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The Solid-phase Polymerisation of Monomers with Conjugated Acetylenic Groups

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Published data on the solid-phase topochemical polymerisation of linear and cyclic monomers containing conjugated acetylenic groups are surveyed and the boundary conditions in this process are discussed. The structure of the monomers, is the intramolecular and supermolecular structures of the polymers, and the specific features of their chemical, physicochemical, physicomechanical, and optical properties are examined.
The bibliography includes 300 references.

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I. INTRODUCTION

Fundamental synthetic studies on the solid-phase polymerisation of diacetylenic monomers containing the $-(C\equiv C)_2-$ (DA) groups were published a fairly long time ago.[1-5] At the present time such investigations have undergone a considerable development in connection with the discovery of a series of unique properties in the polymeric single crystals obtained by this procedure: thermochromism, high mechanical strength, non-linear optical properties, and a considerable anisotropy of the mechanical, optical, electrophysical, etc. properties. The available reviews on this subject, including those which were published during the preparation of this report, are devoted mainly to problems of the kinetics and mechanism of the polymerisation of DA and the magnetic, spectroscopic, and electrophysical properties of polydiacetylenes (PDA).[6-9]

In the present review attention has been concentrated on the characteristics of the structure, crystal chemistry, and morphology of the initial crystalline monomers having the general formula $R-(C\equiv C)_n-R$ ($n = 2-4$) and the corresponding polymers, the characteristic features of the mechanical and chemical properties of the polymeric crystals, and the specific features of the synthesis of soluble polydiacetylenes and DA copolymers. In addition, the reactions of various compounds containing separated $-(C\equiv C)_2-$ groups are considered. In writing this review, the authors endeavoured to cover fairly fully the available literature, reflecting at the same time the chronology of the varying and sometimes contradictory points of view on certain aspects of the solid-phase topochemical polymerisation (TPM) of acetylenes and the properties of the resulting products.

It must be emphasised that by the term topochemical polymerisation we understand a process which consists in a direct transition from the molecules of the crystalline monomer to crystallised polymer chains with retention of the crystallographic centre of gravity and symmetry of the monomeric units. The crystal lattice of the monomer is not disrupted in this process and non-crystalline intermediates are not produced. In the course of the polymerisation of such monomers, a solid solution of polymer chains in the monomer matrix is formed, i.e. the polymerisation is homogeneous.[10-12]

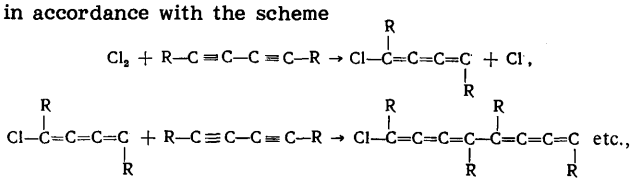
Instances of the breakdown of the crystal lattice with a corresponding change in the monomer polymerisation process are observed in real DA–PDA systems and special attention will be devoted to this aspect.

II. THE SOLID-PHASE POLYMERISATION OF LINEAR SYMMETRICAL DIACETYLENIC MONOMERS

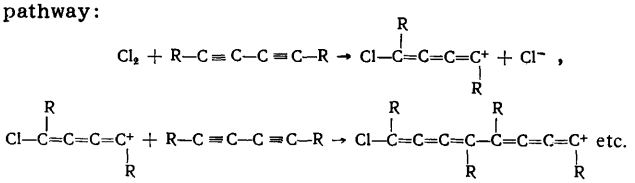
1. General Information

The acquisition of green, red, blue, or other colours by certain solid derivatives of diacetylene, for example, diols and mono- and di-carboxylic acids with a metallic lustre, which has been observed in early investigations[13-15] on illumination or heating, was subsequently interpreted as the topochemical polymerisation of these compounds.[14-16] A study of the infrared spectra of the polymers of deca-4,6-diyne-1,10-diol and its bisnaphthylurethane, the study of the electronic absorption and fluorescence spectra of the hexa-2,4-diyne-1,6-dicarboxylic acid polymer, and the detection of phthalic acid in the products of the decarboxylation and oxidation of this polymer by chromic acid (the material balance of the reaction products has not been published)[17,18] suggested[16-18] that parallel diyne molecules are converted into a polyacene macromolecule. The impossibility of the polymerisation of diynes in solution and in the melt has been explained by the absence of this type of seed outside the crystal.[14,16] Without taking into account the character of the substituents in the DA, this view was in fact reflected in the early reviews.[19-21] Subsequently the above concept was revised. Wegner[1-5] showed that the solid-phase polymerisation of DA (photochemical, radiation-induced, and mechanically initiated or thermopolymerisation at a temperature below the melting point), which proceeds in accordance with the laws of a topochemical reaction, leads to the formation of conjugated linear but not acene polymers. The polymerisation then proceeds only in those DA where the substituents contain groups capable of forming hydrogen bonds or of dipole–dipole interaction.[1,2] The attempts to polymerise such monomers in the liquid phase frequently fail. It has been shown[22] that the polymerisation of DA can be initiated by chemical initiators—gases capable

of forming radicals on the surface or in the bulk of the crystals (Cl_2, Br_2, O_3, NO_2, NOCl, PF_3, or I_2), for example, in accordance with the scheme



although the authors do not rule out an alternative reaction pathway:



Numerous symmetrical conjugated DA of different classes, examples of which are presented in Table 1, have been investigated as the monomers. However, the vast majority of the kinetic studies as well as the investigations of the structures and physicochemical and electrophysical properties of PDA have been carried out on the basis of a fairly limited range of symmetrically substituted monomers with R = CH_2OH (HD), $CH_2OC(O)NHC_6H_5$ (HDDU), $CH_2OSO_2C_6H_4.CH_3$-*p* (TS), CH_3-*N*-carbazolyl (DCHD), and $(CH_2)_nOC(O).NHCH_2C(O)O(CH_2)_mCH_3$, where m = 1 and n = 3 (3ECMU), m = 3 and n = 3 (3BCMU), m = 1 and n = 4 (4ECMU), and m = 3 and n = 4 (4BCMU), as well as a cyclic DA:

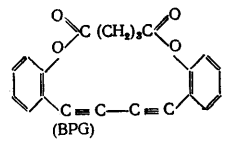


Table 1. Symmetrical DA (R–C≡C–C≡C–R) investigated in solid-phase polymerisation.

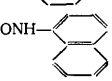
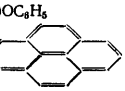
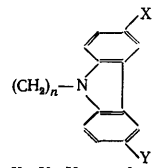
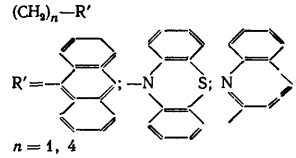
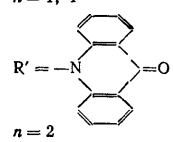
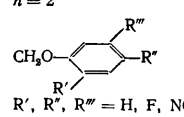
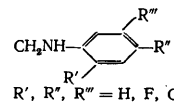
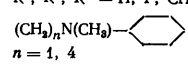
R	Refs.
CH_3	[23, 24]
$C(CH_3)_2H$	[25]
$(CH_2)_nCH_3$ n=11, 12	[26]
$CH_2C_6H_5$	[1, 2, 4]
C_6H_4R' R′=H R′ = *o*-, *m*-, *p*-NO_2, NH_2, $NHCOCH_3$, $NHCOC_6H_5$, $NHCONHC_6H_5$	[5, 24, 25, 27] [5]
R′-*m*-$NHCOCH_3$	[5, 28]
$(CH_2)_nOH$ n=1 n=2 n=6—9	[1, 2, 4, 27, 29, 30] [23, 31, 32] [33]
$CH(CH_3)OH$	[23]
$(CH_2)_nOSO_2C_6H_4R'$; n=1; R′=*n*-CH_3 n=2; R′=*p*-CH_3 n=4; R′=*p*-CH_3 n=1; R′=*p*-OCH_3, H n=1; R′=*p*-F n=1; R′=*p*-Cl, *p*-Br n=1; R′=*m*-CF_3	[4, 23, 34, 29, 35—41] [42] [43] [2, 4, 44, 45] [46—48] [46] [47, 48]
$(CH_2)_nOSO_2C_6H_4$–N=N–C_6H_5 n = 1—4	[49, 50]
CH_2OSO_2–	[51]
$(CH_2)_nOCONHC_6H_5$ n = 1 n = 2 n = 3 n = 4	[1—3, 23, 31, 34, 52, 53] [23] [23, 54, 55] [25, 55—58]
$CH_2OCONHC_6H_4R'$; R′=*p*-CH_3 R′ = *m*-Cl, *p*-Cl	[1, 34, 44] [1]
CH_2OCONH–	[1]
$(CH_2)_nOCONH$– n = 1 n = 2 n = 3	[1, 2, 4, 34] [23] [59]
$(CH_2)_2OCONHCH_3$	[23]
$(CH_2)_nOCONHC_2H_5$ n = 1 n = 2, 3 n = 4	[23, 44] [23, 55] [25, 60, 61]
$CH_2OCONHC_3H_7$	[44]
$(CH_2)_4OCONHCH(CH_3)_2$	[62]
$CH_2OCONH(CH_2)_nCH_3$ n = 3 n = 5, 7, 11	[1, 2, 4] [23]
$(CH_2)_nOCONHC_6H_4$–N=N–C_6H_5 n = 1—4	[49, 50]
$CH(CH_3)OCONHC_6H_5$	[2]
$C(CH_3)_2OCONHC_4H_9$	[2]
$CH_2OCO(CH_2)_nCH_3$ n=17 n=4, 6, 8, 10, 12, 14, 16	[3] [63]
$CH_2OCOC_6H_4R'$ R′=H R′=*o*-COOH	[1, 4, 23] [1, 2]
$CH_2OC(O)OC_2H_5$	[1, 2, 4]
CH_2O–	[64]

Table 1 (contd.).

