mobility at low temperatures can also be detected.[313] Above room temperature, it is possible to detect even two interlayer polarisation processes. One of them (the low-temperature process) is attributed to the formation of a space charge at the boundaries between the amorphous phase and the nonpolar crystals of the α modification, whilst the other 'senses' these boundaries with the polar (β, α_p) modifications.[314,315] In a later study[316] on specimens with crystals of both the polar and nonpolar phases, only one relaxation process, associated with the space charge, was detected. However, at high temperatures three additional current maxima, the temperatures of which are correlated with the melting points of the α, β, and γ modifications of the PVDF crystals, were noted.

Despite the high information content of the electrical methods for the assessment of relaxation process, there have been a number of studies where it was shown that certain forms of mobility in PVDF are inactive. For example, according to the results of McBrierty et al.,[317] the relaxation process, associated with the motion of the folds on the surface of the lamellae and noted in experiments on dynamic mechanical relaxation by the dielectric method, was not observed. A similar conclusion was reached in a study[318] where two mechanical relaxation regions (α_1 and α_2) were found in all the PVDF specimens (isotropic and oriented with the crystals of the α and β modifications) at high temperatures, the higher-temperature region (α_2) being assigned to the

motions preceding the fusion of the crystal. It follows from the results of the study that the mechanisms of the relaxation in mechanical and electric fields in the region of the glass transition of the oriented specimens may differ. This is indicated, in particular, by the finding that, in a mechanical field, the β process is more intense in the case of a parallel disposition of the force vector and the orientation axis,[318] whereas in an electric field the opposite behaviour obtains.[293,297]

An attempt has been made at a detailed comparison of the relaxation processes in PVDF and polyethylene on the basis of the results obtained by mechanical spectroscopy.[319] In the region lying below the glass transition temperature, two relaxation processes (γ_1 and γ_2) were observed in polyethylene, their parameters being close to those of the γ and δ relaxation processes (discussed above) obtained by dielectric measurements. A reasonable agreement between the activation energies and the normalised relaxation time spectra for the processes in both polymers made it possible to postulate that the mechanisms of the γ and δ processes in PVDF are similar to those of the γ_1 and γ_2 processes in polyethylene. According to the results of Yamada et al.,[320] the γ_1 relaxation should be attributed to the local modes of motion of the nonordered chains in the interlamellar regions, whilst the lower-temperature relaxation region (γ_2) should be assigned to the motion in the surfaces of the lamellae.

The same situation occurs also for the region of the high-temperature α relaxation of PVDF, for which the normalised relaxation time spectra agree well with those for the α_2 relaxation in polyethylene. The similarity in the relaxation behaviour of PVDF and polyethylene is also supplemented by the fact that two transitions (α_1 and α_2) can be noted in the high-temperature region for both polymers.[319]

IX. Structural characteristics in the crystallisation of poly(vinylidene fluoride) in blends with other polymers

Examination of the questions associated with the structural characteristics in the crystallisation of PVDF in blends with other polymers will be useful for a number of reasons. One of them is related to the possibility of supplementing and expanding the ideas concerning the characteristic features of the modification of the structure and properties of polymer blends in which one or both components are crystallisable. By crystallising PVDF in blends with other polymers, it is possible to regulate specifically the conformational structure of its chains, which is important in the practical employment of PVDF-based materials for piezoelectric and pyroelectric sensors. The possibility of the modification in such blends of the morphology and optical properties of PVDF is regarded as their additional advantage when they are used as materials with nonlinear optical properties.

Since the blends of PVDF with polymethacrylates have been studied in greatest detail, it is more convenient to begin the analysis of the results precisely with studies in which these blends were investigated. The orientation process in polymeric materials is frequently used to impart improved mechanical properties to the latter. For PVDF, this process is frequently used also for the formation of the ferroelectric β phase, which determines practically important phenomena such as the piezoelectric effect and the second-order optical nonlinearity. However, the orientation of a polymeric material is accompanied by the appearance of birefringence Δn, the magnitude of which is determined by the difference between the refractive indices along (n_1) and across (n_2) the direction of stretching. When a textured material is used for optical elements (windows, discs, lenses, etc.), the birefrigence effect is undesirable. One of the possible ways of suppressing this effect has been noted in relation to blends of atactic poly(methyl methacrylate) (PMMA) with PVDF. Such blends are known to be compatible in the melt and cooling of the latter affords a homogeneous optically transparent material.[320] When the composition of the blend was varied, it was shown that the refractive index of the isotropic phase varies linearly with increase in the fraction of PVDF.[321] This follows from the Lorentz–Lorenz relation for multiphase mixtures, in which the characteristic dimensions of the regions corresponding to different components are smaller than the light wavelength. PVDF is present in a partly crystalline state and is characterised by the densities $\rho_c = 2.0$ g cm^{-3} and $\rho_a = 1.6$ g cm^{-3} in the crystalline and amorphous states; the refractive indices of these phases have been estimated as $n_c = 1.48$ and $n_a = 1.37$. The value of n_c for PVDF is close to that for the amorphous PMMA (1.49). Therefore a decrease in the light scattering effects and an improvement of transparency compared with pure PVDF are to be expected for crystallisable PVDF/PMMA blends with a high content of the first component.

The effect of the deformation-induced birefringence has been observed on noncrystallisable blends with a PVDF content not exceeding 60 mass %. In this case Δn proved to be a linear function of the draw ratio λ, the slope of which depended significantly on the composition of the blend. In the PVDF/PMMA 40/60 and 20/80 blends, Δn was surprisingly low even for high draw ratios. The reason for this may be found by analysing the dependence of Δn on the composition of the blend for $\lambda = 2$ (Fig. 31). For a certain composition of the blend (for $\lambda = 2$, this is a blend having the composition 17/83), Δn proves to be zero. A further decrease in the PVDF concentration leads to negative values of Δn. The components of the above blend have different signs of the double refraction, so that, by varying their ratio, it is possible to select a composition such that the birefringence is compensated for a certain value of λ.

The foregoing is valid for amorphous blends with a particular previous thermal history. These questions have been investigated in detail in a study,[322] where the composition of the components blended in the melt was varied within wider limits. When the components are fully compatible in given proportions in the melt, the cooling of the latter may lead to the crystallisation of PVDF,[323–336] the characteristic features of which may depend also on the annealing temperature.[322] In particular, if the annealing is carried out at temperatures in the range between the glass transition temperatures of PMMA and PVDF crystallisation may be observed in blends containing more than 10% of PVDF.[322] The amorphous phases of both components are apparently fairly compatible since a single glass transition temperature has been noted in the blends. It decreases monotonically with increase in the fraction of PVDF in conformity with the mixing rule for a two-component mixture [337,338]

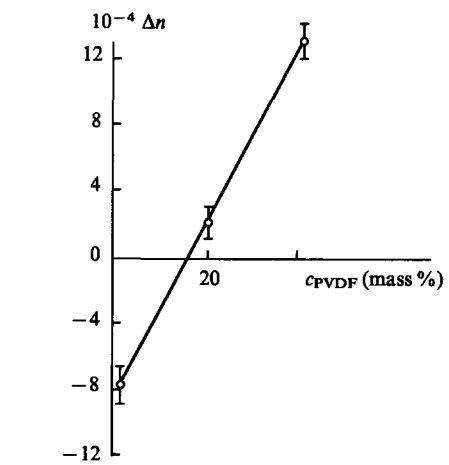


Figure 31. Dependence of the birefrigence refraction on the blend composition in amorphous oriented ($\lambda = 2$) specimens.[321]

$$\lg T_g = \frac{M\Delta C_p \ln T_g + M'\Delta C_p' \ln T_g'}{M\Delta C_p + M'\Delta C_p'}, \quad (27)$$

where T_g, M, and ΔC_p are respectively the glass transition temperature, the mass fraction, and the difference between the heat capacities of VDF in the region of the glass transition of the components; the primed quantities refer to PMMA.

A decrease in the fraction of PVDF in the blend hardly affects the thickness of the lamellae formed (Fig. 32). Under the conditions of reduced crystallinity, this implies that the introduction of PMMA promotes mainly a decrease in the rate of nucleation. It follows from the relations presented in Fig. 32 that, for blends enriched in PMMA, the morphology of the structural elements formed is characterised by an increase in the intercrystallite spacings.

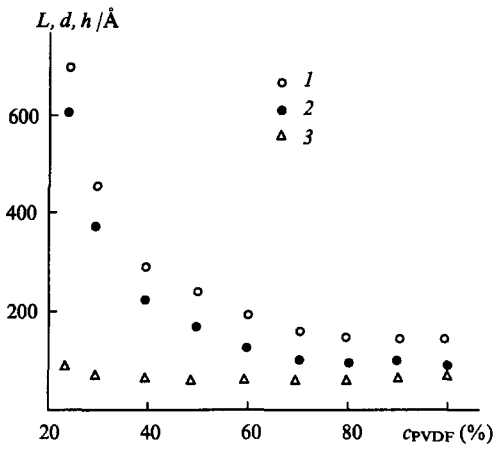


Figure 32. Dependence of the large period (*1*), the size of the amorphous layers (*2*), and the thickness of the lamellae (*3*) on the fraction of PVDF in PVDF/PMMA blends annealed at 140 °C.[322]

The satisfactory compatibility of PVDF with PMMA is confirmed by the negative value of the Flory–Huggins parameter (B). According to numerous data,[330,339–341] blends of PVDF with poly(ethyl methacrylate) (PEMA) are also compatible. The polymers PMMA and PEMA are incompatible and it is therefore difficult to predict the nature of the compatibility of PVDF with PMMA/PEMA copolymers. This problem has been solved in experiments involving the study of the fusion of PVDF in blends with PMMA/poly(ethyl methacrylate) (PEMA) copolymers over a wide range of compositions.[342] The parameter B was estimated from the equation [324,339]

$$T = T_0 + B\frac{V}{\Delta H}T^0\Phi^2, \quad (28)$$

where T_0 and T are respectively the melting points of pure PVDF and in the blend, $\Delta H/V$ is the heat of fusion of PVDF per unit volume (44.0 cal cm^{-3}), and Φ is the volume fraction of the noncrystallisable polymer in the blend.

According to the pair interaction model,[343] the parameter B for such blends may be estimated with the aid of the relation

$$B = B(\text{MMA/VDF})\Phi(\text{MMA}) + B(\text{EMA/VDF})\Phi(\text{EMA}) + B(\text{MMA/EMA})\Phi(\text{MMA})\Phi(\text{EMA}). \quad (29)$$

The experimental values of B for blends of PVDF with the copolymers PMEMA of different composition are presented in Fig. 33. Evidently, with increase in the amount of MMA in the copolymer, B diminishes. Positive values of B(MMA/EMA) in Eqn (29), indicating the repulsive nature of the intramolecular interactions between neighbouring units in the copolymer, yield

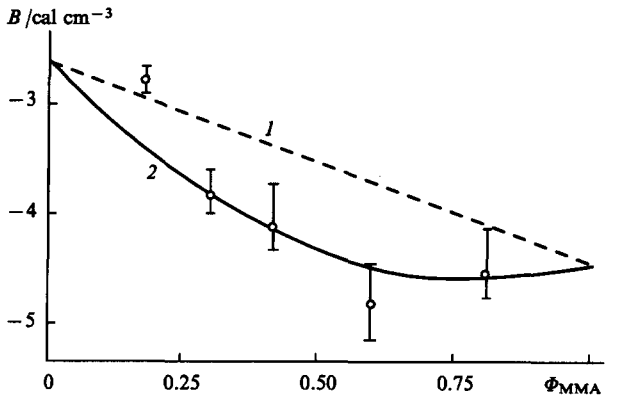


Figure 33. Dependence of the Flory–Huggins parameter for the PVDF/PMEMA blend on the composition of the copolymer. (*1*) B(MMA/EMA) = 0 (*2*) B(MMA/EMA) = 3.25 cal cm^{-3}.

the best agreement between the calculated curve and the experimental points.

The compatibility of PVDF with low homologues of the methacrylate series (PMMA and PEMA) breaks down for higher homologues of this series.[344] Since the concentration of carbonyl groups in the latter diminishes, it has been suggested that these groups in the methacrylates actually play a significant role in the compatibility processes. In this connection, a study has been made[345] of the influence on the compatibility processes of both these and other functional groups and elements, for example oxygen or sulfur in ether groups. For this purpose, questions concerning the compatibility of PVDF with poly(methoxymethyl methacrylate) (PMOMMA) and poly(methylthiomethyl methacrylate) (PMTOMA) were examined. For the former, the existence of a single glass transition temperature indicates the compatibility of the components. The parameter B found from Eqn (28) is -14.5 J cm^{-3}. This is an intermediate value for blends of PVDF with PMMA and PEMA. It was shown that the upper critical miscibility temperature (determined from the turbidity temperature) diminishes almost by 100 °C with increase in the fraction of PMOMMA to 0.5. The PVDF/PMTOMA blends are turbid at all temperatures and two glass transition temperatures are observed for them regardless of composition. This means that these blends are incompatible. The melting point of the PVDF crystals in the blends diminishes slightly with increase in the fraction of PMOMMA, which indicates some change in the dimensions and perfection of the crystals. One may assume that the role of PMTOMA in these blends reduces mainly to the effective suppression of nucleation, since the degree of crystallinity (for a PMTOMA fraction of 0.5) decreases almost by a factor of 2 according to measurements of the heat of fusion. The reasons for such a striking difference in the behaviour of the blends of PVDF with methacrylates, is seen by the authors of the study in the increased volume of the side group in PMTOMA compared with PMOMMA. Yet another cause of the above difference is attributed to the lower electronegativity of the sulfur atom compared with the oxygen atom.