R	Refs.
$(CH_2)_nOCONHCH_2COO(CH_2)_mCH_3$ m = 1, 3; n = 1—4	[65, 66]
$(CH_2)_nCOOM$ n = 1—4; M = H, Li, Na, K	[67, 68]
$(CH_2)_nOCONHCH_2COOM$ n = 3, 4; M = H, Li, Na, K	[67, 68]
$(CH_2)_nCOOR'$ n=6—9 R′=CH_3, C_2H_5, $CH_2C_6H_5$	[33]
$(CH_2)_nR'$ n=6—9 R′=Hal, CN	[33]
 X=Y=H; n = 0 n = 1 n = 3 n = 4 X, Y=Cl, Br, NO; n=0 — 10	[25, 69] [1, 25, 69—73] [74] [69] [75]
$(CH_2)_n$–R′  n = 1, 4	[69]
 n = 2	[69]
 R′, R″, R‴ = H, F, NO_2, CF_3	[76, 77]
 R′, R″, R‴ = H, F, CH_3, CF_3, NO_2	[78]
$(CH_2)_nN(CH_2)$– n = 1, 4	[69]

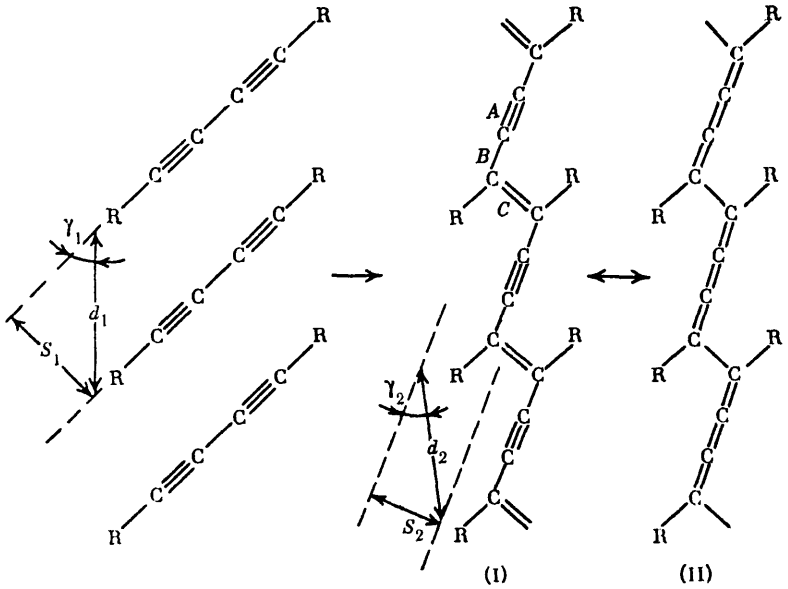


Figure 1. Schematic illustration of the solid-phase polymerisation of monomers with the $-C\equiv C-C\equiv C-$ groups: (I) and (II) are respectively the enyne and butatriene mesomeric forms of the polymer chains; the parameters d, S, and γ describe the topology of the monomer molecules and the polymer chain; B, C, and A are the length of single, double, and triple bonds.[9]

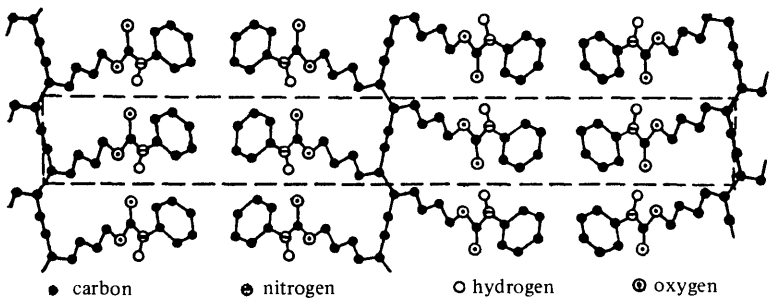


Figure 2. Schematic illustration of the packing of DA [R = $(CH_2)_4OCONHC_6H_5$] in the crystallographic cell. Projection on to the *bc* plane.[81]

Various specially synthesised deuterio-derivatives of TS have been used in the study of the isotope effects in the polymerisation of this DA.[79,80]

2. The Essential Conditions in the Polymerisation of Diacetylenes

The requirements which must be met by the DA polymerising via the TPM mechanism have been discussed in a review.[9] In the present communication the factual data on which these requirements are based have been extended. The changes occurring in the monomer–polymer transition, in conformity with the principles of a topochemical polymerisation of DA, are illustrated in Fig.1. The polymerisation reaction involves the 1,4-*trans*-addition and proceeds via specific rotations of the monomer units about the centres of gravity and via shifts of the centres of gravity. It is determined by the characteristic features of the packing of the monomer in the crystal lattice and proceeds without the evolution of side products and with formation of polymer chains extended parallel to the crystallographic *b* direction (Fig.2).[81]

The absence of the polymerisation of DA molecules in solution and in the melt has in fact been explained by the disordered nature of its molecules.[1,37] However, the presence of polar or interacting (Fig.2) side groups is not a sufficient condition for the occurrence of solid-phase polymerisation, since certain types of substituent hinder it. Indeed, diphenylbutadiyne (DPB) does not polymerise in the

solid phase, since large shifts and rotations of the molecules are required for this purpose.[5,27,28,81] All the symmetrical diamino-derivatives of DPB are also inactive. Nitro-, phenylureido-, acetamido-, or benzamido-groups in the 4- and 4'-positions in DPB hinder the topochemical polymerisation, while those in the 2- and 2'-positions and particularly 3- and 3'-positions of the corresponding DA promote it.[5]

In a series of DA with the substituents R = $CH_2OC(O).(CH_2)_nCH_3$ (n = 4, 6, 8, 10, 12, 14, 16), the rate of polymerisation increases with increasing length of the paraffinic side group, reaching a maximum for n = 8 and then falling owing to the characteristics of the packing of the paraffinic side chains in each member of the series considered.[63]

The presence of α-substituents at the $-(C\equiv C)_2-$ group gives rise to steric hindrance in topochemical polymerisation. Diyne monomers with the substituents R = $CH(CH_3)OC(O).NHC_6H_5$ or $C(CH_3)_2OC(O)NHC_4H_9$ do not therefore polymerise, in contrast to the extremely reactive monomers with the substituents R = $CH_2OC(O)NHC_6H_5$ or $CH_2OC(O)NHC_4H_9$.[1,2,4,23,25]

In view of the need to create a suitable crystal structure in the solid monomer, the polymorphism of the DA assumes a special importance. Thus HDDU, recrystallised from various solvents or their mixtures, has several different crystalline modifications among which only one exhibits a high reactivity.[1,10,82,83] This is caused by the fact that only the monomer recrystallised from a dioxan–water mixture has the necessary packing as a result of the presence of dioxan molecules in the centre of the unit cell forming hydrogen-bonded chains with other neighbouring DA molecules.[84] When dioxan is removed by evacuating the specimens, the monomer loses its reactivity.[84]

Polymerised DA with R = $CH_2OCONHC_6H_4CH_3$-m can be obtained in the form of "orange" and "blue" modifications, whose colour is associated with a small admixture of PDA. After being kept in dioxan vapour, the "orange" modification undergoes a "solvatochromic" solid-phase transition to the more reactive "blue" phase, which is accompanied by an increase of the size of the crystals in one of the directions by ~25%. This is associated with the insertion of dioxan in the single crystal, the formation of hydrogen bonds, and the assumption of a planar conformation by the PDA formed. Extraction of the non-polymerised monomer from the "blue" modification (λ_{max} = 650 nm) leads to the appearance of a red residue (λ_{max} = 550 nm) as a result of the reverse process: the removal of strain from the crystal and the transition of the monomer to a non-planar conformation having different electronic structures.[85]

After being kept in the vapours of polar solvents, the inactive modifications of other urethane DA are also able to undergo a transition into reactive modifications. The transition is accompanied by the appearance of an intense colour associated with the formation of polymer chains in the crystal matrix of the DA and depending on both the structure of the DA and on the type of solvent.[85]

A strong influence of the substituents on the capacity for polymerisation, associated with the packing of the monomer, has been observed also in a series of symmetrical DA (III):

$$RC_6H_4SO_2OCH_2C\equiv C-C\equiv CCH_2OSO_2C_6H_4R \quad \text{(III)}$$

R = H, m-CF_3, p-CH_3, p-OCH_3, p-F, p-Cl, p-Br.

Thus the p-bromo-,[46,47] p-fluoro-,[46] and p-chloro-derivatives of compound (III)[46,47,86] are inactive in solid-phase polymerisation. X-Ray diffraction studies have shown that the lack of reactivity of the chloro-derivative is associated with the unsuitable packing of the monomer.[86] However, a crystalline modification of the p-fluoro-substituted sulphonate, less reactive than TS, has been found.[47] Reactive modifications of compound (III) with R = p-Cl or p-Br, whose melting points are ~50° lower than those of the corresponding inactive forms, have been obtained by crystallisation from a highly supersaturated ethereal solution†. The diacetylenes (III) with R = H, p-OCH_3, or m-CF_3 polymerise in the solid phase and the p-methoxy-derivatives can be obtained in both reactive and inactive forms.[46,47] According to X-ray diffraction studies,[46,47] the side groups in the inactive form rotate above the –O– bond, so that the distance between neighbouring molecules is much greater than that necessary for solid-phase polymerisation. TS (R = p-CH_3) is the most reactive.

The influence of not only the nature of the substituent in the side groups of DA but also of its isotopic composition on reactivity in TPM has been observed. Thus the infrared spectroscopic and differential scanning calorimetric (DSC) studies of the kinetics of the thermal topochemical polymerisation of a series of TS derivatives revealed a decrease of the rate of the autocatalytic stage in a series of DA with different substituents, i.e.

$$CH_2OSO_2C_6H_4CH_3\text{-}p > CH_2OSO_2C_6H_4CD_3\text{-}p > {}^{13}CH_2OSO_2C_6H_4CH_3\text{-}p > CD_2OSO_2C_6D_4CD_3\text{-}p > CD_2OSO_2C_6H_4CH_3\text{-}p,$$

while E_a remained unchanged. During the induction period, the opposite isotope effect was observed. The difference between the rates of reaction has been explained by the variation of the pre-exponential factor for the rate constant, which is attributed to the different lifetimes of the excited state responsible for the chain initiation.[79,80] A decrease of the rate of reaction has also been observed for DA with other substituents: $CH_2OCONHC_6H_5 > CD_2OCONHC_6H_5$.[79]

In order to determine the reactivities of crystallised DA, it is necessary to take into account the contribution of the strain energy of the crystal and the change in chemical energy in the monomer–polymer transition. An estimate of the free energy barrier to molecular movement, required for topochemical polymerisation, is essential in determining the contribution of the energy of the crystal. However, the exact determination of the magnitude of this barrier is very difficult. Allowance for the limitations examined above, arising in the solid-phase polymerisation of DA, led to the development of the principle of the minimum mean square atomic displacement (MMAD) necessary for polymerisation,[81,87] which makes it possible to predict the possibility of the topochemical polymerisation of both different DA and their different crystalline modifications. Parameters most suitable for the description of the topology of the reacting monomer molecules and the resulting polymer chain were selected for this purpose. Such parameters are the vector d_1 and the angle γ_1 in the monomer and the vector d_2 and the angle γ_2 in the polymer, linked by the relation $a = S/\sin\gamma$ (Fig.1). The values of d_1 and γ_1 have been determined for a large number of monomers (Table 2) and have been found to vary in the ranges d_1 = 4.1–8.5 Å and γ_1 = 41–90°. For the polymers, d_2, γ_2, and S_2 are respectively 4.9 Å, 13.4°, and 1.2 Å.

For the most reactive modifications, the monomer parameter S_1 should be ~3.4 Å (twice the van der Waals radius of the carbon atom which can obtain in monomers of the type $HC\equiv C-C\equiv CH$ and $NC-C\equiv C-C\equiv C-CN$). However, owing to the large bulk of the substituent side groups, it actually assumes larger values, reaching ~4.7 Å for the very bulky t-butyl substituents. A polyconjugated chain with the corresponding changes in the geometrical dimensions by the

†V.Enkelmann, J.Mater.Sci., 1980, 50, 951.

amounts Δd and $\Delta\gamma$ is formed in the course of the topochemical polymerisation. The mean square displacements necessary for the polymerisation reaction in solid DPB, HD, and its benzoate were determined by a formula[81]

$$\text{HCAC} = {}^1/_2\left\{\sum_{i=1}^{4}\left[\int_{\gamma_1}^{\gamma_2}(A_i + B_i\sin\theta)^{1/2}\,d\theta\right]^2\right\}^{1/2},$$

where

$$A_i = r_i^2 + {}^1/_4[(d_2-d_1)/(\gamma_2-\gamma_1)]^2;\quad B_i = r_i[(d_2-d_1)/(\gamma_2-\gamma_1)],$$

r_i is the length of the vector joining the centre of the molecule to the ith carbon atom in the linear group C≡C–C≡C in the monomer, and θ varies from γ_1 to γ_2.