The amorphous phase in a blend with a crystallisable polymer is known to decrease the rate of crystallisation of the latter in all cases.[346,347] This law is valid also for the PVDF/PMMA [328] and PVDF/poly(ethyl acrylate) [340] blends. The details of this phenomenon have been investigated in a study [349] where the rate of growth of the spherulites was investigated with variation of both the crystallisation temperature of the PVDF/PMMA blend and of the molecular mass of the second component. It was found that, depending on the temperature, the crystallisation can occur in three regimes, which differ in the rates of secondary nucleation and surface growth. At the same crystallisation temperature, an increase in the molecular mass of PMMA in a blend of one composition leads to a decrease in the rate of growth of the

spherulite. The experimental data are best described within the framework of the modified Hoffman–Lauritzen theory, which takes into account the two-step diffusion-controlled mechanism.

The high-resolution nuclear magnetic resonance (NMR) technique with spinning of the specimen at the magic angle is nowadays frequently employed to analyse the microstructures of polymers in the block state. Potentially this method can be used also for the analysis of the details of the interaction in blends if blending at the molecular level is accompanied by a change in the electronic states for the resonating nuclei. The approximate similarity of the magnetisation parameters for these nuclei in the PMMA and PVDF chains has been demonstrated [350] on the basis of the characteristics of the resonance of the ^{13}C nuclei. When this was taken into account, the experiments involving the ^{13}C and ^{19}F nuclei with cross-polarisation showed that PMMA and PVDF are at least partly blended at the molecular level. This method has been developed (in relation to the blends under consideration) in a study [351] where data involving the resonance of not only the ^{19}F and ^{13}C nuclei but also ^{1}H nuclei were employed.

For PVDF/PMMA blends with a wide range of compositions, the experimental data are best described in terms of the model which takes into account the presence of four different phases. The presence of pure PVDF is postulated in the first phase. On the experimental time scale, the presence of protons arising from PMMA is not detected. The second phase includes the regions in which the chains of both components are mixed at the 'truly molecular' level and the main transfer of magnetisation from protons to fluorine is ensured directly by the $^{1}H-^{19}F$-depolarisation processes. The third phase is close to the previous one but, in contrast to the latter, it should be controlled to a greater extent by spin diffusion processes. Finally, the fourth phase includes regions of pure PMMA, manifesting depolarisation and spin diffusion processes. On the basis of their experiments, the authors [351] were able to calculate the fractions of the first and fourth phases and also to estimate the dimensions and ratios of the components in the domains comprising the second and third phases for blends with a wide range of ratios of the initial components.

Table 17 shows that in the blend with 20% of PMMA the latter is wholly in the blended state. In virtually all the blends, the mixed second and third phases have virtually the same composition as regards the monomer ratio. The 80/20 blend is an exception, which is due to the dilution effect. The dimensions of the domains comprising the above phases also vary only slightly with composition and are respectively 7 and 6 Å.[351]

Later Papavoine et al.[352] demonstrated in relation to the PMMA/PVDF 60/40 blend that the method being developed has a high information content also for the assessment of the kinetics of phase separation. In the experiments, the initial blends were heated under pressure at 200 °C (i.e. above the melting point of the PVDF crystals where the components are fully compatible) and were then rapidly cooled to 77 K. The kinetics of the phase separation were then followed in the isothermal annealing regime (at 120 and 140 °C) by the method described above (the increase in the fractions of the first and fourth phases was estimated). It was found that at both annealing temperatures the attainment of the equilibrium value occurs at approximately the same time in terms of the fractions of both the first and fourth phases. The accumulation of the first phase, i.e. of the regions of pure PVDF, should be accompanied by the crystallisation of the latter. This has been confirmed qualitatively by DSC data (the appearance of the fusion endotherm for annealed specimens). Comparison of the increase in the degree of crystallinity during annealing at 140 °C on the basis of the results obtained by both methods shows that, according to DSC, these values are systematically lower by approximately the same amount. The authors believe that this is not fortuitous and attribute it to the fact that in the NMR method the first phase must include also the interfacial regions at the crystal–amorphous phase boundaries, the presence of which has been demonstrated by numerous dielectric relaxation experiments.

Table 17. The fractions of the first and fourth phases and the monomer ratio in the second and third phases for PVDF/PMMA blends of different composition.[351]

PMMA/PVDF	Fraction of first phase	Fraction of fourth phase	Monomer ratio	Monomer ratio in second and third phases
20/80	0.75	0	0.16	0.65
40/60	0.35	0.10	0.43	0.59
60/40	0.15	0.30	0.96	0.75
80/20	0.10	0.30	2.56	1.99

Shilov et al.[353] investigated the differences between the phase ratios in bulk and on the surfaces of PVDF/PMMA blends. The X-ray photoelectron spectroscopic method, yielding information about the microstructure at depths of 4–5 nm, was employed. Specimens of two types were investigated, one of which consisted of a thin (0.2 μm) film of the 50/50 blend. Heating of the specimen in 40 °C steps directly in the spectrometer chamber demonstrated that up to 373 K the form of the XPES spectra does not change. Annealing at a temperature $T \geqslant 413$ K leads to an increase in the intensities of the lines corresponding to the carbon in the CF_2 bond and, conversely, to a decrease in the intensities of the lines due to the carbon in the C=O group. On fusion of the blend, this process intensifies to an even greater extent as a result of the weakening of the specific interactions between the blend components. All the foregoing considerations can be accounted for solely by a redistribution of the blend components in the above annealing regimes, as a result of which the surface is enriched in PVDF at depths of 5 nm.

This conclusion is confirmed by the results of the study of specimens of the second kind which were of the 'sandwich' type: a thin layer of PMMA was deposited on top of a layer of PVDF. In the initial state, the lower PVDF layer in the specimen was almost fully covered by PMMA, but thermostatic treatment of the specimen at 413 K leads to the redistribution of the intensities of the components of the lines due to carbon in the CF_2 and C=O groups mentioned above. The kinetics of this process are described by a power relation with the exponent $n \approx 0.5$, which is characteristic of diffusion-controlled processes. Since the density of PVDF is higher than that of PMMA the direction of the processes involving the inversion of the distribution of the components in the surface must be opposed to the direction of the force of gravity gradient. According to the authors,[353] a surface energy minimum should correspond to the state of equilibrium, since one is dealing with the structure of the surface. The surface tensions of PMMA and PVDF are respectively 40.2 and 32.7 mN m^{-1}.[354] The surface energy minimum therefore requires the emergence of PVDF onto the surface, which has been noted experimentally.[353]

In connection with the possible formation of polymorphic modifications in PVDF crystals, a test of the influence of the amorphous phase of the blend on the crystallisation of PVDF in a particular modification is of current interest. If PVDF crystallises with formation of α and γ spherulites for low degrees of supercooling, the addition of PMMA leads to a decrease in the concentration of the large (α) spherulites, which in addition become loosely packed.[86] Thus isotropic films become enriched in spherulites formed by the γ phase. According to other data,[345] PMMA can influence also the form of the polymorphic modification of the PVDF crystals produced in the isothermal annealing regime at temperatures above the glass transition temperature of the blend after its quenching from the melt.

DSC, IR spectroscopic, and X-ray diffraction data have shown that the crystallisation of PVDF/PMMA blends leads mainly to the formation of the α phase, but, if the component ratio is 70/30, the ferroelectric β phase is produced. These questions have been investigated in detail for textured films. In

particular the role of PMMA in polymorphic changes has been investigated in the formation of PVDF films under the conditions of a high longitudinal gradient in the flow of the melt.[356] It was shown that, under the above conditions, pure PVDF crystallises as a mixture of the α and β modifications, the fraction data of the former amounting to 62%. Scanning electron microscopic data indicate that this entails the formation of lamellar crystals. When 20 mass% of PMMA is introduced into PVDF, the fraction of the β phase increases by 20% under the same crystallisation conditions, while the morphology becomes mixed, i.e. acicular crystals appear together with lamellar ones. A similar conclusion was reached also in a later study[102] where it was shown that the addition of PMMA also increases the fraction of the β phase formed, while the morphology changes from lamellar to fibrillar. A new feature is the finding that the number of fibrillar β phase crystals increases with increase in the molecular mass of the polymethacrylates.

The influence of the form and concentration of the amorphous component in the blend with PVDF on the nature of the morphology generated on crystallisation of the latter has been investigated in detail.[357] Blends of PVDF with PMMA, the styrene/MMA copolymer (S–MMA), and poly(methyl acrylate) (PMA) were studied. It was noted that, whereas the lower critical miscibility temperature (LCT) in PVDF/PMMA blends is ~350 °C, it is significantly reduced for the PVDF/S–MMA system with increase in the amount of styrene in the copolymer. When the styrene content reaches $\geqslant 0.15$, the blend becomes incompatible, since the LCT becomes comparable to the equilibrium melting point of the α modification of PVDF. As in an earlier study,[86] pure PVDF crystallised at low degrees of supercooling with formation of the α and γ spherulites, but, in contrast to the study quoted, when polymethacrylates were added, fine differences were noted in the supermolecular structures produced. The α spherulites of pure PVDF have a fine fibrillar structure, which the γ spherulites lack.

For the PVDF/S–MMA blends, the α phase spherulites are converted into dendrites, the size of which diminishes, other conditions being equal, with increase in the fraction of the amorphous component. An even higher content of the latter leads to the crystallisation of PVDF in the form of small circular spherulites. The formation of dendrites is explained by the appearance in the growing front of fluctuations in the concentration of PVDF chains and by the transition of the crystallisation process to the diffusion-controlled region. Only circular spherulites are usually observed for PVDF/PMA blends. This is attributed to the lower glass transition temperature of PMA (and hence also of the blend) compared with PMMA, which should lead, other conditions being equal, to the acceleration of the stages involving diffusional control during crystallisation. The last blend is interesting also because it is possible to observe in it the crystallisation of PVDF under the conditions of very high 'dilution', i.e. when its volume fraction is only 0.3.

The above changes in the properties of blends of PVDF with polymethacrylates suggest the occurrence of specific interactions in these components. Their nature has been investigated by IR spectroscopy.[359] Attention was concentrated in the above study[359] on the analysis of the form and frequencies of the stretching vibrations of the carbonyl (C=O) group of PMMA. Preliminary studies on solutions of low-molecular-mass homologues of PMMA in the form of methyl acetate (MAC) and methyl pivalate (MPA) have shown that the solvent polarity may alter significantly the characteristics of the above band up to its splitting. The occurrence of significant interactions may be deduced by analysing the form of the absorption band due to the vibrations of the carbonyl group in MAC and MPA, which were introduced into the matrices of different polymers (Fig. 34). Evidently in the case of inert matrices (PE, PTFE) the absorption bands remain narrow and are displaced towards higher frequencies. In contrast to this, bands due to the PVDF matrix are significantly broadened and are displaced appreciably towards

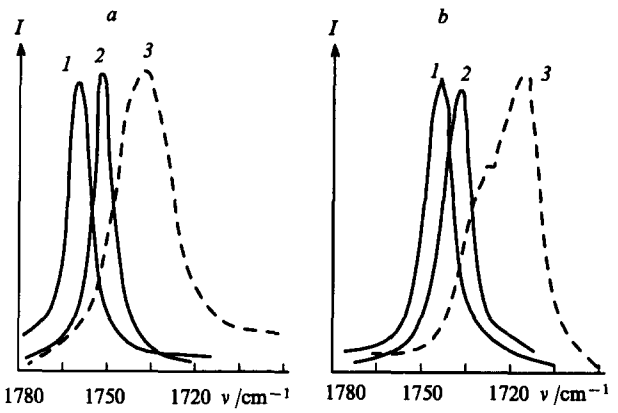


Figure 34. The form and position of the band due to the stretching vibrations of the C=O group of methyl acetate (*a*) and methyl pivalate (*b*) in various matrices.[359]
(*1*) PTFE; (*2*) PE; (*3*) PVDF.[359]

low frequencies. The authors formulated in greater detail the mechanism of the specific interactions in blends, having considered the system comprising the VDF/chlorotrifluoroethene copolymer swollen in deuterated MAC.

By following the doublet absorption in the region of symmetrical and antisymmetrical stretching vibrations of the methylene groups in PVDF in the copolymer, it was shown that the swelling of the copolymer in MAC leads to a significant bathochromic shift of the bands. It was therefore concluded that the C=O groups may form hydrogen bonds with VDF units. When account is taken of similar data for low-molecular-mass compounds, the enthalpy of such bonds, calculated from the frequency shift of the absorption bands, is found to be ~1 kcal mol^{-1}. This conclusion has been confirmed also on passing from model systems to polymer blends. The changes in the region of the absorption bands due to the carbonyl group for pure PMMA and PMMA in the PVDF/PMMA 50/50 blend show that in the latter case the band shifts somewhat towards lower frequencies, which can be seen distinctly from the difference spectra for specimens of the annealed and quenched blends, having the same composition. The excess absorption on the high-frequency side and the negative absorption on the lower-frequency side imply in this case that this annealing, leading to the crystallisation of PVDF, diminishes the number of specific contacts between PMMA and PVDF.