Although the above analysis does not include certain details, for example, the anisotropy of the intermolecular forces and the allowance for the difference between the lengths of the polymer chain and between the numbers of the initial monomer molecules (i.e. the principle holds best for low degrees of conversion), nevertheless the calculations yielded a satisfactory agreement with the experimental result: the mean square displacements increased with decrease of the polymerisation capacity of the monomers estimated in the investigations.[81]

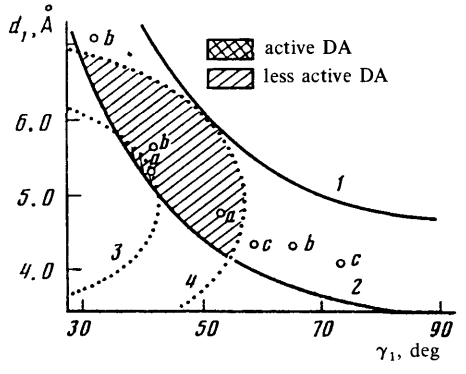


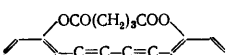
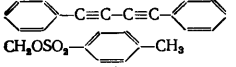
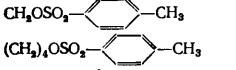
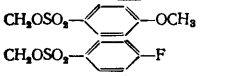
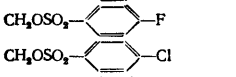
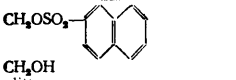
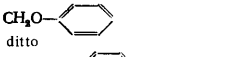
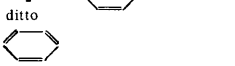
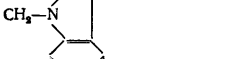
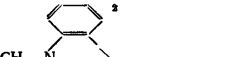
Figure 3. Determination of the ranges of the structural parameters, d_1 and γ_1 corresponding to the reactive and inactive modifications of DA: *a*) hexadiynediol; *b*) hexadiyne; *c*) hexadiyne dibenzoate; 1) S_1 = 4.7 Å; 2) S_1 = 3.4 Å; 3) MMAD = 0.72 Å; 4) MMAD = 1.08 Å.[81]

Fig.3 [81] presents as an example the structural parameters (dashed lines) for two values of MMAD: 0.72 Å (corresponds to the most reactive crystalline HD phase) and 1.08 Å (corresponds to crystalline DPB which is almost inactive in topochemical polymerisation; although the crystals become coloured, the polymer can be isolated). The crystalline modifications of monomers with coordinates lying to the right of the MMAD = 1.08 Å curve are inactive in topochemical polymerisation, which agrees with experimental observations. In addition, curves (continuous lines) representing the $d_1 = S_1/\sin\gamma_1$ relation for two values of S_1 are plotted in Fig.3. The circles in Fig.3 denote the coordinates of d_1 and γ_1 observed for the crystalline modifications of monomers with approximately the same minimum separations S_1. Thus the curves plotting in Fig.3 make it possible to determine the regions in which the parameters d_1 and γ_1 correspond to high (narrower region) and low (broader region) reactivities.

For example, in the case where S = 3.4 Å (curve *2*) the region of the parameters corresponding to a very high reactivity is bounded by the ranges $\gamma_1 \cong 36$–$42°$ and $d_1 \cong 5.0$–5.9 Å, while the region corresponding to a lower reactivity is bounded by the broader ranges of the parameters $\gamma_1 \cong 29$–$55°$ and $d_1 \cong 4.2$–6.9 Å.

Analysis of Fig.3 shows that one cannot except an appreciable topochemical polymerisation of monomers with $S_1 \geq 4.7$ Å, since the curves corresponding to the MMAD and S_1 = 4.7 Å (curve *1*) are hardly overlapped. Indeed, reactive phases of DA of the type R–C(CH$_3$)$_2$–C≡C–C≡C–C(CH$_3$)$_2$–R are unknown.[2,31]

Table 2. Specific features of the packing in the single crystals of the DA R^1–C≡C–C≡C–R^2 and the possibility of topochemical polymerisation (R^1 = R^2).

R^1	Parameter from Fig.1		Reactivity in TPM	Refs.
	d_1, Å	γ_1, deg		
	4.93	46	+[4]	[88]
	5.42	90	—	[88]
	5.11	44	+	[89]
	5.19	47.9	+	[90]
	5.80	45	—	[91]
	5.18	—	+	[47]
	5.03	67	—	[86]
	5.42	62	—	[51]
CH$_2$OH	4.76	41	+[4]	[92]
ditto	4.09	73.4	—[5]	[92]
CH$_2$OH[1]	4.87	49.6	+[4]	[93]
CH$_3$	5.65	42	+[6]	[81]
ditto	4.31	65.3	—[5]	[81]
CH$_2$CH$_2$OH	4.85	48	+[4]	[94]
	8.53	77	—	[95]
ditto	7.47	73	—	[95]
	4.35	58	+[6]	[96]
ditto	8.48	40	—	[96]
	6.04	50.9	+[6]	[27]
	4.66	90	—	[97]
	4.55	60	+[7]	[98]
	4.35	61.5	—	[99]
	4.36	61.0	—	[99]
CH$_2$OCONHC$_6$H$_5$	5.05	43	+	[100]
(CH$_2$)$_4$OCONHC$_6$H$_5$	5.23	42	+	[101]
(CH$_2$)$_8$CH$_3$[3]	4.76	45	+	[102]

Remarks: [1]R^2 = CH$_3$. [2]R^2 = CH$_2$(9-anthryl). [3]R^2 = (CH$_2$)$_8$COOH. [4]Complete conversion is not attained. [5]Topochemical polymerisation is impossible according to the MMAD principle. [6]Reactive under pressure. [7]Phase transition in the course of topochemical polymerisation.

It has been suggested that this principle for the determination and comparison of the reactivities in topochemical polymerisation with the aid of the MMAD principle can be extended also to other systems as well. It has been shown experimentally that the most reactive DA are those which have the following parameters: $d_1 \cong 5$ Å, $\gamma_1 \cong 45°$, and S_1 in the range $3.4 < S_1 < 4.0$ Å (Table 2). For example, the non-polymerising DA (III) with R = *p*-Cl has $d_1 \cong 5$ Å, which corresponds to a high reactivity of the monomer.[86] However, $\gamma_1 \cong 67.0°$ is outside the limits corresponding to a reactive modification of DA.[81] On the other hand, in one of the modifications of DA with R = $CH_2OC(O)NHC_6H_4CH_3$-*m* the vectors of the neighbouring molecules are not parallel, intersecting at an angle of 72°, which is inconsistent with the mechanism of topochemical polymerisation. However, the short distance between the neighbouring terminal carbon atoms is sufficient for the reaction to occur albeit with a low yield. The exposure of this modification to dioxan vapour leads to the formation of a highly reactive modification containing the solvent.[85]

The second factor influencing the specific features of the topochemical polymerisation of the monomers and the morphology of the resulting PDA is the inconsistency between the parameters of the crystal cells of the monomer and the polymer, which leads to strain and hence to defects in the single crystal on polymerisation of the monomer, which diminished the degree of conversion of DA and prevents the formation of a polymer having a high molecular weight.

The influence of this factor has been observed by means of X-ray diffraction for HD [27] in the course of the polymerisation of which (^{60}Co γ-radiation, dose 5–100 Mrad, dose rate 1 Mrad h^{-1}) the linear parameters and the angle γ of the unit cell varied continuously with the corresponding variation of the density of the crystal (Fig.4). The distance between the centres of the reacting monomer molecules then diminished by 0.44 Å and the axis of the conjugated C≡C–C≡C bonds was rotated by an angle of ~28°.

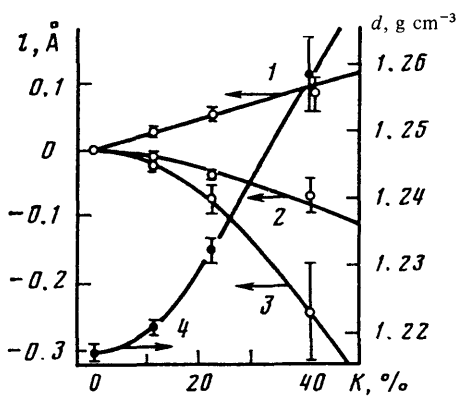


Figure 4. Variation of the parameters *l* of the unit cell [1) Δ*a*; 2) Δ*c*; 3) Δ*b*] and the density *d* (curve 4) as a function of the degree of conversion *K* of hexa-2,4-diyne-1,6-diol.[27]

The polymerisation reaction results in the formation of a solid solution of the polymer chains in the monomer matrix. However, when a specimen of this kind polymerised up to low degrees of conversion (50 Mrad) is kept for two months at room temperature, phase separation takes place, yielding separately the monomer and the amorphous phase of the polymer.[27] The conversion of PDA into the amorphous form also takes place on topochemical polymerisation of the monoclinic HD phase up to high degrees of conversion. The reason for this is the deviation of the centre of the monomer unit of the polymer chain from the centre of the corresponding monomer molecule as a result of a continuous translational movement initially over a distance $d_1 - d_2 = 0.44$ Å and then, as the polymer chain grows, over a longer distance. The enhancement of the amorphous X-ray scattering with increasing conversion in the range 0–69% corresponds experimentally to this process. A similar inhomogeneous course of the solid-phase polymerisation has been observed by Raman spectroscopy for HD biscaprilate.[45] A similar behaviour is observed on thermal polymerisation of HD.[30] Because the shifts are $d_1 - d_2 \cong 0$ for the HDDU phase containing dioxan, appreciable amorphous scattering does not occur up to quantitative conversion.[10,83]

Since the distribution of well-separated polymer chains along their lengths is irregular for long $d_1 - d_2$ distances and high degrees of conversion, the synthesis of PDA single crystals with $d_1 - d_2 \neq 0$ should probably be carried out at a suitable higher temperature where the molecular mobility essential for the longitudinal rearrangement of the system increases.

Another example of the synthesis of amorphous PDA is provided by the solid-phase polymerisation of HD bis-stearylurethane with subsequent extraction of the monomer which has not reacted and the isolation of the polymer having the character of a nematic liquid crystal.[3] The authors believe that the thermodynamically unfavourable strained or kinetically stable polymer conformation having a high free energy can exist only in the presence of a monomer lattice, ensuring thereby an "enforced" isomorphism of the polymer and monomer. The isolation of such a polymer leads to its conversion into an amorphous form with the corresponding decrease in its free energy.