It was possible to demonstrate the occurrence of specific interactions also in relation to other functional groups, in particular for the methyl ether group O–CH_3 and the α-methyl group of PMMA. An increase in temperature leads to a decrease in the intensities of the above absorption bands for pure PMMA. The addition of 15 mass % of PVDF leads to exactly the same change. As a result of specific interactions, the latter effectively weakens the intermolecular interactions in PMMA chains. This is reflected also by the decrease in the glass transition temperature of the blends with increase in the fraction of PVDF noted above [see Eqn (27)]. Shilov et al.[353] also concluded that specific interactions occur in PVDF/PMMA blends, where the carbonyl group of PMMA should be involved. This conclusion is based on the analysis of the X-ray photoelectron spectral lines.

The specific interactions between PMMA and PVDF may be the cause of an unusual phenomenon noted for the PVDF/PMMA 80/20 blend. The study by Tsutsumi et al.[360] was devoted to the estimation of the internal field E_i in the polarised specimen. The method involving the introduction of small amounts of a dye (dimethylaminonitrostilbene) was used and measurements were made of the differences between the absorption spectra in the visible region before and after poling in a field with a strength E. For sufficiently high poling fields, the internal field proved to be higher than the poling field (Fig. 35 *a*). In the highest poling fields,

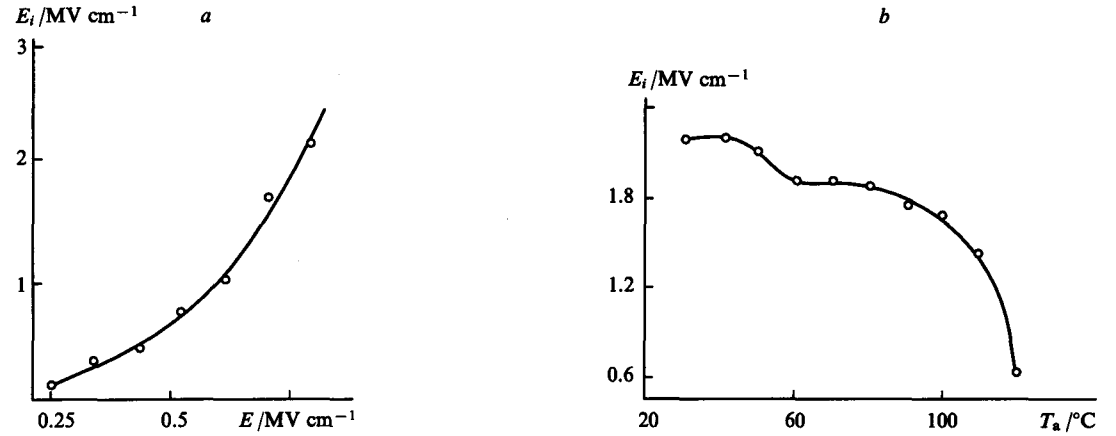


Figure 35. Dependence of the internal field E_i on the strength of the poling field (*a*) and the annealing temperature (*b*) in PVDF/PMMA 80/20 blends.[360]

the field ratio may be more than two, this conclusion being confirmed also for another type of dye.[361]

As a result of the specific interactions between the PVDF and PMMA chains in the amorphous phase, the glass transition temperature in the blend of the above composition becomes 60 °C.[360] At a poling temperature of 80 °C, these interactions are weakened and the poling field causes the preferential orientation of not only the ferroelectric crystals but also of the polar segments in the amorphous phase. Cooling of the specimen after poling in the presence of a field to room temperature creates a new situation for the blend compared with the VDF homopolymer. Indeed, since $T_g = -40$ °C for the latter, it follows that at room temperature the ordered dipoles in the amorphous phase should undergo depolarisation after the removal of the field and the internal field is then generated only by crystallites. In contrast to this, for the above blend at room temperature the ordered dipoles of the amorphous phase should be frozen, since its glass transition temperature is 60 °C. For this reason, the resultant internal field at room temperature is generated in this case, in contrast to PVDF, both by the polar crystals and by the ordered domains in the amorphous region. This hypothesis is confirmed by the data presented in Fig. 35*b*. Evidently heating of the specimen of the poling blend lowers E_i precisely in the region of the glass transition temperature, where the specific interactions between the PVDF and PMMA chains are effectively weakened. It can also be seen from the same figure that the main contribution to the depolarisation process comes nevertheless from crystals in which the appearance of mobility at temperatures above 100 °C leads to a more significant decrease in E_i.

The study of Tsutsumi et al.[360] was also concerned with the problem of the influence of PMMA on the polymorphism of PVDF. X-Ray diffraction data have shown that, whereas the homopolymer crystallises as the α phase, its blends with PMMA having the composition specified above are characterised by the presence of the β phase after quenching from the melt. This has also been noted in other studies.[345,357] However, it would be premature to reach an unambiguous conclusion concerning the role of PMMA as regards polymorphism, since many results indicate some uncertainty. For example, when the blend is prepared by deposition from a compatible polar solvent (dimethylacetamide), then, as for the pure homopolymer, it crystallises as the γ modification.[362] In the absence of α phase crystals, it is impossible to observe the high-temperature $\alpha(\alpha_c)$ relaxation. However, later data[363] showed that the form of the crystallographic modification may depend also on the type of the support on which the film is deposited. In particular, the case of the PVDF/PMMA 60/40 blend from solution onto an aluminium support promotes crystallisation as the α modification.

Together with indirect data on the polymorphism in PVDF, the dielectric relaxation method applied to blends can also yield new information about the details of the morphology produced. This is illustrated by the results of a series of studies where the relaxation processes in compatible PVDF blends were investigated by the dielectric method. The temperature dependences of the loss factor at a frequency of 100 kHz were analysed for pure PVDF and its blends with PMMA having different compositions.[365-367] Two relaxation regions can be clearly distinguished for the homopolymer. They are attributed, in order of increasing temperatures, to the $\beta(\alpha_a)$ and α_c processes. For blends, the kinetics of both processes are the same as the fraction of PMMA increases to 60% their intensity diminishes steadily without a change in the temperature of the ε'' maximum. The latter factor for the high-temperature process can be readily accounted for from the standpoint of the mechanisms of the α_c relaxation in PVDF. Indeed, as already mentioned, it can be attributed to motions of the chains in the crystals of the α modification of PVDF. A decrease in the fraction of the latter is therefore equivalent to a decrease in the number of crystals, which should lead to the observed decrease in the intensity of the peak without its displacement as regards temperature. The $\beta(\alpha_a)$ process is unusual. As mentioned above, according to the unanimous view of all investigators this process is attributed to the micro-Brownian motion of the chains in the amorphous region during glass transition. If the low-temperature peak for blends is also related to the glass transition, then it is impossible to account for the independence of the temperature of the above process as the fraction of PMMA in the blend increases. If the amorphous phase of PVDF is compatible with that in PMMA (this is indicated by the presence of a single glass transition temperature), then, as the fraction of the latter increases, the glass transition region should shift towards higher temperatures, as indicated by Eqn (27). The observed constancy of the low-temperature relaxation peak clearly conflicts with these conclusions.

This factor as well as the fact that the $\beta(\alpha_a)$ relaxation is observed distinctly only when the α_c process is detected made it necessary to postulate that the observed low-temperature process has to be related not to glass transition but to the motion in the interfacial region along the crystal–amorphous PVDF phase boundaries. The same idea has been developed in a study[368] in which compatible PVDF blends were investigated, but this time with PEMA. Fig. 36 presents the temperature variations of the loss factor ε'' for this blend at a frequency of 200 kHz.

In contrast to PMMA, poly(ethyl methacrylate) has a lower glass transition temperature (60 °C), so that yet another relaxation region (β_1) is observed together with the $\beta(\alpha_a)$ and α_c dispersions for blends with a high PVDF content. Comparison of DSC data shows that this relaxation region has to be attributed to the glass transition process in the mixed regions of the amorphous phase of PVDF and PEMA. It was found that the temperature variations of the relaxation frequencies for the

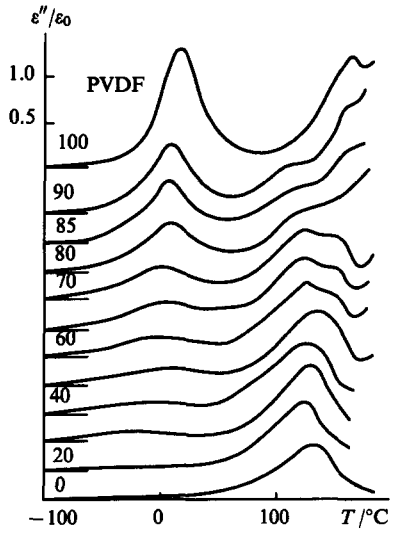


Figure 36. Temperature dependence of the loss factor at a frequency of 200 kHz in PVDF/PEMA blends.[368] The numerals on the curves represent the fraction of PVDF in the blend.

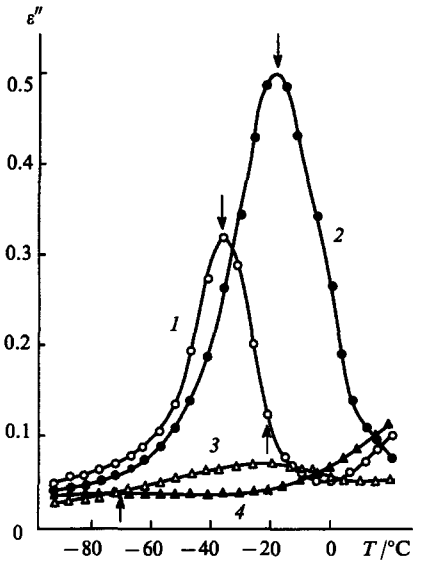


Figure 37. Temperature dependence of the loss factor in PVDF (*1*, *2*) and in the PVDF/PMMA 60/40 blend (*3*, *4*) at frequencies of 100 Hz (*1*, *4*) and 10 kHz (*3*, *2*).[369]

homopolymer and the slowly cooled blends enriched in PVDF fit satisfactorily on a single relation. This made it possible to claim that the low-temperature relaxation region in PVDF and in its crystallisable blends with PEMA is associated with the mobility in the interfacial regions of the crystal. Furthermore, the fraction of such regions W_i may be estimated from the relation[368]

$$W_i = W-(W_c-W_m), \tag{30}$$

where W is the overall fraction of PVDF in the blend, W_c the fraction of the crystalline phase, and W_m the fraction of PVDF in the blended state. The last was estimated from T_g for the blend, while W_c was calculated from the enthalpy of fusion. The values of W_i were compared with the relaxation force $\Delta\varepsilon$. It was shown that there is a linear relation between them. The maximum value of $\Delta\varepsilon$ (5.5) corresponds to the relaxation in the homopolymer, for which the fraction of interfacial regions reaches 0.35. As can be seen, this value may constitute more than half the degrees of crystallinity in PVDF usually reported.

However, the view of Yoon et al.[367] and Ando et al.[368] concerning the nature of the low-temperature relaxation region in PVDF blends is not shared by everyone. Thus Saito and Stuhn[369] questioned the validity of the conclusions reached. This is based on, for example, the temperature variations of the loss factor ε'' at two frequencies for pure PVDF and in blends with PMMA having the 60/40 composition (Fig. 37). Evidently the regions of the ε'' maximum for low-temperature relaxation at a high frequency are approximately the same for the homopolymer and the blend, as mentioned in the earlier studies.[367,368] However, at a frequency of 100 Hz the differences between the temperatures of the maxima are very striking. This served as a basis for the conclusion that it is not the α_a process but some other process which contributes to the low-temperature relaxation.

Fig. 38 presents comparative frequency dependences of ε'' in the glass transition region for pure PVDF and its blend with PMMA. Evidently, the peak for the homopolymer exhibits a high-frequency asymmetry, which was attributed to the contribution by the local mobility in the region of $\beta(\gamma)$ relaxation. The overall curve was subdivided into two components (α_a and β) by adjusting the experimental points to agree with the calculated ones with the aid of the empirical Havriliyak–Negami relation:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty)}{[1 + (i\omega\tau)^\alpha]^\gamma}\ , \tag{31}$$

where the parameters $0 \leqslant \alpha$ and $\gamma \leqslant 1$ describe respectively the broadening and asymmetry of the relaxation time distribution function, while ε_0 and ε_∞ are the extrapolated static and high-frequency relative permittivities. At the temperature indicated in Fig. 38, the curve for the β process in PVDF is described satisfactorily by the parameters $\Delta\varepsilon = 0.69$, $\lg\nu_m = 4.0$ $\alpha = 0.32$, and $\gamma = 1$.