However, for example, in the case of poly-TS, an increase of the degree of crystallisation of the extracted PDA with increasing degree of conversion has been noted.[36] This phenomenon is caused by the isolation of the polymer chains in the polymer matrix at lower conversions. With increase of the amount of polymer, neighbouring chains appear. Calculations based on the random formation of nuclei have demonstrated a significant increase in the number of adjoining chains and hence of the degree of crystallinity in the extracted polymer for conversions in excess of 10%, which has in fact been observed.[36]

In a general form, the criteria of phase stability have been examined[81] from the standpoint of the dependence of the overall free energy of the system on the degree of conversion. Here it is assumed that the overall free energy is made up of intramolecular and intermolecular components and should decrease with increased degree of conversion. Since the intramolecular contribution can be represented as a linearly diminishing function of the monomer–polymer transformation (both the monomer and the polymer must then exist in conformations with the minimum free energy), the change in the overall free energy of the system is influenced significantly by the character of the variation in the intermolecular contribution. Fig.5 presents an example of a free energy diagram, conforming to these general postulates, for the case where topochemical polymerisation proceeds with phase separation.[64]

The third general condition governing the possibility of topochemical polymerisation is the correspondence between the symmetries of the structural units in the monomer and

polymer crystals. In conformity with the possible types of symmetry for the monomer units in PDA and with the retention of the specificity of the solid-phase reaction, there exist specific types of symmetry of the monomer necessary for the synthesis of specific PDA chains: the monomer symmetries are of the 1, $\bar{1}$, 2, *m*, 2/*m* types for the synthesis of *trans*, *trans*-polymers and 1, 2, *m*, *mm*2 for the synthesis of *cis*, *trans*-polymers. Examination of the types of symmetry for a series of DA (HDDU and HD) and DA with R = $CH_2OC(O)C_6H_5$ and C_6H_5 has shown that their topochemical polymerisation can proceed with formation of *trans,trans*-PDA. Furthermore, in theory the type of symmetry of the crystalline HDDU phase should enable it to polymerise with formation of *cis,trans*-PDA single crystals (it has been established experimentally that this monomer polymerises with formation of only *trans,trans*-PDA).[84] However, in practice all the conjugated DA, including cyclic DA, are packed in crystals in such a way that the solid-phase polymerisation yields either the *trans*, *trans*-polymer or the monomer does not polymerise.[103]

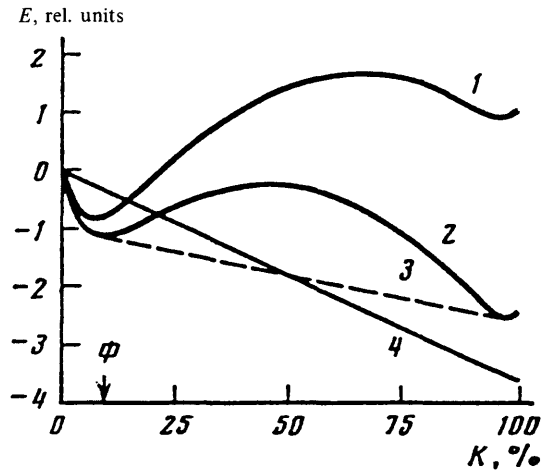


Figure 5. The free energy (*E*) diagram for the case where the solid-phase polymerisation cannot occur up to high degrees of conversion *K* owing to phase separation into isomorphous or non-isomorphous phases: 1) intermolecular contribution (one phase); 2) total free energy (one phase); 3) total free energy (two phases); 4) intramolecular contribution. The point Φ denotes the limiting conversion without phase separation.[64]

It has been observed that polymerisation with formation of a single crystal does really occur in the case of HDDU but not for TPB and HD dibenzoate,[1,5,23,27] since in the last two cases polymerisation requires excessive molecular displacements. In other words, the topochemical polymerisation of TPB and HD dibenzoate is allowed by symmetry conditions but is prohibited by the minimum displacement principle. The solid-phase polymerisation of HD is likewise not prohibited by the symmetry criterion and occurs in practice at least up to low degrees of conversion.[27] However, as reported above, owing to the displacement of the centres of the monomer units (by $d_1 - d_2$), the correspondence between the topologies of the polymer chain in the monomer units subsequently breaks down and the final polymer is amorphous. In such cases the "recrystallisation" of the reactive form in the direction of the PDA chains is necessary to increase the degree of conversion and the degree of crystallinity.

Thus the set of the specific requirements mentioned above which must be met by the topochemical polymerisation of diacetylenes may be formulated as the following criteria:[81,87] the occurrence of the minimum displacements of the atoms of the reacting molecules, phase stability of PDA in the DA matrix, and the retention of crystallographic symmetry elements in the DA → PDA transition. Only the simultaneous fulfillment of these criteria permits the actual occurrence of the topochemical polymerisation of the monomers.

The solid-phase polymerisation (γ-irradiation; 6.3 Mra; -78 °C) of thin films of butadiyne, i.e. DA having the smallest R = H substituents, has been described. However, the infrared spectra indicate the aromatic character of the monomer which implies, according to the authors,[104] the isotactic linear 1,2-addition to the C≡C bond and subsequent cyclisation.

The characteristic features of the DA polymerisation processes as well as the specificity of the structure and properties of the intermediate compounds and the final PDA have been investigated by various methods: gravimetrically with extraction of the monomer,[11,25,35-38,79,105,106] contraction of single crystals,[76,107,108] flash photolysis,[102] method employing X-ray diffraction,[27,30,35] proton spin–lattice relaxation,[110] DSC,[25,27,76,77,105,111-115] Brillouiin scattering,[56,116] photoacoustic methods,[117-119] optical spectroscopy,[35,82,105,120-123] scattered reflected light spectroscopy,[35,38,46,124] EPR,[30,125-132] infrared spectroscopy,[80,133] Raman spectroscopy,[31,35,41,45,46,134,135] and molecular weight distribution.[136] When particular conditions are met, various methods for the investigation of the topochemical polymerisation kinetics (for example, the gravimetric method, DSC, and electronic spectroscopy) yield satisfactorily concordant results.[105]

3. The Crystal and Molecular Structures of Diacetylenes and Their Polymers

The solid-phase reactions of DA which satisfy the criteria for topochemical polymerisation result in the formation of crystalline linear polymers. Well formed acicular crystals up to 5 cm long have been obtained by the method described on the basis of HDDU,[53] while large crystals weighing more than 1 g have been synthesised from TS.[125,137] The possibility of obtaining larger PDA crystals (up to 15 cm long and weighing up to 10 g) has been reported.[87]

Studies by optical and electron microscopy of the etched characteristic surfaces of the preferred cleavage planes of TS single crystals[36,138,139] revealed specific ellipsoidal pits, caused by dislocations, arranged in certain preferred directions having a long axis in the [010] direction, which subsequently becomes the direction of the principal PDA chain. Photographs and schemes for different types of the observed defects have been published[138,139] and the possible role of active centres (chain propagation initiators) has been discussed. Thermal polymerisation, in which dislocations play an important role, then begins at localised sites corresponding to the centres of the elliptical pits, while all the polymer chains grow in only one direction—"plus" or "minus" depending on the sign of the Burgers vector of the dislocation lines. This hypothesis is confirmed by the additional appearance near the deformation zones of numerous characteristic dislocations, which arise as a consequence of the compression of TS in the [010] direction and at which polymerisation begins.[36,139] Evidence for the occurrence of localised polymerisation either at the dislocation sites or at the sites of macroscopic deformation, for example, scratches,

has not been obtained for a photoinitiated reaction. Thus the defects do not control the photopolymerisation, since each absorbed photon of energy should lead to reaction regardless of the presence of defects in the crystal.[138,139] As a consequence of this, the energy of the photon initiating the topochemical polymerisation (~370 kJ mol^{-1}) should be much higher than the energy stored in the dislocation centres (not more than 90–180 kJ mol^{-1} according to calculations) and should be comparable to the activation energy for thermal polymerisation (80–120 kJ mol^{-1}).[139]

All the PDA crystals synthesised are cleaved in specific directions. For example, HDDU is cleaved along the (100) and (102) planes, forming smooth surfaces suitable for spectroscopic and electrophysical studies. Various types of dislocations have been observed on these surfaces although it is not clear whether they appear in the course of cleavage, or whether they are already present in the single crystal, or whether they arise in the course of the topochemical polymerisation.[138] Detailed microscopic studies of single crystals of poly-TS taking into account the crystal structure[35,36,138–140] permitted the solution of a number of problems: a scheme has been devised for the slip systems, deformation twinning of the crystals has been observed, and the characteristics of the distribution of the polymer chains and defects in the single crystals have been determined. The results of studies of the morphology of poly-TS in a number of investigations have been examined critically.[141]

The structure of the dislocations in TS and poly-TS has been investigated in detail with the aid of Laue diagrams. The growth of dislocations in the TS crystal during topochemical polymerisation and the influence of dislocations on the polymerisation process have been analysed.[142] The characteristic features of the optical spectra of a specially synthesised high-defect poly-TS have been attributed to the presence of dislocations at which short polymer chains have been terminated.[143] It is believed[144] that dislocations are present in the TS crystals and are then fixed during polymerisation, affecting the topochemical polymerisation process and mechanical and electrical properties. For example, the anisotropy of the mobilities of the current carriers in the direction of the polymer chains and at right angles to them is associated with the one-dimensional character of the PDA. However, the difference between the ratios of the corresponding mobilities $\mu_\parallel/\mu_\perp$, which are 10 [145] and $(8 \pm 3) \times 10^2$,[146] can be attributed to dislocations.

Furthermore, the mobilities of current carriers $\mu_\parallel$, determined in different studies, differ in magnitude (1 – 5 $cm^2 V^{-1} s^{-1}$,[147–149] 6×10^3 $cm^2 V^{-1} s^{-1}$,[150] and 2×10^5 $cm^2 V^{-1} s^{-1}$ [151]) and can also be attributed to different contents of dislocations functioning as current carrier traps.[144] Indeed the edge dislocations in poly-TS with the Burgers vector parallel to the direction of the chain are present in an amount of 10^{13} m^{-2}.[144] An approximate calculation showed the following: if each dislocation (with a density of 10^{12}–10^{13} m^{-2}) disrupts a chain when the chain passes through a dislocation nucleus, the length of the undeformed section of the chain is 0.1 – 1 mm, which corresponds to the distance traversed by an electron in poly-TS.[151] Dislocations can be arranged in lines at right angles to the direction of the chain. When the density of the dislocations along the line become sufficiently great, low-angle grain boundaries are formed.[144]

Fibrillar crystals with a diameter not exceeding 1000 Å and having a length of several μm have been obtained by the crystallisation from solution of partly polymerised TS. The direction of the molecules in the crystals have not been determined, but it has been noted that the crystal structure of fibrillar crystals differs from that of lamellar crystals obtained by the polymerisation of DA single crystals.[152,153]

The conversion into an amorphous form of the poly-TS crystals formed by forging and rolling is not caused by chemical changes but is due to the chain defects (loops and bends), leading to the appearance of segments with different conjugation lengths along the chain.[154,155]

The deformations along the crystal lattice defects have been discovered with the aid of asymmetric high-resolution X-ray topography in DA and PDA with $R = (CH_2)_4OCONHC_6H_5$. The defects are preserved in the course of topochemical polymerisation and the degree of deformation along them does not increase.[156]

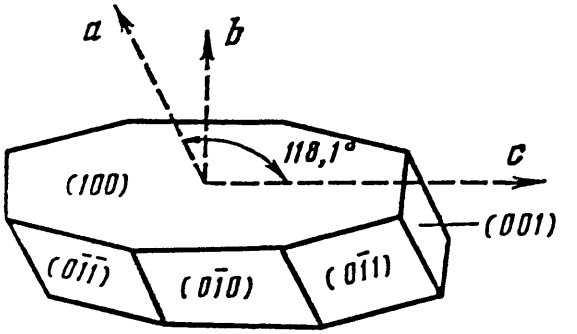


Figure 6. A TS crystal for dilatometric measurements; the (010) and (001) surfaces have been obtained by polishing.[108]

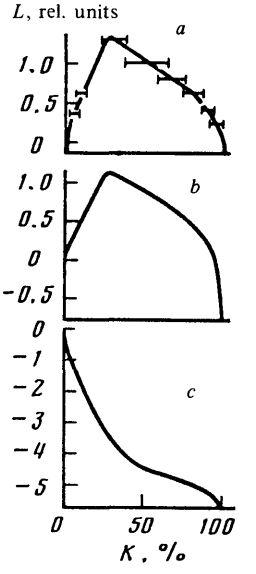


Figure 7. Variation of the dimensions L of a TS crystal with the degree of conversion K: *a*) $100\Delta d_{(100)}/d_{(100)}$; *b*) $100\Delta d_{(001)}/d_{(001)}$; *c*) $100\Delta b/b$.

The presence of a well formed TS crystal made it possible to investigate dilatometrically the kinetics of thermal (at 333.2 K) topochemical polymerisation. Direct measurements of the geometrical dimensions of the crystal (Fig.6)[108] at 276 and 294 K on the basis of the formulae

$$\frac{\Delta d_{(100)}}{d_{(100)}} = \frac{\Delta a}{a} + \Delta\beta \cot \beta,$$
$$\frac{d\Delta_{(010)}}{d_{(010)}} = \frac{\Delta b}{b},$$
$$\frac{\Delta d_{(001)}}{d_{(001)}} = \frac{\Delta c}{c} + \Delta\beta \cot \beta$$

were used to calculate the varying unit cell parameters. The existence of maxima in the parameter a and c in the region of 30% conversion has been observed, while the parameter b diminishes continuously (Fig.7).[108] The continuous variation of the parameter b during topochemical polymerisation has also been noted in another study.[116] However, examination of the unit cell parameters derived from X-ray diffraction data showed that the thermal polymerisation of TS (59.4 °C) is accompanied by a jump in b for the unit cell in the region of the transition from the induction period in topochemical polymerisation to the autocatalytic stage (~15% conversion) with a corresponding alteration of the reaction rate constant from 4.8×10^{-7} to 1.6×10^{-4} s^{-1}.[157,158]

X-Ray diffraction analysis of the products of the low-temperature phototopochemical polymerisation of symmetrical DA with R = $(CH_2)_4OSO_2$––CH_3, carried out at T = 110 K, revealed the homogeneous character of the polymerisation up to 20% conversion of the monomer.[159]

On the other hand, in the case of the γ-initiated topochemical polymerisation at 20 °C all the DCHD unit cell parameters vary in jumps (see above) in the range of conversions of the monomer 30–50%, which is believed[98,160] to be a consequence of a phase transition.

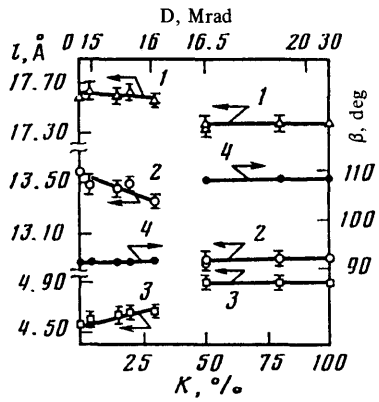


Figure 8. Variation of the parameters l of the DCHD crystal unit cell with the degree of conversion K and the γ-radiation dose D: 1) c; 2) a; 3) b; 4) β.[98]

The study of a poly-TS crystal by wide angle X-ray diffraction under a pressure $p \leq 16.5$ kbar revealed the variation of the parameters a and c as well as the angle β of the monoclinic unit cell with increasing pressure.[161] The compressibilities obtained have the following values:

Parameter	a	b	c	β
Compressibility, $kbar^{-1}$	$2.6 \cdot 10^{-3}$	0.0	$3.2 \cdot 10^{-3}$	$2.4 \cdot 10^{-4}$

The formation of PDA single crystals makes possible their complete X-ray diffraction analysis together with the calculation of the coordinates of all the atoms, the lengths of the valence bonds, and the angles, which means that one can determine the type of unit in the main chain. At the beginning of the development of the research into the solid-phase polymerisation, the isomorphism of the monomeric and polymeric crystals enabled the authors to regard the polymerisation process as one involving the rupture of two C≡C bonds via a mechanism involving the 1,4-addition of monomeric units to the polymer chain (Fig.1) with formation of an enyne (I) structure, or the cumulene (II) structure mesomeric relative to the former, which some workers[1–3,5,34,37] have found to be preferable.

However, calculations of bond length based on the results of the X-ray diffraction analysis of the HDDU,[84] TS,[162] and DCHD[163] polymers were found to agree better with the concept of the polymer chain as a flat zig-zag containing conjugated C=C and C≡C bonds. Not only in these but also in all other polymers investigated, the existence of only the *trans*-confugurations of a macromolecule relative to the C=C bond has been noted. Later X-ray diffraction analysis showed that the cumulene structure makes a greater contribution at least for PDA with R = $(CH_2)_4OCONHC_6H_5$ and for BPG.[164–166] Crystallographic data for a series of DA and PDA as well as the bond lengths in the PDA main chains are listed in Table 3.

Differences have been detected between the expansion coefficients of a crystal of a BPG monomer and the polymer chain in the study of the temperature variation of the position of the maximum in the electronic transition.[181]

The study of the reflection spectra of PDA with R = $(CH_2)_4$.$OC(O)NHC_2H_5$ deposited on ceramic discs with a high thermal expansion coefficient revealed a phase transition between liquid helium temperature to room temperature, induced by the removal of mechanical stress and accompanied by the structural change (II) → (I).[182] The thermochromic transition (green → red) observed for the same PDA at temperatures in the range 115–130 °C has been explained by a first-order phase transition accompanied by the structural change (I) → (II). The reverse process occurs in the region of 70 °C.[60]

A phase transition, caused by a rearrangement of the side groups at 142 K, has been observed for a carbazolyl-containing PDA with the aid of ultraviolet and Raman spectroscopy.[71]

X-Ray diffraction studies on poly-TS crystals revealed a reversible second-order phase transition below 170 K. The unit cell of the high-temperature phase

($P2_1/c$, a=14.493; b=4.910, c=14.930 Å; β=118.14°; Z=2)

contains two symmetrically arranged polymer chains extended along the b direction.[162] The transition to the low-temperature phase is characterised by the rotation of the side group in the neighbouring polymer chains in the opposite directions. Although the bond lengths and angles in the main chain are not altered in this process, two varieties of polymer chains appear in the unit cell and the latter is in fact doubled without change in the perfection of the single crystal

($P2_1/c$; a=14.92; b=4.910; c=25.56 Å; β=92°; Z=4).

The low-temperature splitting in the optical and Raman spectra of poly-TS has been explained by the existence of two types of polymer chain.[183–187] The monomeric TS undergoes two phase transitions.[158]

Table 3. Crystallographic data for DA and PDA.

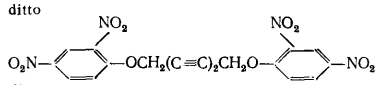
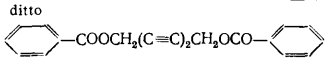
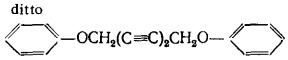
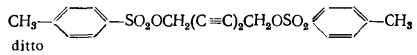
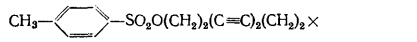
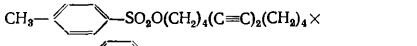
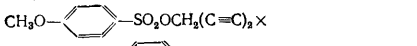
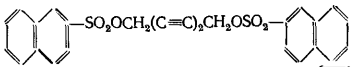
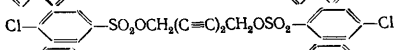
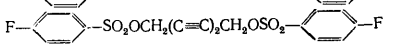
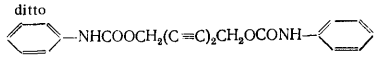
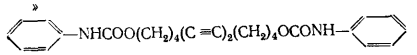
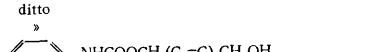
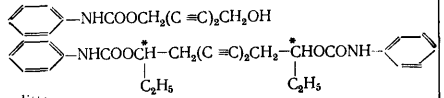
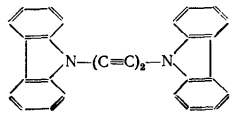
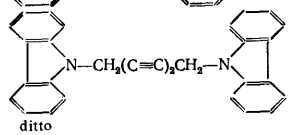
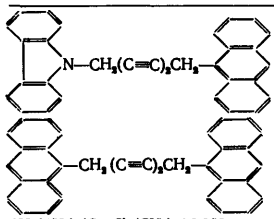
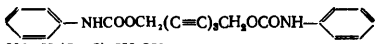
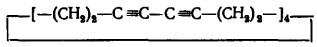
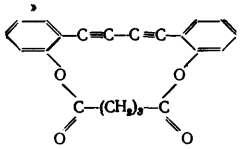
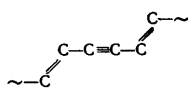
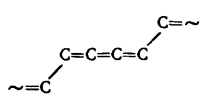
Monomer	DA or PDA	Unit cell parameters				Z	Space group	Factor R	Crystal system	Bond length (Fig.1), Å			Refs
		a, Å	b, Å	c, Å	β, deg					A	B	C	
$HOCH_2(C{\equiv}C)_2CH_2OH$	DA[1]	4.08	15.99	4.76	106.5	2	$P2_1/c$	—	monocl.	—	—	—	[92]
ditto	DA[1]	4.093	16.028	4.74	106.34	2	$P2_1/c$	—	ditto	—	—	—	[27]
»	PDA	4.176	15.785	4.703	110.34	2	$P2_1/c$	—	»	—	—	—	[27]
$HOCH_2CH_2(C{\equiv}C)_2CH_2CH_2OH$	DA	4.847	19.58	8.130	95.41	4	$P2_1/c$	0.042	»	—	—	—	[94]
$HOCH_2(C{\equiv}C)_2CH_3$	DA	4.893	28.471	4.131	101.67	4	$P2_1/c$	—	»	—	—	—	[93]
ditto	DA[2]	4.375	28.117	4.028	102.24	4	$P2_1/c$	0.13	»	—	—	—	[93]
	DA	5.194	11.942	14.745	98.45	2/m	$P2_1/c$	—	»	—	—	—	[77]
ditto	PDA	4.930	11.977	14.877	95.09	2/m	$P2_1/c$	—	»	1.205	1.410	1.471	[77]
	DA[1,3]	14.02	4.352	15.14	118.9	2	$P2_1/c$	0.064	»	—	—	—	[96]
ditto	DA[1]	9.665	8.479	11.03	114.0	—	$P2_1/c$	0.085	—	—	—	—	[96]
	DA[1]	11.179	14.979	8.527	—	4	P_{cab}	—	orthorhomb.	—	—	—	[95]
ditto	DA	7.469	11.368	8.591	109.42	2	$P2_1/c$	—	monocl	—	—	—	[95]
	DA	14.60	5.15	15.02	118.4	2	$P2_1/c$	—	ditto	—	—	—	[35]
ditto	PDA[4]	14.93	4.91	25.56	92	4	$P2_1/c$	0.10	»	—	—	—	[167]
»	PDA	14.493	4.910	14.936	118.14	2/n	$P2_1/c$	0.055	»	1.191	1.428	1.356	[162]
	DA[1]	7.034	9.590	9.692	111.7	1	—	0.055	tricl.	—	—	—	[168]
	DA	20.60	11.79	5.19	89.3	—	—	—	ditto	—	—	—	[90]
ditto	PDA[5]	20.13	6.11	4.91	93.7	—	—	—	»	—	—	—	[90]
»	PDA[5]	20.01	6.02	4.91	93.7	—	—	—	»	—	—	—	[90]
	DA[1]	9.875	10.226	5.798	76.92	1	—	0.045	»	—	—	—	[91]
	PDA	4.902	8.543	12.724	77.220	1	—	—	»	1.223	1.400	1.265	[169, 170]
	DA[1]	13.446	5.421	15.903	100.96	2	—	0.054	monocl.	—	—	—	[51]
	DA[1]	8.941	11.170	5.030	91.19	1	—	0.045	tricl.	—	—	—	[86]
	DA	13.94	5.18	14.09	114.1	2	—	—	monocl.	—	—	—	[47]
ditto	PDA	13.93	4.90	14.06	113.3	2/n	—	—	ditto	—	—	—	[47]
	PDA[1,6]	23.5	7.86	18.82	94.5	8	—	—	»	—	—	—	[10]
ditto	PDA[7]	4.89	12.53	16.78	96.81	—	$P\bar{1}$	—	»	1.21	1.41	1.36	[84]
»	DA[8]	23.51	7.80	18.47	94.0	8	$C2/c$	0.065	»				[171, 172]
	PDA	6.229	39.027	4.909	106.85	4	$P2_1/c$	—	»	1.17	1.38	1.45	[101]
ditto	PDA	»	»	»	»	4	»	0.081	»	1.24	1.37	1.44	[57,166]
»	DA[8]	18.97	5.19	11.60	92.0	4	$P2_1/c$	0.09	»	—	—	—	[171, 172]
	DA[1]	21.908	9.982	9.352	108.03	4	$C2/c$	0.078	»	—	—	—	[85]
$CH_3CH_2NHCOOCH_2(C{\equiv}C)_2CH_2OCONHCH_2CH_3$	DA	16.82	17.72	4.70	96.6°	4	$P2_1/a$	—	»	—	—	—	[98]
ditto	DA[1]	9.39	17.84	8.64	105°	4	$P2_1/a$	—	»	—	—	—	[98]
»	PDA	15.14	17.96	4.88	98.42°	4	$P2_1/a$	—	»	—	—	—	[98]
	PDA	38.77	23.64	4.86	—	16	$Pna2_1$	—	orthorhomb.	—	—	—	[87]
	DA	45.982	10.879	9.601	—	8	$Pbca$	—	ditto	—	—	—	[173]
ditto	DA	5.181	36.629	6.827	113.17	2	$P\bar{2}_1/c$	—	monocl.	—	—	—	[173]
	DA[1]	15.306	13.742	4.656	—	2	$P2_12_12_1$	—	orthorhomb.	—	—	—	[97]
	DA[10]	13.38	4.20	18.44	92	4	$P2_1/c$	0.13	monocl.	—	—	—	[99, 160]
ditto	DA	13.60	4.55	17.60	94	4	$P2_1/c$	0.13	ditto	—	—	—	[99, 160]
»	PDA	12.865	4.907	17.403	108.3	4/n	$P2_1/c$	0.086	»	1.21	1.44	1.33	[163]