The same frequency dependences of ε'' for the blend at the same temperature are presented in Fig. 38*b*, where the high-frequency maximum is described (after separation from the postulated low-frequency maximum) by the parameters $\Delta\varepsilon = 0.43$, $\lg\nu_m = 4.3$ $\alpha = 0.34$, and $\gamma = 1$ As can seen, the parameters of the β process for the homopolymer and the blend are virtually identical. This justifies the assumption that the low-temperature relaxation in PVDF/PMMA blends is determined by the contribution not of the α_a process but of the local mode of motion (β process). The temperature dependence of the relaxation frequencies in the blend and in the homopolymer are presented in Fig. 39. They confirm the above conclusion, since in both cases the relaxation frequencies and the activation energies (determined from the slopes of the relations presented) for the β and α_c process are virtually identical.

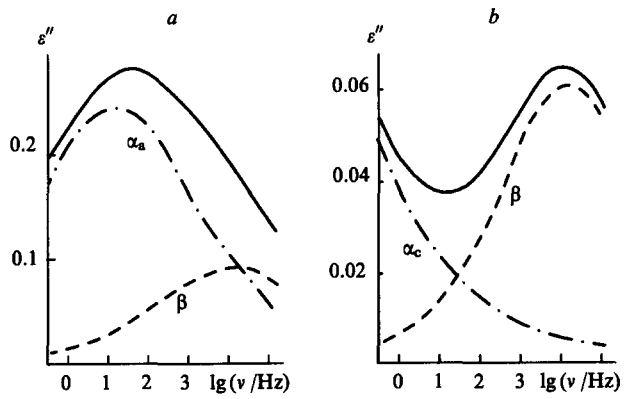


Figure 38. Frequency dependences of the loss factor at −40 °C for pure PVDF (*a*) and for the PVDF/PMMA 60/40 blend (*b*).[369]
α_a, α_c, β — contributions of the corresponding relaxation regions.

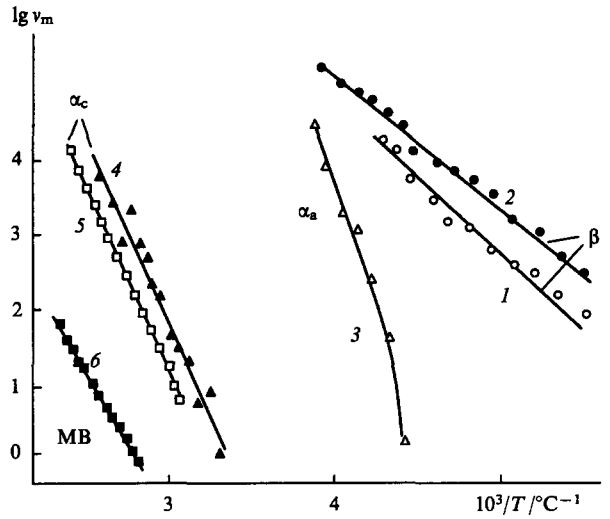


Figure 39. Temperature dependences of the relaxation frequencies in pure PVDF (*1*, *3*, *4*) and in the PVDF/PNMA 60/40 blend (*2*, *5*, *6*).[369] α_a, α_c, β, MW — contributions of the corresponding relaxation regions.

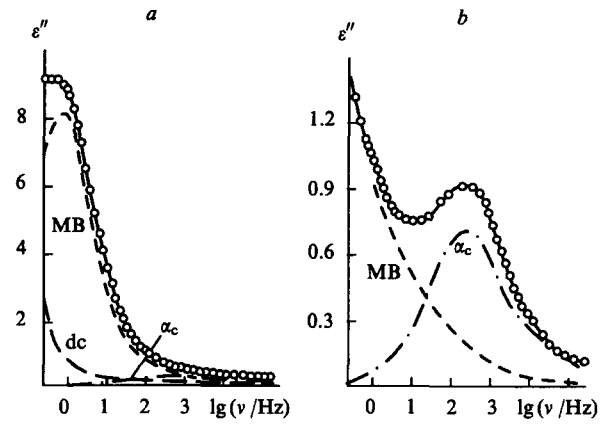


Figure 40. Frequency dependences of the loss factor at 90 °C in the PVDF/PMMA 60/40 blend (*a*) and in pure PVDF (*b*).[369] Components: dc — dc conductivity; M = Maxwell–Wagner relaxation; α_c — α_c relaxation.

The α_a process in the homopolymer cannot be described by the Arrhenius relation, as noted also by Ando et al.[368] Ando et al.[368] thought that one of the main arguments in support of their hypothesis is the agreement between the correlation frequencies for the homopolymer and the blend, which cannot be observed in the case of PVDF/PMMA according to the data of Saito and Stuhn.[369] However, one can assume that there are no special contradictions in the experimental data of the two studies.[368,369] Indeed, the sections of the curve corresponding to the relaxation frequencies in the ranges $\nu > 10^4$ Hz and $\nu < 10^4$ Hz were discussed in the first and second studies respectively (Fig. 39). Evidently, with increase in frequency, the α_a and β relaxation processes approach one another and one may expect that they would coincide. Despite the rigorous quantitative analysis of the results for the low-temperature relaxation in PVDF/PMMA blends, the conclusions reached by Saito and Stuhn [369] are nevertheless regarded as controversial. Indeed, if the low-temperature relaxation in the PVDF/PMMA blend is induced mainly by the contribution of the local β process in PVDF, then, under the conditions of the compatibility of the amorphous phases of both components, one has to postulate that the β(γ) process in PVDF is associated with the local mobility precisely in the amorphous regions. However, this conclusion is not always confirmed experimentally, since there are data (see, for example, Osaki and Ishida [275]) showing that this process has to be related to the crystalline phase.

The demonstration by Saito and Stuhn [369] that the characteristics of the interfacial regions at the amorphous phase–crystal boundary in the homopolymer and in the PVDF/PMMA blend differ significantly is more valuable. This is confirmed by the frequency dependences of ε'' at 90 °C for the PVDF/PMMA blend and the homopolymer (Fig. 40). Evidently they differ significantly: a maximum associated with the α_c relaxation, on which an intense rise in ε'' due to the occurrence of a vigorous low-frequency relaxation process via the Maxwell–Wagner (MW) interlayer polarisation mechanism is superimposed, has been observed for PVDF. As can be seen from Fig. 40*a*, the above relaxation process can be distinguished in the case of a blend, since the experimental ε'' points in the low-frequency region are satisfactorily fitted for the superposition of the MW process and when account is taken of the dc-conductivity. Compared with the homopolymer, the MW polarisation process in the blend is displaced towards higher frequencies. This made it possible to describe the given relaxation process in terms of the parameters of Eqn (31): $\Delta\varepsilon = 22.5$, $\lg\nu_m \approx 0.3$, $\alpha = 0.72$, and $\gamma = 1$.

Thus the difference noted between the parameters of the MW polarisation in the homopolymer and in its blend with PMMA makes it possible to assume that, owing to the increased affinity of the chains of both components, PMMA fragments are inserted not only in the PVDF amorphous phase proper but also into the regions of the interfaces noted above. Only this hypothesis can explain (at least qualitatively) the observed differences, since the ratio of the relative permittivities and the mobility of the carriers in the region of the interfaces, which in fact control the MW polarisation processes, should change under these conditions.

It is of interest to examine the characteristics of the blending of PMMA not only with PVDF but also with its copolymers. In the first place, attention was turned to the VDF/TrFE copolymer, which gives rise to a ferroelectric phase immediately on crystallisation from the melt.[370] The VDF/TrFE 78.5/21.5 copolymer was used and the blends were prepared by precipitation from solution in dimethylacetamide. As for the PVDF/PMMA blend, in the case of the copolymer an increase in the fraction of the amorphous component lowers the melting point of the PVDF crystals formed. Taking this into account, the Flory–Huggins parameter was estimated from Eqn (29) as −0.329, which is less then in the case of the homopolymer. This means that the introduction of TrFE into the VDF chain of the monomer promotes an intensification of the interaction between these blend components. It may be that this accounts for a series of the features noted below.

X-Ray diffraction data have shown that an increase in the fraction of PMMA in the blend with the copolymer hardly affects the unit cell parameters of the ferroelectric phase and leads merely to a decrease in its volume fraction. Crystallisation persists even in 65/35 blends and both the Curie and melting points change little under these conditions. The degree of crystallinity diminishes linearly with increase in the fraction of PMMA to 40% and for its higher values the blend is obtained in the amorphous state. Comparison of IR spectroscopic data and the concentrations of the groups of the copolymer in the 'planar zigzag' and $TGT\bar{G}$ conformations showed that the introduction of PMMA into the copolymer promotes an increase in the concentration of the former.

The copolymer considered comprises two polar comonomers. It is of interest to proceed to the consideration of a VDF copolymer in which the second comonomer is nonpolar. A fairly high fraction of this comonomer may affect the mechanism of the interaction of the blend components, since specific interactions between the PMMA chains and a nonpolar comonomer may be disturbed. The most suitable compound for this purpose is the copolymer of VDF with tetrafluoroethylene, which, like the

previous copolymer, can give rise to a ferroelectric phase in the isotropic state.[371]

The use of the VDF/TFE 80/20 copolymer, the properties of which are similar to those of the VDF/TrFE copolymer, made it possible to test the role of the polarity of the second monomer. The monotonic variation of the refractive index and the single glass transition temperature obtained on varying the composition ratio indicate that the above blends are compatible. Analysis of X-ray data has shown that crystallisation ceases when the fraction of the copolymer is less than 70%. Evidently this corresponds approximately to the critical value for VDF/TrFE copolymer in a blend with PMMA (~65%). This similarity is most probably associated with the fact that in both copolymers crystallisation proceeds with formation of the polar ferroelectric β phase. For higher contents of PMMA in the blend with the VDF/TFE copolymer, the latter no longer crystallises. The nature of the amorphous halo indicates the compatibility of the components in the nonordered state: with increase in the fraction of PMMA, the angular position the halo shifts monotonically towards lower angles as a consequence of the increase in the average distances between the molecules.

The different chemical composition of the second comonomer is, however, manifested in a different way. Yet another endotherm, associated with the phase separation process, which is recorded also from the appearance of the turbidity point, has been noted on the DSC curves in the range of temperatures above the melting paint. Both methods yielded approximately similar characteristic temperatures, but, what is most interesting, the turbidity point varied very significantly. The variation may be described by a curve with a minimum as a function of the increase in the fraction of the copolymer in the blend. It has been shown that a maximum variation of the enthalpy of phase separation corresponds to the region of the minimum in the phase separation point. The Flory–Huggins parameter is then found to depend on the composition, but remains negative over the entire concentration range. The increase in this parameter as the concentration of the copolymer is reduced shows that PMMA-enriched blends are characterised by a weaker interaction of the components. This has also been noted for the PVDF/PMMA blend [332] on the basis of small angle X-ray scattering data. The specific role of the nonpolar comonomer TFE in PVDF chains most probably attributes to the fact that the lowest values of B are found to be higher than for the blend of pure PVDF and PMMA.

From the practical point of view, it is important to have compatible PVDF blends with a high glass transition temperature. For this purpose, it is of interest to consider as the blend component the noncrystallising highly polar polyvinylpyrrolidinone (PVP), the glass transition temperature of which is ~200 °C . The above components are satisfactorily compatible in the melt.[372, 374] It was observed that the introduction of PVP greatly reduces the melting point of the PVDF crystals, the formation of which is fully inhibited for a PVP content of ~40 mass %. The melting point depends on the molecular mass of PVP and decreases with increase in the fraction of the latter. Analysis of the details of the dynamic relaxation in the above systems shows that a decrease in the fraction of PVP in noncrystallising heterogeneous blends with PVDF leads to a significant decrease also in the glass transition temperature: for a PVP fraction of 0.4, it diminishes to ~120 °C.[374]

If the PVDF/PVP blends crystallise, then the presence of three-phases is noted: the crystals of PVDF, homogeneously blended domains with a quasi-constant composition, and the purely amorphous PVDF phase. In view of the very low Flory–Huggins parameter, very strong interactions are postulated between the components of the blend in the second phase.

The possibility of regulating the energy of the specific interactions of the components can be ensured by introducing ions into the polymer chain. In this connection, it is of interest to examine the questions concerning structure formation in a blend of PVDF with the tetrafluoroethene–perfluorovinyl ether copolymer with a sulfonic acid group at the end [Nafion (NAF)].[375] In the study of the morphology on crystallisation of PVDF in such a blend, obtained by precipitation from dimethylacetamide and dimethylformamide, it was shown that the average size of the spherulite is always greater when the component ratio is approximately equal. Mixed spherulites of the α and γ modifications have been observed for the PVDF/NAF 40/60 and 60/40 blends, as in pure PVDF under certain crystallisation conditions. The size and shape of the spherulites formed depend not only on the blend composition but also on the film deposition temperature. α Spherulites grow predominantly at 150 °C, whereas the small spherulites of the γ phase grow mainly at 70 and 90 °C. The latter property is new compared with pure PVDF and is apparently due to the presence of the ionomer.