Table 3 (contd.).

Monomer	DA or PDA	Unit cell parameters				Z	Space group	Factor R	Crystal system	Bond length (Fig.1), Å			Refs.
		a, Å	b, Å	c, Å	β, deg					A	B	C	
	DA	14.33	4.36	18.00	91.1	4	$P2_1/c$	0.09	»	—	—	—	[99]
	DA	14.60	4.35	17.92	97.0	4	—	0.098	»	—	—	—	[99]
$CH_3(CH_2)_8(C{\equiv}C)_2(CH_2)_8COOH$	DA	4.76	5.42	42.30	90	—	—	—	»	—	—	—	[102]
$CH_3(CH_2)_{11}(C{\equiv}C)_2COOH$	DA	4.91	5.36	32.7	91.6	2	$P\bar{1}$	—	tricl.	—	—	—	[174]
ditto	DA^{11}	4.77	7.09	33.2	91.6	3	$P\bar{1}$	—	ditto	—	—	—	[174]
$CH_3(CH_2)_{12}(C{\equiv}C)_2COOH$	DA^{11}	4.74	7.15	36.4	92.1	—	—	—	—	—	—	—	[174]
ditto	PDA^{11}	4.866	7.066	34.34	94.8	—	—	—	—	—	—	—	[174]
$HOCH_2(C{\equiv}C)_2CH_2OH$	polymer	4.11	19.59	4.80	109	2	$P2_1/c$	—	monocl.	—	—	—	[175]
	polymer	24.65	30.74	4.89	92.2	8	$P2_1/c$	—	ditto	—	—	—	[175]
$HOCH_2(C{\equiv}C)_4CH_2OH$	monomer	4.005	23.00	4.73	106.08	—	$P2_1/c$	—	»	—	—	—	[87]
$HC{\equiv}C[(CH_2)_5(C{\equiv}C)_2]_n(CH_2)_5C{\equiv}CH$	nDA^{12}	7.88	21.00	5.67	90.8	—	$P2_1$	—	»	—	—	—	[176]
ditto	PDA^{13}	4.65	17.5	4.85	101.7	—	$P2_1/n$	—	»	—	—	—	[176]
$HC{\equiv}C[(CH_2)_8(C{\equiv}C)_2]_n(CH_2)_8C{\equiv}CH$	nDA^{12}	13.25	14.15	7.63	118.5	—	$P2_1/n$	—	»	—	—	—	[176, 177]
ditto	PDA^{13}	9.17	12.25	9.92	123.5	—	$P2_1/n$	—	»	—	—	—	[176, 177]
	DA	24.54	4.98	25.38	93.2	4+1	C2, Cm or C2/m	—	»	—	—	—	[178]
ditto	PDA	12.43	4.8	25.34	—	2+2	—	—	orthorhomb.	—	—	—	[178]
»	PDA^{14}	12.05	4.8	25.23	—	—	—	—	—	—	—	—	[178]
»	PDA	12.4	4.8	24.8	—	2+2	Pgg	—	orthorhomb.	—	—	—	[179]
	DA	22.66	7.88	9.85	108.0	8	C2/c	0.078	monocl.	—	—	—	[88]
	DA^1	21.68	13.83	5.42	90.17	4	$P2_1/n$	0.062	ditto	—	—	—	[88]
ditto	PDA	23.12	7.87	9.69	111.29	4	C2/c or Cc	0.075	»	1.29	1.38	1.42	[57, 164, 166]
»	PDA	20.8	8.0	9.7	106	4	2C/c or Cc	—	»				[103]
	calculation for the ideal enyne PDA chain									1.20	1.45	1.34	[180]
										1.21	1.43	1.34	[84]
	calculation for the ideal cumulene PDA chain									1.26	1.35	1.48	[180]
										1.28	1.32	1.46	[84]

Remarks: [1]The monomer is inactive or its activity is low. [2]T = 110 K. [3]Polymerises at high pressure. [4]T < 170 K. [5]T = 110 K. [6]Crystallised from anisole. [7]Crystallised from the dioxan–water system. [8]T = 120 K. [9]The angle γ is quoted. [10]T < 142 K. [11]2:1 complex with phenazine. [12]Macromonomer. [13]Cross-linked macromonomer. [14]Polymer washed free of monomer.

The study of the polymerisation of TS led to the hypothesis[38] that the structure (II) obtains in the polymer for a low degree of conversion owing to the discrepancies between the unit cells of the monomer and polymer in the direction of the chain (the TS chain should increase in length by ~5%). The absorption spectra of TS at low conversions resemble those of PDA having the cumulene structure (II).[56] With increase of the degree of conversion, the strain energy diminishes and the enyne structure (I) becomes preferable. The induction period is then replaced by the autocatalytic stage involving an increase of the topochemical polymerisation rate constant by a factor of 100–400.[38,112,113] It is expected that only enyne structures are formed in the autocatalytic stage, while the cumulene structures are converted into the enyne structures. The consecutive transition of the structures is confirmed by the results of optical and EPR spectroscopic measurements.[130,155]# The results of the investigation of poly-TS by resonance Raman spectroscopy can apparently be accounted for by the contributions of different types of structures.[137] It has been suggested that, apart from the main *trans*-structure, there is another impurity structure which consists of a perturbed planar fully *trans*-structure and not a *cis*-structure.[137]

The majority of the workers who have investigated the optical infrared and Raman spectra of PDA have described the structure of their chains in terms of a mesomeric structure, the extreme manifestations of which are the cumulene and enyne units.[23,56,133] For example, in conformity with

#H.Gross and H.Sixl, Mol.Cryst.and Liquid Cryst., 1983, 93, 261.

the calculation for the Coulson and Dewar models, the fraction of the cumulene structure in poly-HDDU is 8–25% and diminishes when the chain conformation deviates from the planar zig-zag as a result of structural disorder.[23] The contributions of structures of different types depend on the chemical structure of the substituent in the monomer and also on the conditions in the preparation and state of the monomer whose variation can entail the reversible interconversion of these structures. However, regardless of the electronic structure of the chain, all the PDA have one common feature: a marked anisotropy of the physicochemical, electrolphysical, and other properties associated with the orientation of the polymer chain along the crystallographic *b* direction (Fig.9).[7]

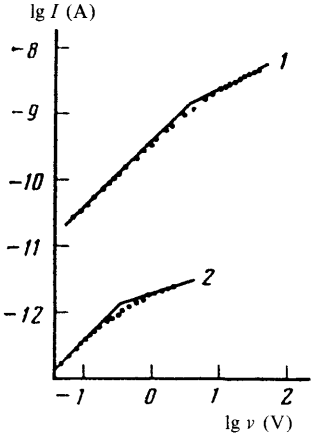
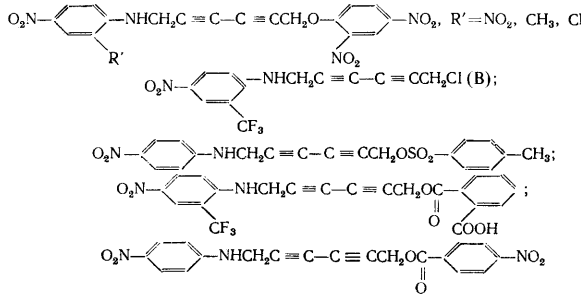


Figure 9. Variation of the photocurrent with the stress in a poly-TS single crystal; the light is polarised parallel (curve *1*) and at right angles (curve *2*) to the polymer chains (to the crystallographic *b* axis).[7]

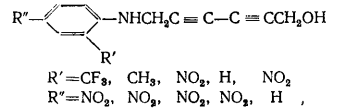
III. SPECIAL CASES OF THE SOLID-PHASE POLYMERISATION OF MONOMERS WITH $-(C\equiv C)_n-$ GROUPS

1. Polymerisation of Asymmetric Diacetylenes

A large number of polymeric single crystals have been synthesised from asymmetric DA of the type $R^1-C\equiv C-C\equiv C-R^2$ (Table 4). The study of the polymerisation of nitroanilino-substituted DA having the structure

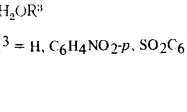
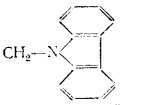
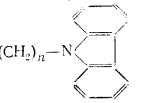


has shown that only the monomers (A) and (B) are reactive in the solid phase. The monomer (A) polymerises on heating and under the influence of ultraviolet radiation and X-rays, while the monomer (B) polymerises only under the influence of X-rays.[195] Among a series of asymmetric DA having the general formula



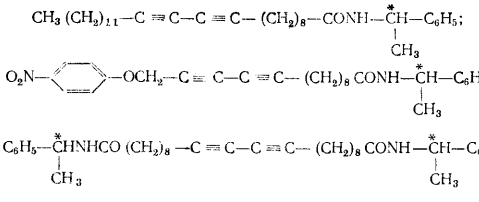
only those with $R' = CF_3$ and $R'' = NO_2$ polymerise under the influence of ultraviolet light and X-rays ($Cu K_\alpha$, 3 days, 73% conversion), although all the monomers are electronically and sterically similar.[196]

Table 4. The asymmetric DA $R^1-C\equiv C-C\equiv C-R^2$ investigated in the solid-phase polymerisation.

R^1	R^2	Refs.
CH_2OH	CH_3	[23,31,32,39,188]
$CH_2OCONHC_6H_5$	CH_3	[23]
$CH_2CH(C_2H_5)OCONHC_6H_5$	CH_3	[23]
$CH_2OCONHC_2H_5$	CH_3	[23,87]
$CH_2OCONHC_6H_5$	CH_2OH	[87]
$CH_2OCONHC_6H_5$	$CH_2OCONHCH_3$	[87]
COOH	$(CH_2)_{11}CH_3$	[133]
$(CH_2)_8COOH$	$(CH_2)_8CH_3$	[32,102,189–192]
$(CH_2)_nCOOH$	$(CH_2)_nCH_3$	
	$n = 4,7,11,13,15$	[190,191,193]
CH_2OR^3	CH_2OR^4	
R^3 = H, $C_6H_4NO_2$-*p*, $SO_2C_6H_4CH_3$-*p*	R^4 H, 	[76]
CH_2Cl	CH_2O— 	[76]
	$C_{12}H_{25}$	[74]
	$(CH_2)_nR^4$	[194]
$n = 0–10$; X and Y = H, Cl, Br, NO	$n = 0–10$; $R^4 = CH_3$, OH, $OCONHR^5$ (R^5 = Alk, Ar)	

Polymerisation in single crystals and monolayers of DA having the structures $CH_3(CH_2)_{17}C\equiv C-C\equiv CCOOM$ ($M = H^+$, Cu^+, or Ag^+) and $HC\equiv C-C\equiv(CH_2)_{17}COOH$ led to the formation of blue and red polymers respectively.[197] The instability of the copper salt in the crystalline state has been noted.

DA with chiral substituents, derivatives of *d*(+)-α-methylbenzylamine, are highly sensitive to ultraviolet light and X-rays:

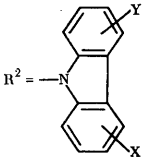


It has been observed that the asymmetric DA with the $CH_3(CH_2)_{11}$ end groups has a higher quantum efficiency (1×10^{12}) than the corresponding pentacosa-10,12-diynoic acid (1.6×10^{11}). It has been suggested that it be used to cross-link polymeric materials (for example glycidyl methacrylate) and also in photography and lithography.[198]

Carbozole-containing polymers based on the monomers

$$R^1(CH_2)_mC{\equiv}C{-}C{\equiv}C(CH_2)_nR^2,$$

in which m and n = 0–10 and R^1 = CH_3, OH, OC(O)NHR^3 [R^3 = alkyl (C_1–C_{18}), phenyl, tolyl, naphthyl, or $CH_2OC(O)C_qH_{2q+1}$ (q = 2–4)] have been proposed as materials with non-linear optical properties:[194]



X and Y = H, Cl, Br, NO_2.

The photopolymerisation of the tetrachlorocadmates $(RNH_3)_2CdCl_4$ (where R = $CH_2C{\equiv}CC{\equiv}CCH_2Cl$) with organic cations is known.[199] The use of asymmetric DA containing simultaneously hydrophilic and hydrophobic substituents made it possible to obtain and investigate polymeric monolayers and multilayers with unique structures.[200]

Infrared spectroscopic study of the blue products of the polymerisation of hepta-2,4-diynoic acids[133] (^{60}Co γ-radiation: 120 Mrad; 0.135 Mrad h^{-1}) showed that during solid-phase polymerisation a single crystal contains three components (the monomer, the insoluble polymer, and a segregated soluble oligomer), which give rise to two individual solid solutions over the entire range of conversions: the phase enriched in the monomer [with frequencies 1420, 905, and 600 cm^{-1} for the $(CH_2)_n$ groups], which is converted into a phase enriched in the polymer [with frequencies 1350 and 835 cm^{-1} for the $(CH_2)_n$ groups]. It is of interest that the authors proposed a cumulene structure of the chain unit for the intermediate oligomer.

The presence of two different non-chiral substituents in the monomeric molecule makes possible the existence of additional, compared with symmetrical diacetylenes, types of structure in the PDA molecules: "head to tail", "head to head", or both simultaneously. For the polymers obtained (using ^{60}Co γ-radiation) from the asymmetric diacetylenes

$$CH_3C{\equiv}C{-}C{\equiv}CCH_2OCONHC_6H_5;\ HOCH_2C{\equiv}C{-}C{\equiv}CCH_2OCONHC_6H_5;$$
$$CH_3NHCOOCH_2C{\equiv}C{-}C{\equiv}C{-}CH_2OCONHC_6H_5$$

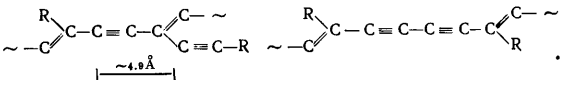
only the first type of addition has been observed with a regular alternation of "head–tail" side groups and the occurrence of entirely the *trans*-conformation in the polymer chain.[87]

Being formally symmetrical, a DA having chiral groups can give rise to several types of addition of units. The mixture of the DA $R{-}C{\equiv}C{-}C{\equiv}C{-}R$, $S{-}C{\equiv}C{-}C{\equiv}C{-}S$, and $R{-}C{\equiv}C{-}C{\equiv}C{-}S$ [R and S are the chiral groups $-CH_2\overset{*}{C}H(CH_2CH_3){-}OCONHC_6H_5$ of different sign], synthesised by Wilson et al.,[173] crystallises in two crystallographic modifications one of which is a racemic mixture, while the other is optically inactive. Their polymerisation leads to the corresponding PDA having the structures $[{=}C(R)C{\equiv}CC(R){-}C(S)C{\equiv}CC(S){=}]_n$ and $[{=}C(R)C{\equiv}CC(S){=}]_n$.

Certain general criteria of the solid-phase polymerisation of asymmetric diacetylenes have been stated by Baughman and Yee.[87]

2. Polymerisation of Linear Monomers with the $-(C{\equiv}C)_n-$ Groups

The polymerisation of triynes having the general formula $R{-}(C{\equiv}C)_3{-}R$ can proceed via a 1,4-addition reaction with formation of asymmetric side substituents R and $C{\equiv}C{-}R$ and via the 1,6-addition reaction with formation of symmetrical substituents R or, via a combination of both processes:



Examination of the MMAD principle in relation to triynes demonstrated a higher probability of the formation of fully *trans*-polymers in the case of both 1,4- and 1,6-addition than that of the formation of the corresponding *cis*-polymers. Furthermore, it has been noted that higher MMAD are required for the 1,6-addition reaction than for the 1,4-addition.[87] It must be emphasised that the polymer formed can have the type of symmetry corresponding to the monomer type of symmetry, which agrees with the specificity of both the 1,6-addition reaction of triynes and the 1,4-addition of symmetrical diynes. However, for the topochemical asymmetric 1,4-addition reaction of triynes, which should be preferred in conformity with the MMAD principle, the monomer type of symmetry corresponding to the possible occurrence of such topochemical polymerisation is 1 or m, which has in fact been observed.[87] The absence of the topochemical polymerisation of dimethyltriacetylene, the molecular symmetry of which ($\bar{3}m$) [81,201] rules out the occurrence of a specific reaction of this monomer via both 1,4- and 1,6-additions in agreement with the criteria concerning the type of symmetry formulated above.

Table 5. Polymerisation of the triynes $R{-}(C{\equiv}C)_3{-}R$.[193]

R	Photopolymerisation[1]		Thermal polymerisation		
	yield[2] of polymer	colour[3]	T, °C	τ, h	yield of polymer, %
CH_2OH	+++	purple-red	60	52	87
			100	0—1	—[4]
$CH_2OCONHC_6H_5$	+++	dark-blue	60	50	6—7
			70	70	14
			100	22	71
$CH_2OCONH(CH_2)_5CH_3$	++	blue	70	70	0
$CH_2OCOC_6H_5$	+	brown	100	20	88
$CH_2OSO_2C_6H_4$ (p-CH_3)	++	violet	70	70	0
			83	40	—[5]
			100	1	—[5]

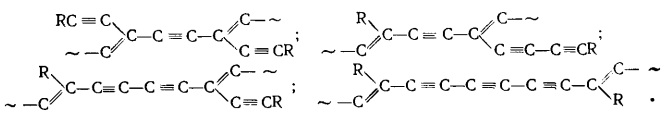
Remarks. [1]Moderate-pressure mercury lamp, room temperature, 3 h. [2]– = no polymerisation, + = low yield (<1%), ++ = moderate yield (<10%), +++ = high yield (>20%). [3]Unresolved polymer–monomer mixture. [4]Rapid carbonisation takes place. [5]Elimination of sulphonate groups (according to infrared spectroscopic data).

Examination of the polymerisation reactivity of octa-2,4,6-triyne-1,8-diol and some of its derivatives in topochemical polymerisation showed that the diol is the most reactive monomer (it polymerises readily even on recrystallisation in the dark at room temperature). The diphenylurethane of the diol polymerises to a crystalline polymer on heating and also on irradiation with ultraviolet light and X-rays, but its reactivity is lower. The dibutylurethane and the dibenzoate

are inactive in the photochemical reaction, although heating of the dibenzoate at 100 °C gives rise to a black polymer in 88% yield. On the other hand, the bistoluenesulphonate is photochemically reactive but does not undergo thermal polymerisation. The reactivity of triynes in photopolymerisation thus diminishes in the sequence diol > phenylurethane > toluenesulphonate > butylurethane > benzoate, the most reactive form of the phenylurethane derivative having been obtained by recrystallising the monomer from a petroleum ether–benzene mixture (Table 5). Triynes with large α-substituents [R = $C(CH_3)_2OH$] do not photopolymerise.[175]

Depending on the structure of the macromolecules, the repeat period of the chain may range from 1 (~4.9 Å) to 4 (19.6 Å) monomer units. The study of the structure of the polymers synthesised (Table 3)[87,175] showed that *trans*-polymerisation does indeed take place fully, while 1,4-addition with formation of structure (I) in the topochemical polymerisation of the biphenylurethane of octatriynediol leads to a crystalline polymer, while the polymerisation of octatriynediol up to a high degree of conversion results in a polymer with a perturbed three-dimensional order.