An increase in temperature in a film of a blend with a spherulitic morphology to 185 °C is accompanied by the disappearance of spherulites when the system melts. However, a further increase in temperature leads to a catastrophic growth of scattering intensity (for parallel polarisers) and a displacement of the scattering region towards small angles. This is attributed to the thermoinduced phase separation of the spinodal type. By resorting to dielectric relaxation data in the region of the α_c transition, it was possible to establish that the temperature of the maximum increases linearly with increase in the fraction of NAF. On this basis, it is concluded that this pair of components is partly compatible as a result of the specific interactions between the PVDF groups and NAF ions. A detailed study of the kinetics of the phase separation (above the melting point of PVDF) showed that the characteristic point may depend significantly on the heating rate. At a constant heating rate (0.2 K min^{-1}), the turbidity point varies as a function of blend composition along a curve with a minimum for a blend with 60 mass% of NAF. Treatment of the experimental data from the standpoint of the scaling theory has shown that, for a small thickness of the blend films (10 μm), the growth of domains with concentration fluctuations in the region of the phase separation is more likely to be two-dimensional in character.

One may deal separately with the results of several studies in which problems of compatibility in blends of PVDF with an other crystallisable polymer were considered. The blends of PVDF with poly(vinyl fluoride) (PVF) have been investigated in greatest detail in this connection.[376, 377] The results of X-ray analysis have shown that the phenomenon of isomorphism (crystallisation of both components with the same lattice) is characteristic of them for virtually any component ratio.[376] The reason for this is apparently the identity of the chemical bonds in the repeat units of the monomers and hence the similarity of the lattices of each polymer. Thus the most intense intermolecular reflection due to the β phase is characterised by the interplanar spacings d = 4.31 Å in PVF and 4.39 Å in PVDF. It is significant that even small amounts of PVF added to PVDF stabilise the 'planar zigzag' conformation in the latter.[376]

The same feature has been noted also for the blend of PVDF with another crystallisable polymer — poly(ethylene glycol).[378] The manifestation of cocrystallisation effects has also been observed for the blend of PVDF with the chlorotrifluoroethylene/VDF 77/23 copolymer. Under the conditions of the preparation of blend films from a common solvent, a single melting endotherm due to the fusion of the PVDF crystals is manifested, the melting point shifting insignificantly towards lower temperatures as the PVDF fraction is diminished. At the same time, this leads to an appreciable decrease in the degree of crystallinity and in the size of the spherulites. The authors tend to see the significant difference between the degrees of crystallinity α in the blend with 10% of PVDF compared with the pure homopolymer, taking into account its fraction in the blend, as the manifestation of the cocrystallisation effects in the above blends: whereas α = 53% for PVDF, for the blend with 10% of the homopolymer (in the case of a noncrystallisable copolymer) α should be 5.3%, but the actually observed value is 9.9%.

The practical tasks in the search for new materials with high piezoelectric characteristics suggest the creation of composite systems with classical inorganic ferroelectric fillers (of the type of $BaTiO_3$), which are introduced into the organic polymer matrix. In this connection, the specific interactions between PVDF and PMMA, in particular, may be reflected also in the final piezoelectric properties. Indeed, the three-layer dielectric in the form of PVDF combined with PMMA (filled with $BaTiO_3$) has a high piezoelectric constant d_{33}, which, however, is insufficiently stable. An increase in d_{33} may be attained in another system, where the buffer layer consists of a polyetherurethane elastomer,[380] the highly polar groups of which may stabilise the structure and hence the piezoelectric properties as a result of the interaction with the corresponding fragments of the PVDF chains.

The filling of PVDF simply with $BaTiO_3$ particles is also of practical interest, since the latter have a higher Curie temperature, which makes it possible, in principle, to obtain a combined material not only with high piezoelectric characteristics but also with a wider range of temperatures at which it can be employed. Possible structural modifications both in PVDF and in the particles of the added filler have been suggested for this purpose.[381, 382] The X-ray diffraction method, employed for the same purpose, has been applied over a wide range of scattering angles in order to isolate nonoverlapping reflections from individual blend components. Pure PVDF crystallised as the α modification while the introduction of even 10% of $BaTiO_3$ greatly reduced the intensity of the corresponding reflections, which can be explained by a decrease in the degree of crystallinity. The observation of the characteristic reflections for $BaTiO_3$ with increase in its content in the blend indicates that they are somewhat displaced into the region of smaller angles. This is treated as evidence for the appearance of internal stresses in such composites.

Finally, one should deal with yet another study on PVDF blends with inorganic fillers. This concerns PVDF composites with γ-Fe_2O_3 particles.[383] The author's aim was to test the occurrence of the thermal decomposition of $Fe(CO)_5$ in a chemically inert matrix. However, this study may be regarded as a contribution to the development of a new method for the preparation of materials with an interesting combination of electrical and magnetic properties.

The formation of fine γ-Fe_2O_3 particles as a result of the decomposition reactions of the initial compounds is accompanied primarily by the formation of an insoluble polymer. These processes are most probably actually responsible for the fact that, on crystallisation of PVDF, the large spherulites (which arise in the homopolymer) are no longer observed in the blend, while the mechanical characteristics of the latter change significantly in the region of the high elasticity plateau. Optical microscope and small angle X-ray scattering data indicate that the degree of crystallinity in blends diminishes significantly. Analysis of the morphology of the blends produced clearly indicates the occurrence of processes involving the phase separation of the components. The cluster structure was typically analysed by the method of X-ray probes and it was found that the concentration of iron within the particles is higher than in the surrounding polymer matrix. Analysis of X-ray and electron diffraction indicates the possibility of the occurrence of reactions between the magnetic particles and PVDF with formation of FeF_2 compounds. It is believed that the latter are produced in the course of the formation of a three-dimensional network in the polymer matrix. On the other hand, most of the disperse phase has the γ-Fe_2O_3 structure. The proposed method is promising for the preparation of organic materials containing small magnetic particles (the size of the latter is 50–100 Å).

X. Conclusion

The possibilities of the polymorphic transformations in PVDF and in its copolymers under the influence of various external factors have been analysed in the present review. It has been shown that a particular crystallographic modification may be obtained not only as a result of the operation of various physical factors but also as a result of the introduction into the PVDF chain of, for example, 'head to head' defects or certain comonomers. It is significant that the specific effects of the solvent can also be used as an effective factor in the formation of particular structure of PVDF films from appropriate solutions. It is emphasised that the concentration and type of ionogenic impurities in solution can then affect the type of the polymorphic modification formed.

The operation of factors such as high pressure and tensile deformation are used for practical applications, where one needs to obtain polar modifications of PVDF, for example for pyro- and piezo-electric transducers. Examination of the polymorphism in PVDF induced by high electric fields may be used, on the one hand, to discover the fundamental characteristics of the behaviour of polymeric dielectrics in electric fields and, on the other, for recommendations concerning the practical preparation of the active elements used in the energy converters mentioned above. It has been shown in relation to a series of recent studies that yet another (nontraditioned) method for the modification of the structure of PVDF and crystallising polymers in general is irradiation.

The characteristics of the dynamics of polymer chains in PVDF and its copolymers may serve as a basis for the prediction of the occurrence of relaxation processes in the systems considered, which is important for the creation of materials with stable and specified properties.

It is shown that specific modification of the structures of the polymer systems considered may be achieved also with the aid of blends with polymers and nonpolymeric components. In a number of cases, it is possible to improve by this procedure certain optical characteristics of the materials formed, which makes them competitive in relation to other materials used in elements with nonlinear optical properties.

References

1. H Kawai *Jpn. J. Appl. Phys.* **8** 975 (1969)
2. G M Sessler *J. Acoust. Soc. Am.* **70** 1596 (1981)
3. V V Kochervinskii *Usp. Khim.* **63** 383 (1994) [*Russ. Chem. Rev.* **63**
4. C W Wilson *J. Polym. Sci. Part A, Polym. Chem.* **1** 1305 (1963)
5. R C Ferguson, E G Brame *J. Phys. Chem.* **83** 1397 (1979)
6. V A Lovchikov, A M Shlyakov, I M Dolgopol'skii *Issledovanie Stroeniya Makromolekul Metodom YaMR Vysokogo Razresheniya* (Investigation of the Structure of Macromolecules by the High-Resolution NMR Method) (Moscow: TsNIIITEI Nefteperer. Neftekhim. Prom., 1983)
7. R C Ferguson, D W Ovenall *Am. Chem. Soc. Polym. Prepr.* **25** 340 (1984)
8. A E Tonelli, F C Schilling, R E Cais *Macromolecules* **15** 849 (1982)
9. F A Bovey, F C Schilling , T K Kwey, H L Frish *Macromolecules* **10** 559 (1977)
10. A E Tonelli, F C Schilling, R E Cais *Macromolecules* **14** 560 (1981)
11. F C Schilling *Am. Chem. Soc. Polym. Prepr.* **22** 407 (1981)
12. M Bruch, F A Bovey, R E Cais *Macromolecules* **17** 2547 (1984)
13. R E Cais, J M Kometani *Macromolecules* **18** 1334 (1985)
14. V P Sass, A S Shashkov, A I Konkin, R I Rabinovich, I M Dolgopol'skii, V S Sokolov *Vysokomol. Soed., Ser. A* **17** 1086 (1975)
15. T Yagi, M Tatemoto *Polym. J.* **11**. 429 (1979)
16. E M Murasheva, A S Shashkov, A A Dontsov *Vysokomol. Soed., Ser. A* **23** 632 (1981)
17. R E Cais, J M Kometani *Anal. Chim. Acta.* **189** 101 (1986)
18. J Ando, H Kobayashi, R Chuio, in *Proceedings of the US-Japanese Polymer Symposium* (New York: Springer, 1984) p. 173
19. B Servet, D Bruussoux, F Micheron, R Bisaro, S Res, P Merenda *Rev. Techn. Thomson-CSF* **12** 761 (1980)
20. E L Gal'perin, Yu V Strogalin, M P Mlenik *Vysokomol. Soedin.* **7** 933 (1965)
21. G Cortili, G Zerbi *Spectrochim. Acta* **23A** 285 (1967)

22. G Cortili, G Zerbi *Spectrochim. Acta* **23A** 2216 (1967)
23. F J Boerio, J G Koenig *J. Polymer Sci., Part A, Polym. Chem.* **9** 1517 (1971)
24. G Cessae, J G Curro *J. Polym. Sci., Polym. Phys. Ed.* **12** 695 (1974)
25. M Kobayashi, K Tashiro, H Tadokoro *Macromolecules* **8** 158 (1975)
26. M Bachmann, W J Gordon, J I Koenig, J B Lando *J. Appl. Phys.* **50** 6106 (1979)
27. M Kobayashi, K Tashiro, H Tadokoro *Macromolecules* **14** 1757 (1981)
28. M Latour, A Montaner, M Galtier, G Geneves *J. Polym. Sci, Polym. Phys. Ed.* **19** 1121 (1981)
29. L Lanchlan, J F Rabolt *Macromolecules* **19** 1049 (1986)
30. L N Pirozhnaya, O B Zubkova, L A Gribov *Zh. Prikl. Spektrosk.* **48** 65 (1988)
31. G Borinetti, G Zannoni, G Zerbi *J. Mol. Struct.* **224** 425 (1990)
32. V V Kochervinskii, V A Glukhov, V G Sokolov, V F Romadin, E M Murasheva, Yu K Ovchinnikov, N A Trofimov, B V Lokshin *Vysokomol. Soed., Ser. A* **30** 1969 (1988)
33. V V Kochervinskii *Vysokomol. Soed., Ser. A* **33** 2106 (1991)
34. N N Makarevich *Zh. Prikl. Spektrosk.* **7**. 341 (1965)
35. N N Makarevich, N I Sushko *Zh. Prikl. Spektrosk.* **11** 917 (1969)
36. W W Doll, J B Lando *J. Macromol. Sci., Phys.* **B2** 205 1968
37. S Weinhold, M A Bachmann, M H Litt, J B Lando *Macromolecules* **15** 1631 (1982)
38. M Latour, N Abo Dorro, J L Galigne *J. Polym. Sci., Polym. Phys. Ed.* **22** 345 (1984)
39. K Okuda, T Yoshida, M Sugito, M Asahina *J. Polym. Sci., Polym. Phys. Ed.* **5** 465 (1967)
40. E L Gal'perin, B P Kosmynin, R A Bychkov *Vysokomol. Soed., Ser. B* **12** 555 (1970)
41. E L Gal'perin, Doctoral Thesis in Chemical Sciences, Karpov Physicochemical Research Institute, Moscow, 1980
42. E L Gal'perin, V F Mindrul, N I Nikanorova, N I Titanskaya *Vysokomol. Soedin., Ser. B* **14** 37 (1972)
43. R L Miller, J J Raisoni *J. Polym. Sci., Polym. Phys. Ed.* **14** 2325 (1976)
44. D T Grubb, K W Choi *J. Appl. Phys.* **52** 5908 (1981)
45. D T Grubb, P Cebe, K W Choi *Ferroelectrics* **57** 12 (1984)
46. A Chapiro, Z Mankowski, N Schmitt *J. Polym. Sci., Polym. Chem. Ed.* **20** 1791 (1982)
47. V V Kochervinskii, V A Glukhov, V G Sokolov, L Ya Modorskaya, B V Lokshin *Vysokomol. Soed., Ser. A* **31** 2590 (1989)
48. V V Kochervinskii, V A Glukhov, V G Sokolov, B I Ostrovskii *Vysokomol. Soed., Ser. A* **31** 154 (1989)
49. A J Lovinger *Polymer* **22** 412 (1981)
50. A S Lovinger *Macromolecules* **14** 322 (1981)
51. C M Balik, R Farmer, E Baer *J. Mater. Sci.* **14** 1511 (1979)
52. E L Gal'perin, S S Dubov, E V Volkova, M P Mlenik, L A Bulygina *Vysokomol. Soedin.* **8** 2033 (1966)
53. E L Gal'perin, B P Kosmynin, V F Mindrul, V K Smirnov *Vysokomol. Soed., Ser. B* **12** 594 (1970)
54. W W Doll, J B Lando *J. Appl. Polym. Sci.* **14** 1767 (1970)
55. J Hoshi *Mod. Plast.* **48** 110 (1971)
56. R Liepins, J R Surles, N Morosoff, V J Stannett *J. Polym. Sci., Polym. Chem. Ed.* **16** 3039 (1978)
57. L N Pirozhnaya, V Ya Maksimov, L I Tarutina, L Ya Madorskaya *Zh. Prikl. Khim.* **55** 2758 (1982)
58. L Ya Madorskaya, N I Loginova, N E Shadrina, M S Kleshcheva, Yu A Panshin *Vysokomol. Soed., Ser. B* **22** 904 (1980)
59. L Ya Madorskaya, N N Loginova, A M Lobanov, Yu A Panshin *Vysokomol. Soed., Ser. A* **25** 2144 (1983)
60. E G Erenburg, L V Pavlova, A I Konshin, A M Greis, I P Dolgopol'skii, I T Poddubnyi *Vysokomol. Soed., Ser. A* **25** 365 (1983)
61. L Ya Madorskaya, M V Samoilov, G A Otradina, M P Agapitov, V P Budtov, T G Maksenko, E Yu Kharcheva, N H Loginova *Vysokomol. Soed., Ser. A* **26** 2577 (1984)
62. V V Kochervinskii, T E Danilyuk, L Ya Modorskaya *Vysokomol. Soed., Ser. A* **28** 619 (1986)
63. L Ya Madorskaya, N N Loginova, L P Kastorskii, O V Kuz'michev, V L Maksimov, A M Lobanov *Vysokomol. Soed., Ser. A* **28** 1284 (1986)
64. R E Cais, N J A Sloane *Polymer* **24** 179 (1983)
65. G A Otradnaya, L Ya Madorskaya, V M Belyaev, K A Vylegzhanina, O K Belomutskaya, T V Kornilova *Vysokomol. Soed., Ser. A* **32**. 872 (1990)
66. S Weinhold, M A Backmann, M H Litt, J B Lando *Macromolecules* **15** 1631 (1982)
67. W W Doll, J B Lando *J. Macromol. Sci.* **4B** 309 (1970)
68. S Weinhold, M H Litt, J B Lando *J. Appl. Phys.* **51** 5145 (1980)
69. S Weinhold, M H Litt, J B Lando *Macromolecules* **13** 1178 (1980)
70. M A Bachmann, J B Lando *Macromolecules* **14** 40 (1981)
71. G Welch, R L Miller *J. Polym. Sci., Polym. Phys. Ed.* **14** 1683 (1976)
72. C Mancarella, E Martuselli *Polymer* **18** 1240 (1977)
73. Y S Yadav, P C Jain *J. Macromol. Sci., Phys.* **25** 335 (1984)
74. L T Chen, C W Frank *Ferroelectrics* **57** 51 (1984)
75. P J Flory *Trans. Faraday Soc.* **51** 848 (1955)
76. J C Sanchez, R K Eby *J. Res. Natl. Bur. Stand. A, Phys. Chem.* **77** 353 (1973)
77. B L Farmer, A J Hopfinger, J B Lando *J. Appl. Phys.* **43** 4293 (1972)
78. K Nakagawa, Y Ishida *J. Polym. Sci., Polym. Phys. Ed.* **11** 2153 (1973)
79. S Osaki, Y Ishida *J. Polym. Sci., Polym. Phys. Ed.* **13** 1071 (1975)
80. W M Prest, D J Luca *J. Appl. Phys.* **46** 4136 (1975)
81. W M Prest, D J Luca *J. Appl. Phys.* **49** 5042 (1978)
82. A J Lovinger, H D Keith *Macromolecules* **12** 919 (1979)
83. A J Lovinger *J. Polym. Sci., Polym. Phys. Ed.* **18** 793 (1980)
84. A J Lovinger *Polymer* **21** 1317 (1980)
85. A J Lovinger, M Freed *Macromolecules* **13** 989 (1980)
86. B S Morra, R S Stein *J. Polym. Sci., Polym. Phys. Ed.* **20** 2261 (1982)
87. L T Chen, C W Frank *Macromolecules* **18** 2163 (1985)
88. N C Banik, F P Boyle, T J Sluckin, P L Taylor, S K Tripathy, A J Hopfinger *Phys. Rev. Lett.* **43** 456 (1979)
89. N C Banik, P L Taylor, S K Tripathy, A J Hopfinger *Macromolecules* **12** 1015 (1979)
90. N C Banik, F P Boyle, T J Sluckin, P L Taylor, S K Tripathy, A J Hopfinger *J. Chem. Phys.* **72** 3191 (1980)
91. Y Takahashi, M Kohyama, H Tadokoro *Macromolecules* **9** 870 (1976)
92. Y Takahashi, H Tadokoro *Macromolecules* **13** 1316 (1980)
93. Y Takahashi, H Tadokoro, A Odajima *Macromolecules* **13** 1318 (1980)
94. Y Takahashi, Y Matsubara, H Tadokoro *Macromolecules* **13** 334 (1982)
95. Y Takahashi *Kobunshi* **33** 696 (1984)
96. Y Takahashi *Polym J.* **15** 733 (1983)
97. Y Takahashi, H Tadokoro *Ferroelectrics* **57** 187 (1984)
98. A J Lovinger *J. Appl. Phys.* **52** 5934 (1981)
99. C C Hsu, P H Geil *J. Appl. Phys.* **56** 2404 (1984)
100. C C Hsu, P H Geil *Polym. Commun.* **27** 105 (1986)
101. D-C Yang, Y Chen *J. Mater. Sci. Lett.* **6** 599 (1987)
102. D-C Yang, Y Chen, D-D Song *Chem. J. China. Univ.* **14** 1325 (1993)
103. Y Oka, N Koizumi *Bull. Inst. Chem. Res. Kyoto Univ.* **63** 192 (1985)
104. K Loufakis, B Wunderlich *Polymer* **26** 1875 (1985)
105. R Loufakis, B Wunderlich *Macromolecules* **20** 2471 (1987)
106. Y Takahashi *Polym. J.* **15** 733 (1983)
107. T Yagi *Kindzoku Khemen Gidzyutsu (J. Metal. Finish. Soc. Jpn.)* **37** 640 (1986)
108. A J Lovinger, G T Davis, T Furukawa, M G Broadhurst *Macromolecules* **15** 323 (1982)
109. K Tashiro, K Takano, M Kobayashi, Y Chatani, H Tadokoro *Polymer* **25** 195 (1984)
110. H Yasegawa, M Kobayashi, H Tadokoro *Polym. J.* **3** 591 (1972)
111. R Hasegawa, Y Takanashi, Y Chatani, H Tadokoro *Polym. J.* **3** 600 (1972)
112. Y Oka, Y Murata, N Koizumi *Polym. J.* **18** 417 (1986)
113. K Tashiro, H Kaito, M Kobayashi *Polymer* **33** 2915 (1992)
114. B B Kochervinskii V A Glukhov, V F Romadin, V G Sokolov, B V Lokshin *Vysokomol. Soed., Ser. A* **30** 1916 (1988)
115. V V Kochervinskii, N N Kuz'min, A N Zadorin *Vysokomol. Soedin.* (1997) (in the press)

116. V V Kochervinskii, N N Kuzmin, in *Proceedings of the Fifth Russian-Japanese Symposium on Ferroelectricity* (Moscow: Moscow State Univ., 1994) p. 132
117. V V Kochervinskii, N N Kuz'min *Neorg. Mater.* **31** 859 (1995)
118. V V Kochervinskii, N N Kuz'min, in *Proceedings of the International Symposium "Ferro-Piezoelectric Materials and their Applications"* (Moscow: Karpov Physicochemical Research Institute, 1994) RO-2-22
119. S Roussel, K L Mgelroy, L N Judovits *Polym. Eng. Sci.*, **32** 1300 (1992)
120. R Gregorio M Cestari *J. Polym. Sci., Part B, Polym. Phys.* **32** 859 (1994)
121. J B Lando, H G Olf, A Peterlin *J. Polym. Sci., Polym. Chem. Ed.* **4** 941 (1966)
122. B P Kosmynin, E L Gal'perin, D Ya Tsvankin *Vysokomol. Soed., Ser. A* **12** 1254 (1970)
123. B P Kosmynin, E L Gal'perin, D Ya Tsvankin *Vysokomol. Soed., Ser. A* **14** 1365 (1972)
124. K Matsushige, T Takemura *J. Polym. Sci., Polym. Phys. Ed.* **18** 1665 (1980)
125. U Kofer, R Hirte, Ch Ruscher *Acta Polym.* **34** 352 (1983)
126. U Kofer, R Hirte *Acta Polym.* **33** 434 (1982)
127. K Matsushige, T Takemura, in *Proceedings of the 55th Meeting of the American Chemical Society, Atlanta, 1983* No 4, p. 1
128. E L Nix, L Holt, J C Mcgrath *Ferroelectrics* **32** (1–4) 103 (1981)
129. V V Kochervinskii, V F Romadin, V A Glukhov, V G Sokolov, M A Saidakhmetov *Vysokomol. Soed., Ser. A* **31** 1381 (1989)
130. V V Kochervinskii, V A Glukhov, V G Sokolov, V F Romadin, B I Ostrovskii, S Yu Kuznetsova *Vysokomol. Soed., Ser. A* **31** 2311 (1989)
131. J Clements, G R Davies, I M Ward *Polymer* **26** 208 (1985)
132. D K Das-Gupta, D B Shier *J. Appl. Phys.* **49** 5685 (1978)
133. B Servet, D Broussoux, F Micheron *Rev. Tech. Thomson-CSF* **12** 796 (1980)
134. B Servet, D Broussoux, F Micheron *J. Appl. Phys.* **52** 5926 (1981)
135. B Servet, D Broussoux, F Micheron, R Bisaro, S Ries, P Merenda *Rev. Techn. Thomson-CSF* **12** 761 (1980)
136. C H Wang, D B Cavanaugh, Y Hashidaki *J. Polym. Sci., Polym. Phys. Ed.* **19** 941 (1981)
137. J Humpreys, I M Ward, E L Nix, J C McGrath *J. Appl. Polym. Sci.* **30** 4069 (1985)
138. T Mizuno, K Nakamura, N Murayama, K Okuda *Polymer* **26** 853 (1985)
139. T C Hsu, P H Geil *J. Mater. Sci.* **24** 1219 (1989)
140. T Konaka, S Nakagawa, S Yamakawa *Polymer* **26** 462 (1985)
141. Y Takeuchi, K Nakagawa, S Yamikawa *J. Polym. Sci., Polym. Phys. Ed.* **23**. 1193 (1985)
142. Y Takeuchi, K Nakagawa, F Yamamoto *Polymer* **26** 1929 (1985)
143. K Nakagawa, M Amano *Polym. Commun.* **27** 310 (1986)
144. K Spector, R S Stein *Macromolecules* **24** 2083 (1991)
145. A G Kolbek, D R Uhlmann *J. Polym. Sci., Polym. Phys. Ed.* **15** 27 (1977)
146. W T Mead, A E Zachariades, T Shimada, R S Porter *Macromolecules* **12** 473 (1979)
147. T Shimada, A E Zachariades, W T Mead, R S Porter *J. Cryst. Growth* **48** 334 (1980)
148. E M Berg, D C Sun, J H Magill *Polym. Eng. Sci.* **29** 715 (1989)
149. A J Lovinger, T T Wang *Polymer* **20** 725 (1979)
150. D T Grubb, F R Kearney *J. Polym. Sci., Part B, Polym. Phys.* **28** 2071 (1990)
151. J C Mcgrath, L Holt, D M Jones *Ferroelectrics* **50** 339 (1983)
152. G W Andrews, A R Piercy *J. Mater. Sci. Lett.* **5** 969 (1986)
153. P Leaver, M I Cunmingham *J. Mater. Sci. Lett.* **6** 705 (1987)
154. E L V Levis, I M Ward *J. Polym. Sci., Part B, Polym. Phys.* **27** 1375 (1989)
155. V V Kochervinskii *Neorgan. Mater.* **31** 851 (1995)
156. V V Kochervinskii, in *Proceedings of the International Symposium "Ferro-Piezoelectric Materials and their Applications"* (Moscow: Karpov Physicochemical Research Institute, 1994) 0-7-6
157. V V Kochervinskii, V A Glukhov, V G Sokolov, B V Lokshin *Vysokomol. Soedin., Ser. A* **31** 282 (1989)
158. R M Cohil, J Petermann *Polymer* **22** 1612 (1981)
159. Y Takahashi, A Odajima *Rep. Progr. Polym. Phys. Jpn.* **23** 161 (1980)
160. V V Kochervinskii, V G Sokolov *Vysokomol. Soedin., Ser. A* **33** 1625 (1991)
161. J Frile *Makromol. Chem., Makromol Symp.* **72** 131 (1993)
162. Y Takahashi, T Zakoh, N Hanatani *Colloid Polym. Sci.* **269** 781 (1991)
163. V V Kochervinskii, V A Głukhov, S Yu Kuznetsova *Vysokomol. Soed., Ser. A* **29** 1530 (1987)
164. W W Doll, J B Lando *J. Macromol. Sci., Phis.* **B2** 219 (1968)
165. W W Doll, J B Lando *J. Macromol. Sci., Phis.* **B4** 889 (1970)
166. W W Doll, J B Lando *J. Macromol. Sci., Phis.* **B4** 897 (1970)
167. R Hasegawa, Y Tanabe, M Kobayashi, H Tadokoro *J. Polym. Sci., Part A, Polym. Chem.* **8** 1079 (1970)
168. J Scheinbien, C Nakafucu, B A Newman, K D Pae *J. Appl. Phys.* **50** 4399 (1979)
169. B A Newman, C H Yoon, K D Pae *J. Mater. Sci.* **14** 2391 (1979)
170. K D Pae, C Vijayan, R Renfree, K T Chung, J I Schenbeim, B A Newman *Ferroelectrics* **57** 245 (1984)
171. K Matsushige, K Nagata, T Takemura *Jpn. J. Appl. Phys.* **17** 467 (1978)
172. K Matsushige, T Takemura *J. Polym. Sci., Polym. Phys. Ed.* **16** 921 (1978)
173. K Matsushige, T Takemura *J. Cryst. Growth* **48** 343 (1980)
174. K Matsushige, T Takemura *J. Polym. Sci., Polym. Phys. Ed.* **18** 1665 (1980)
175. K Matsushige, K Nagata, I Imada, T Takemura *Polymer* **21** 1391 (1980)
176. A I Ozerin, M B Konstantinopol'skaya, Yu A Zubov *Vysokomol. Soed., Ser. A* **16** 2511 (1974)
177. K Sakuoku, T Itoh, S Kunimura *Jpn. J. Appl. Phys. Pt 2* **24** 175 (1985)
178. G A Samara *J. Polym. Sci., Part B, Polym. Phys.* **27** 39 (1989)
179. T Horiashi, K Matsushige, T Takemura *Jpn. J. Appl. Phys.* 25 L 465 (1986)
180. E Akacuge, S Taki, T Horiuchi *Kyusyu Daigaku Kagaku Syukho* **59** 655 (1986)
181. H Ohigashi, T Watanabe, G R Li, T Hattori, S Takanashi *Jpn. J. Appl. Phys. 1* **30** 111 (1991)
182. M Hikosaka, K Sakurai, H Ohigashi, T Koizumi *Jpn. J. Appl. Phys. 1* **32** 2029 (1993)
183. M Hikosaka, K Sakurai, H Ohigashi, A Keller *Jpn. J. Appl. Phys. 1* **33** 214 (1994)
184. R G Kepler, R A Anderson *J. Appl. Phys.* **49** 1232 (1978)
185. D K Das-Gupta, K Doughty *J. Phys. J. Appl. Phys.* **11** 2415 (1978)
186. D K Das-Gupta, K Doughty *IEEE Trans. Ind. Appl.* **1A-14** 448 (1978)
187. D Naegele, D Y Yoon, M G Broadhurst *Macromolecules* **11** 1297 (1978)
188. G T Davis, J E Mckinney, M G Broadhurst, S S Roth *J. Appl. Phys.* **49** 4998 (1978)
189. G T Davis, H Scugh *Polymer* **20** 772 (1979)
190. D K Das-Gupta, K Doughty, D B Shier *J. Electrost.* **7** 267 (1979)
191. J P Luongo *J. Polym. Sci., Polym. Chem. Ed.* **10** 119 (1972)
192. R D Southgate *Appl. Phys. Lett.* **28** 250 (1976)
193. D Naegele, D Y Yoon *Appl. Phys. Lett.* **33** 132 (1978)
194. D Broussoux, B Servet, F Micheron *Rev. Tech. Thompson-CSF* **13** 2 (1981)
195. B Servet, S Ries, D Broussoux, F Micheron *J. Appl. Phys.* **55** 2763 (1984)
196. N C Banik, P L Taylor, A I Hopfinger *Appl. Phys. Lett.* **37** 49 (1980)
197. F J Lu, D A Waldman, T Hsu *J. Polym. Sci., Polym. Phys. Ed.* **22** 827 (1984)
198. A J Lovinger *Macromolecules* **14** 225 (1981)
199. H Dvey-Aharon, P L Taylor, A I Hopfinger *J. Appl. Phys.* **51** 5184 1980
200. J D Clark, P L Taylor, A I Hopfinger *J. Appl. Phys.* **52** 5903 (1981)
201. D U Reneker, J Mazur *Bull. Am. Phys. Soc.* **29** 324 (1984)
202. D U Reneker, J Mazur *Polymer* **24** 1387 (1983)
203. B Tynenska, A Galeski, M Kryszewski *Polym. Bull.* **4** 171 (1981)
204. R Danz *Acta Polym.* **33** 1 (1982)
205. R Danz *Polym. Bull.* **7** 497 (1982)
206. T T Wang *J. Appl. Phys.* **53** 1828 (1982)
207. R G Kepler, R A Anderson, R R Lagasse *Phys. Rev. Lett.* **48** 1274 (1982)

208. F J Lu, S L Hsu *Polymer* **25** 1247 (1984)
209. M Latour *Polymer* **18** 278 (1977)
210. M Latour, H Abo Dorra, J L Galogne *J. Polym. Sci., Polym. Phys. Ed.* **22** 245 (1984)
211. I J Guy, J Unsworth *J. Appl. Phys.* **61** 5374 (1987)
212. S L Hsu, F J Lu, A Waldman, M Mathukumar *Macromolecules* **18** 2583 (1985)
213. F J Lu, S L Hsu *Macromolecules* **19** 326 (1986)
214. N M Reynolds, K J Kim, C Chang, S L Hsu *Macromolecules* **22** 1092 (1989)
215. M A Marcus *IEEE Trans. Electr. Insul.* **E1-21** 519 (1986)
216. D Geschke, P Holstein, M Mendler *Acta Polym.* **39** 206 (1988)
217. K Frigge, D Geiss, A Janke, W Konstler *Acta Polym.* **39** 169 (1988)
218. F Ishii, T Sawatari, A Odajima *Jpn. J. Appl. Phys.* **27** 1047 (1988)
219. L C Kopferberg *J. Appl. Phys.* **64** 2316 (1988)
220. Y Takase, J I Scheinbeim, B A Newman *J. Polym. Sci., Part B, Polym. Phys.* **27** 2347 (1989)
221. Y Takase, J I Scheinbeim, B A Newman *J. Polym. Sci., Part B, Polym. Phys.* **28** 1593 (1990)
222. D Geiss, C Rusher *Progr. Colloid. Polym. Sci.* **80** 119 (1989)
223. A Biichmann, D Geiss *Polymer* **32** 215 (1991)
224. H L Marand, R S Stein, G M Stack *J. Polym. Sci., Part B, Polym. Phys.* **26** 1361 (1988)
225. H L Marand, R S Stein *J. Polym. Sci., Part B, Polym. Phys.* **27** 1089 (1989)
226. H Sussner, K Dransfeld *J. Polym. Sci., Polym. Phys. Ed.* **16** 529 (1978)
227. P Saikiewicz *J. Polym. Sci., Part B, Polym. Phys.* **32** 313 (1994)
228. K Koga, N Nakano, T Hattori, H Ohigashi *J. Appl. Phys.* **67** 965 (1990)
229. Y Takahashi *Jpn. J. Appl. Phys., Part. 1* **33** 202 (1994)
230. B Servet, J Rault *J. Phys. (Paris)* **40** 1145 (1979)
231. B A Newman, J I Scheinbein *Macromolecules* **16** 60 (1983)
232. M Weinhold, M Litt, J B Lando *Ferroelectrics* **57** 277 (1984)
233. Y Takahashi *J. Appl. Phys.* **67** 4060 (1990)
234. A Sen, J I Scheinbein, B A Newman *J. Appl. Phys.* **56** 2433 (1984)
235. A Wedel, R Danz, D Geiss, A Leets *Wiss. Z. Elektrotech.* **26** 222 (1988)
236. V V Kochervinskii, V G Sokolov, V M Zubkov *Vysokomol. Soed., Ser. A* **33** 530 (1991)
237. V V Kochervinskii, E M Murasheva *Vysokomol. Soed., Ser. A* **33** 2096 (1991)
238. Z F Il'icheva, I A Slovokhotova, I G Akhvlediani *Vysokomol. Soed., Ser. A* **18** 209 (1976)
239. B K Passal'skii, D A Sachuk, L N Goichenko, Ya I Lavrentovich *Vysokomol. Soed., Ser. B* **22** 107 (1980)
240. I Klier, A Vokal *Radiat. Phys. Chem.* **38** 457. (1991)
241. T B Vinogradova, V K Matveev, A G Sirota, V T Shirinyan *Vysokomol. Soed., Ser. B* **30** 691 (1988)
242. T Sasuga, S Kawanishi, T Seguchi, I Kohno *Polymer* **30** 2054 (1989)
243. M A Said, C M Balik, J D Carlson *J. Polym. Sci., Part B, Polym. Phys.* **26** 1457 (1988)
244. V K Matveev, N A Smirnova, L Ya Madorskaya, N N Loginova, V K Milinchuk *Vysokomol. Soed., Ser. B* **32** 762 (1990)
245. Y Nabata *Jpn. J. Appl. Phys. 1* **29** 2755 (1990)
246. S K Bhabeja, E H Andrews *J. Appl. Polym. Sci.* **34** 2809 (1987)
247. M Norkis, I Raiter, S Sholnik, A Siegmann, P Eyster *J. Macromol. Sci., Phys.* **26** 37 (1987)
248. V M Aslamian, V S Vardanian, M N Avetisian, S S Filikian, S R Ayvasian *Polymer* **29** 755 (1987)
249. L Minkova *Colloid Polym. Sci.* **266** 6 (1988)
250. S K Bhateja, E N Andrews, S M Yarbouugh *Polymer* **21** 739 (1989)
251. S K Bhateja, S M Yarbouugh, E N Andrews *J. Macromol. Sci., Phys.* **29** 1 (1990)
252. A M Hindeleh, R Hosemann, G Hinricsen, H Springer *J. Polym. Sci., Part B, Polym. Phys.* **28** 267 (1990)
253. I Nishimoto, S Haisupakin, T Imui *Radiat. Phys. Chem.* **32** 413 (1992)
254. A D Pae, S K Bhateja, B A Gilbert *J. Polym. Sci., Part B, Polym. Phys.* **25** 717 (1987)
255. Z Zhao, J Chu, X Chen *Radiat. Phys. Chem.* **43** 523 (1994)
256. K A Verkhovskaya, V V Kochervinskii *Vysokomol. Soed., Ser. A* **32** 1669 (1990)
257. V V Kochervinskii *Vysokomol. Soed., Ser. A* **35** 1978 (1993)
258. B P Kosmynin, E L Gal'perin *Vysokomol. Soed., Ser. A* **14** 1603 (1972)
259. E L Gal'perin, B P Kosmynin *Vysokomol. Soed., Ser. A* **15** 2556 (1973)
260. A Collins, R De Batist, R Gevers *Radiat. Phys. Chem.* **16** 225 (1980)
261. Sh T Tuigiev, A N Kuznetsova, A M Mukhamadieva *Vysokomol. Soed., Ser. AB* **27** 375 (1985)
262. P P Khlyabich, A G Sirota, V P Budtov *Vysokomol. Soed., Ser. A* **32** 1444 (1990)
263. A Odajima, Y Takase, T Ishibashi, K Yuasa *Jpn. J. Appl. Phys. 2* **S24** 881 (1985)
264. A J Lovinger *Macromolecules* **18** 910 (1985)
265. B Daudin, M Dubus, J F Legrand *J. Appl. Phys.* **62.** 994 (1987)
266. F Macchi, B Daudin, J F Legrand *Nucl. Instrum. Methods Phys. Res. B* **46** 324 (1990)
267. F Macchi, B Daudin, J Hillairet, J Lanzier, J B Ngoma, J Y Cavaille, J F Legrand *Nucl. Instrum. Methods, Phys. Res. B* **46** 334 (1990)
268. B Daudin,J F Legrand, F Macchi *J. Appl. Phys.* **70** 4037 (1991)
269. Y Tsugita, T Nose, T Hata *Polymer* **3** 580 (1972)
270. S P Kabin, S G Malkevich, G P Mikhailov, B I Sazhin, A L Smolyanskii, L V Chernikovich *Vysokomol. Soed.*, **3** 618 (1961)
271. T Wentink *J. Appl. Phys.* **32** 1063 (1961)
272. Y M Jshida, M Watanabe, K Yamafuji *Kolloid-Z.* **200** 48 (1964)
273. S Yano *J. Polym. Sci., Part A, Polym. Chem.* **8** 1057 (1970)
274. H Sasabe, S Saito, M Asahina M Kakutani *J. Polym. Sci., Polym. Chem. Ed.* **7** 1405 (1969)
275. S Osaki, Y Ishida *J. Polym. Sci., Polym. Phys. Ed.* **12** 1727 (1974)
276. H Arisawa, O Yano, Y Wada *Ferroelectrics* **32** 39 (1981)
277. Y Nabata *Jpn. J. Appl. Phys.* **29** 319 (1990)
278. N Koizumi, J Hagino, Y Murata *Ferroelectrics* **32** 141 (1981)
279. G Williams, D C Watts *Trans. Faraday Soc.* **66** 80 (1970)
280. M G Brereton, G R Davies, A Rushworth, J Sprence *J. Polym. Sci., Polym. Phys. Ed.* **15** 583 (1977)
281. N Koizumi, S Yano, K Tsunashima *J. Polym. Sci., Polym. Phys. Ed.* **7** 59 (1969)
282. V K Matveev, S E Vaisberg, V L Karpov *Plast. Massy* (9) 45 (1971)
283. K Nakagawa, Y Ishida *J. Polym. Sci., Polym. Phys. Ed.* **11** 1509 (1973)
284. S Tasaka, K Miyasato, M Yoshikawa, S Miyata, M Ko *Ferroelectrics* **57** 267 (1984)
285. S Tasaka, N Inagaki, T Okutani, S Miyata *Polymer* **30** 1639 (1989)
286. S Utoh *Jpn. J. Appl. Phys.* **30.** L1516 (1991)
287. Y Abe, M Kakizaki, T Hideshima *Jpn. J. Appl. Phys.* **24** 1074 (1985)
288. M Kakizaki, Y Abe, T Hideshima *Jpn. J. Appl. Phys.* **25** 485 (1986)
289. T Anada, M Kakizaki, T Hideshima, in *IUPAC the 32nd International Symposium on Macromolecules, Kyoto* 1988
290. T Anada, M Kakizaki, T Hideshima *Jpn. J. Appl. Phys.* **29** 322 (1990)
291. T Anada, M Kakizaki, T Hideshima *Rep. Progr. Polym. Phys. Jpn.* **33** 361 (1990)
292. A Peterlin, J D Holbrook-Elwell *J. Mater. Sci.* **2** 1 (1967)
293. M E Baird, P Blackburn, B W Delf *J. Mater. Sci.* **10** 1248 (1975)
294. G K Rashmi, P K C Pillai *J. Mater. Sci.* **22** 2006 (1987)
295. H Kukutani *J. Polym. Sci., Polym. Chem. Ed.* **8** 1177 (1970)
296. S Shen, L Wu, B Chen, B Wu *Gaofenzi Tunsun* (4) 241 (1984)
297. B I Sazhin, M P Eidel'nant, V I Shul'gin *Vysokomol. Soed., Ser. B* **11** 384 (1969)
298. Y Myjamoto, H Mijaji, K Asai *J. Polym. Sci., Polym. Phys. Ed.* **18** 597 (1980)
299. S Osaki, S Uemura, Y Ishida *J. Polym. Sci., Polym. Chem. Ed.* **9** 585 (1971)
300. S Uemura *J. Polym. Sci., Polym. Phys. Ed.* **12** 1177 (1974)
301. S Yano, K Tadano, K Adki *J. Polym. Sci., Polym. Phys. Ed.* **12** 1875 (1974)
302. N Koizumi, T Hanai *Bull. Inst. Chem. Res. Kyoto Univ.* **42** 115 (1964)
303. D K Das Gupta, K Douguty *Ferroelectrics* **32** 69 (1981)

304. S Osaki, T Kotaka *Ferroelectrics* **32** 1 (1981)
305. K W Wagner *Arch. F. Electrotech.* **2** 371 373 383 (1914)
306. N Koizumi, N Nakawa, H Habuka *Ferroelectrics* **57** 99 (1984)
307. M-C Felux-Vandorpe, M Maitrot, R Ongaro *Phys. J. Appl. Phys.* **18** 1385 (1985)
308. M Kozaki, H Obeshima, M Ieda *J. Phys. Soc. Jpn.* **29** 1012 (1970)
309. A J Lovinger, D J Freed *Bull. Am. Phys. Soc.* **25** 221 (1980)
310. H P Jillis, K M Boyle, R L Long *Am. Chem. Soc. Polymer. Prepr.* **19** 468 (1978)
311. P K Wu, G -R Yang, X F Ma, T -N Lu *Appl. Phys. Lett.* **65** 508 (1994)
312. M Abkovitz, G Pfister *J. Appl. Phys.* **46** 2559 (1975)
313. T Takamatsu, E Fukada *Rep. Progr. Polym. Phys. Jpn.* **13** 363 (1970)
314. T Muzutani, T Yamada, M Ieda *J. Phys. J. Appl. Phys.* **14** 1139 (1981)
315. T Mizutani, T Yamada, M Ieda *J. Phys. J. Appl. Phys.* **15** 289 (1982)
316. L S Wu, H Shen, in *Proceedings of the International Conference on Properties and Applied Dielectric Materials, Xian* 1985, Vol. 2 (1), p. 437
317. V S Mc Brierty, D C Douglass, T A Weber *J. Polym. Sci., Polym. Phys. Ed.* **14** 1271 (1976)
318. R Sakamoto, Y Abe, S Yano *Rep. Progr. Polym. Phys. Jpn.* **23** 353 (1980)
319. Y Abe, M Kakizaki, T Hedeshima *Ferroelectrics* **57** 9 (1984)
320. Y Yamada, M Kakizaki, T Hideshima *Jpn. J. Appl. Phys.* **21** 352 (1983)
321. B R Hahn, J H Wendorff *Polymer* **26** 1619 (1985)
322. W Ulmann, J H Wendorff *Compos. Sci. Technol.* **23** 97 (1985)
323. J S Noland, N N C Hsu, R Saxon, J M Schmitt *Adv. Chem. Ser.* **99** 15 (1971)
324. T Nishi, T T Wang *Macromolecules* **8** 909 (1975)
325. D R Paul, J O Altamirano *Adv. Chem. Ser.* **142** 371 (1975)
326. M M Coleman, J Zarian, D F Varnell, P S Painter *J. Polym. Sci., Polym. Lett. Ed.* **15** 745 (1977)
327. D J Hourston, J D Hughes *Polymer* **18** 1175 (1977)
328. T T Wang, T Nishi *Macromolecules* **10** 421 (1977)
329. E Roerdink, G Chala *Polymer* **19** 173 (1978)
330. D R Paul, J W Barlow, R E Bernstein, D C Wahrmund *Polym. Eng. Sci.* **18** 1225 (1978)
331. E Roerdink, G Challa *Polymer* **21** 509 (1980)
332. J H Wendorff *J. Polym. Sci., Polym. Phys. Ed.* **18** 439 (1980)
333. T K Kwei, H L Frisch *Macromolecules* **11** 1267 (1978)
334. B S Morra, R S Stein *J. Polym. Sci., Polym. Phys. Ed.* **20** 2243 2261 (1982)
335. B S Morra, R S Stein *Polym. Eng. Sci.* **24** 311 (1984)
336. C Nakafuku, M Yasuniwa *Polym. J.* **19** 845 (1987)
337. P R Couchman *Macromolecules* **11** 1156 (1978)
338. P R Couchman *Macromolecules* **13** 1272 (1980)
339. P L Inken, D R Paul, J W Barlow *Polym. Eng. Sci.* **16** 593 (1976)
340. T K Kwei, G D Patterson, T T Wang *Macromolecules* **9** 780 (1976)
341. M Galin, L Maslinko *Eur. Polym. J.* **23** 923 (1987)
342. S H Goh, K S Slow *Polym. Bull.* **20** 393 (1988)
343. D R Paul, J W Barlow *Polymer* **25** 487 (1984)
344. D C Wahrmund, R E Bernstein, J W Barlow, D R Paul *Polym. Eng. Sci.* **18** 677 (1978)
345. S H Goh, S Y Lee, Y F Chang *Polym. Bull.* **25** 257 (1991)
346. R M Briber, P Knoury *Polymer* **28** 38 (1987)
347. C J Ong, F P Price *J. Polym. Sci., Polym. Symp.* **63** 59 (1978)
348. G C Alfonso, T P Russel *Macromolecules* **19** 1143 (1986)
349. H Saito, T Okada, T Hamam, T Inoue *Macromolecules* **24** 4446 (1991)
350. C N Klein Douwel, W E J R Maas, W S Veeman, G H Werumeus-Buning, J M J Vancan *Macromolecules* **23** 406 (1990)
351. W E J R Maas, W A C Vander Heijden, W S Veeman, J M J Vankan, G H Werumeus-Buning *J. Chem. Phys.* **96** 4698 (1991)
352. C H M Papavoine, W E J R Maas, W S Veeman, G H Werumeus Buning, J M J Vankan *Macromolecules* **26** 6611 (1993)
353. V V Shilov, V N Bliznyuk, S A Tyurin, V I Povstugar, S G Bystrov *Vysokomol. Soedin., Ser. A* **30** 1633 (1988)
354. V P Privalko *Spravochnik po Fizicheskoi Khimii Polimerov. Svoistva Polimerov v Blochnom Sostoyanii* (Handbook on the Physical Chemistry of Polymers. Properties of Polymers in the Block State) (Kiev: Nauk. Dumka, 1984) Vol. 2, p. 273
355. C Leonard, J L Kalary, L Monnerie, D Broussoux, B Servet, F Miciuron *Polym. Commun.* **24** 110 (1983)
356. W Kaufmann, J Petermann, N Reynolds, E L Thomas, S L Hsu *Polymer* **30** 2147 (1989)
357. D Braun, M Jacobs, G P Hellmann *Polymer* **35** 706 (1994)
358. R E Bernstein, C A Cruz, D R Paul, J W Barlow *Macromolecules* **10** 681 (1977)
359. C Leonard, J L Halary, L Monnerie *Polymer* **26** 1507 (1985)
360. N Tsutsumi, Y Ueda, T Kiyatsuki, A S Dereggi, G T Davis *J. Appl. Phys.* **74** 3366 (1993)
361. T Tsutsumi, G T Davis, A S De Reggi *Macromolecules* **24** 6392 (1991)
362. R G K Narula, P K C Pillai *J. Macromol. Sci., Phis.* **B26** 185 (1987)
363. G K Narula, P K C Pillai *J. Mater. Sci. Lett.* **8** 608 (1989)
364. G K Narula, P K C Pillai *J. Mater. Sci. Lett.* **9** 130 (1990)
365. B R Hahn, J H Wendorff, D Y Yoon *Macromolecules* **17** 718 (1985)
366. B R Hahn, O Hermann-Schonherr, J H Wendorff *Polymer* **28** 201 (1987)
367. D Y Yoon, Y Ando, S Rojstaczer, S K Kumar, G C Alfonso *Makromol. Chem., Makromol. Symp.* **50** 183 (1991)
368. Y Ando, T Hanada, K Saiton *J. Polym. Phys.* **B32** 179 (1994)
369. H Saito, B Stuhn *Polymer* **35** 475 (1994)
370. K Saito, S Tasaka, S Miyata *Nippon Kagaku Kaishi* (10) 1909 (1985)
371. N Hamazaki, J W Cho, S Mijata *Polym. J.* **23** 333 (1991)
372. M Galin *Macromol. Chem., Rapid Commun.* **9** 119 (1984)
373. M Galin *Makromol. Chem.* **188** 1391 (1987)
374. G Caccorolli, M Pizzoli, M Scandola, G G Alfonso, A Turturro *Polymer* **30** 1251 (1989)
375. T Kyu, J-C Yang *Macromolecules* **23** 176 182 (1990)
376. G Natta, G Allegra, T W Bassi, D Siamsu, G Caporiccio, E Torti *J. Polym. Sci., Polym. Chem. Ed.* **3** 4263 (1965)
377. G Guerra, F Karasz, W J Mecnight *Macromolecules* **19** 1935 (1986)
378. Yu S Lipatov, G M Semenovich, S S Makovei *Dokl. Akad. Nauk Ukr. SSR* **6** 43 (1986)
379. A Siegmann, G Cohen, Z Baraam *J. Appl. Polym. Sci.* **37** 1481 (1989)
380. K Mazur *IEEE Trans. Electr. Insul.* **27** 782 (1992)
381. G Muralidhar, P K C Pillai *J. Mater. Sci. Lett.* **6** 33 (1987)
382. C Muralidhar, P K C Pillai *J. Mater. Sci.* **23** 410 (1988)
383. S Reich, E P Goldberg *J. Polym. Sci., Polym. Phys. Ed.* **21** 869 (1983)