In the polymerisation of tetraynes the PDA chains can have four types of units and can also consist of a combination of two or more structures:

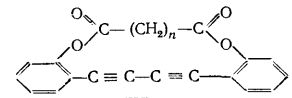


in the presence of asymmetric substituents in the main PDA chain [for example, R and RC≡C] there is a possibility of the "head to head" and "head to tail" addition of the monomer molecules which increases the number of possible variants of the polytetrayne structure. The structure becomes still more complicated when the substituents possess optical activity.

According to infrared and Raman spectroscopic and X-ray diffraction data (Table 3), the symmetrical tetrayne with $R=CH_2OCONHC_2H_5$ polymerises thermally and under the influence of γ-radiation without changes in the side groups forming the polymeric skeleton $(=RC-C\equiv C-CR'=)_n$, in which the length of the repeating fragment is 4.75 Å. Nevertheless it has not been established whether symmetrical polymerisation with formation of C≡C–R side groups or asymmetric polymerisation with formation of the R and $C\equiv C)_2$–R side groups takes place.[87] X-Ray diffraction has shown that the unit cell parameters vary gradually during the reaction with increasing degree of conversion and that a new phase does not appear. Such absence of phase separation is a necessary condition for the solid-phase synthesis of polymeric single crystals. However, the three-dimensional order of the monomeric phase is not retained in the polymer from which the monomer has been extracted and depends on the method of initiation of the reaction: the γ-initiated reaction leads to an amorphous polymer with extended chains, while the thermal reaction results in the formation of a polymer having two-dimensional order but a perturbed periodicity in the direction of the chain.[87] The γ-initiated topochemical polymerisation of the symmetrical diol $HO-CH_2-(C\equiv C)_4CH_2-OH$, which crystallises as an isomorphous phase with triacetylenic and diacetylenic diols, breaks up the three-dimensional order in the monomeric phase. This results in the formation of a monomer having an extended chain in which the repeating fragment is 4.9 Å long, in good agreement with the 1,4-addition of the monomer molecules involving the formation of a fully *trans*-polymer.[87]

3. Polymerisation of Cyclic Monomers

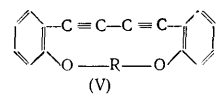
The synthesis of cyclic compounds containing conjugated C–C bonds established that some of these compounds are just as unstable in the solid phase as linear diacetylenes although they are fairly stable in solutions.[202–204] In both cyclic and linear diynes, the structure of the substituents R has been found to have a stong influence on the reactivity of the monomer.



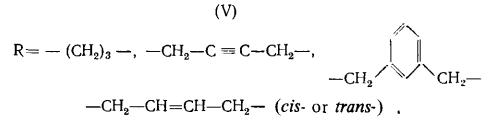
(IV)

$n = 3, 4, 5, 7$.

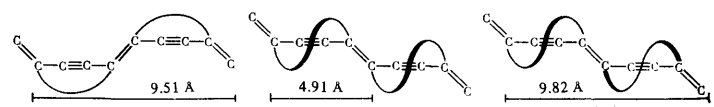
Monomers of type (IV) are sensitive to light only for $n = 3$.[202] The strongly strained ethers (V) are fairly stable in the solid state under illumination but are sensitive to heating:[203]



(V)



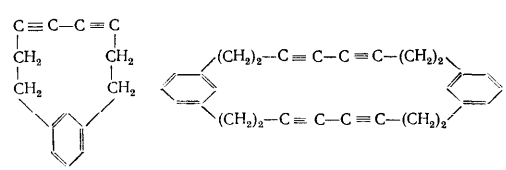
The polymerisation of *oo*-buta-1,3-diynylenediphenyl glutarate (BPG) (IV) ($n = 3$) under the influence of ultraviolet light or γ-radiation affords, after the extraction of the monomer which failed to react, an asbestos-like infusible insoluble PDA in yields up to 35–40%.[57,103,164,181] The non-extracted product of the polymerisation reaction is a solid solution of the polymer in the monomer matrix, the axis of the monomer being rotated by 33° in the course of the topochemical polymerisation and the side groups undergoing a change in orientation. The structure of poly-BPG can be represented by the following units:



(VI)

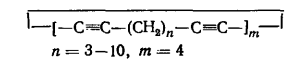
It has been established by X-ray diffraction (Table 3), optical dichroism, and infrared and Raman spectroscopy[103,164,205] that the macromolecules consist of a flat zig-zag (fully *trans*-polymer) with helically coiled substituents [structure (VI)]. The repeating interval in the achiral chain then consists of a double unit (~9.7 Å), which is satisfactorily consistent with calculations carried out taking into account the valence angles and bond lengths (9.82 Å).[103] Studies have shown[103,181,206] that the polymer contains conjugated C≡C– and C≡C– (*trans*) bonds, although there is a possibility of a contribution by the cumulene structure.

The exceptionally unstable compound (VII) polymerises in several seconds to give an insoluble red polymer even in the dark, while the cyclic compound (VIII) is stable.[203]



(VII) (VIII)

The macrocyclic compounds (IX) have been proposed for the synthesis of three-dimensional polymers having fully conjugated parallel chains and hence exhibiting a strong dichroism.[207]



$n = 3-10,\ m = 4$ (IX)

The ladder polymers based on compound (IX) should have had higher moduli of elasticity and thermal stabilities than the linear PDA.

The study of a series of cyclic monomers (IX) ($n = 4$, $m = 2-4$), obtained by the oxidative dehydrocondensation of octa-1,7-diyne,[208] showed that the monomer with $m = 4$ exhibits the greatest capacity for topochemical polymerisation. Crystalline modifications both photochemically inert and reactive polymerising under the influence of γ-radiation, ultraviolet light, heat, or mechanical action, with formation of pink polymeric crystals, have been obtained from different solvents.[179,208] Elemental analysis has shown that the "active" form crystallises with inclusion of 1 mole of chloroform per cyclotetrameric unit. It is of interest that the "inactive" crystals contain 1 mole of benzene per mole of the cyclotetramer according to infrared spectroscopic and ^1H NMR data. When the "active" colourless acicular crystals are kept in the dark *in vacuo*, chloroform is removed and the crystals are converted into a yellow amorphous modification with a melting point close to that of the monomer but do not undergo solid-phase polymerisation. Accordingly, it is recommended that the monomer be polymerised under pressure of chloroform vapour in order to prevent the evaporation of chloroform from the single crystal. The infusible, insoluble polymer obtained retains the form of the crystals of the initial monomer and exhibits a strong dichroism with the dichroism axis parallel to the axis of the acicular crystal. According to Raman spectroscopic data, the polymerisation occurred as a 1,4-addition reaction of the diacetylenic groups of the monomer.[179,207,208] The unit cell of the polymer incorporating two monomeric units and two chloroform molecules has the parameters $a = 12.4$ Å, $b = 24.8$ Å, and $c = 4.8$ Å, where c represents the direction of the polymer chain. Comparison of these results with molecular models made it possible to assume that the most preferred of the three possible conformations (crown, boat, and chair) is the chair conformation, which is less strained and has a repeat period of ~4.9 Å.[179]

The total insolubility of the polymerised specimen shows that the cyclotetramer polymerises (γ-radiation, 50 Mrad) quantitatively. However, the low degree of crystallinity (40%), the positive temperature coefficient of linear expansion, and a lower mechanical strength than that of the linear PDA showed that the polymer might have contained $-(C\equiv C)_2-$ groups which failed to react. It has been established that resonance Raman spectroscopy does not always make it possible to determine the degree of conversion of the monomer, since, for example, the characteristic band of PDA with $R = (CH_2)_3OCONHC_6H_5$ might not have been observed in the spectrum of a mixture containing 75% DA and 25% of its polymer. In addition, the DSC curve for the polycyclic compound revealed an exothermic peak with a maximum at 197 °C corresponding to the exothermic 1,4-addition reaction of the $-(C\equiv C)_2-$ groups which failed to react in the course of the polymerisation, whose heat overlaps the endothermic heat of evolution of the solvent.[179]

4. Polymerisation at High Pressure

Diacetylenes in the single crystals where the distances between the terminal carbon atoms of the C≡C bonds in neighbouring molecules are greater than a certain critical value do not polymerise. A factor promoting the polymerisation of such monomers is an increase of pressure. A typical example of DA which is difficult to polymerise is provided by HD dibenzoate, which crystallises in two forms which are and are not capable of polymerising under high pressure.[23,96] X-Ray diffraction studies of the two forms have shown that this is caused by a difference between the distances separating the carbon atoms in the C≡C bonds in neighbouring reacting molecules (4.02 and 5.36 Å respectively).[96]

The study of the solid-phase polymerisation of DPB, HD, and hexadiyne under a pressure of 75 kbar (the specimen was placed in a solid medium which transmitted the pressure) and at temperatures up to 260 °C showed that the smallest amount of polymer detectable at 21 °C after 1 h is obtained at minimum pressures of 60, 20, and 60 kbar respectively.[24] Assuming that the compressibilities of the monomer crystals are identical, the authors believe that the crystal lattices of the monomers are distorted in the course of topochemical polymerisation until the attainment of the structural parameters optimal for polymerisation. The polymers from which the monomer has been removed by extraction are amorphous. The remaining hydrogen bonds in the partly polymerised HD are disrupted on extraction of the monomer. The infrared spectra of PDA indicate the occurrence of 1,4-addition with formation of units of type (II) in poly-DPB and of type (I) in the HD and hexadiyne polymers. Ogo and Okuri attributed the same structure to poly-HD.[209]

The sterically hindered α-substituted DA, such as octa-3,5-diyne-2,7-diol and its bisphenylurethane and bistoluenesulphonate, become capable of polymerising with increase of pressure to 30 kbar. The yield of the polymers depends more on the pressure than on time and temperature. A structure of type (II) has been proposed for the main chain.[210]

Detailed study of the kinetics of the thermal topochemical polymerisation of TS under hydrostatic pressure[107,211] demonstrated the disappearance of the autocatalytic effect at a pressure $p \geq 2-4$ kbar. Since the autocatalytic effect has been attributed to the difference between the dimensions of the monomeric and polymeric crystals, the influence of pressure was explained by the equalisation of the monomeric and polymeric lattices with its aid; at $p = 1$ kbar the length of the repeating fragment in PDA single crystals is smaller by 0.25 Å (~5%) than in the monomer single crystals, while the corresponding length at $p \geq 4-2$ kbar is smaller by 0.1 Å.[211]

The photopolymerisation of TS, carried out in an optical cuvette under a hydrostatic pressure up to 4 kbar, and also the study of the resulting specimens by scanning electron microscopy showed that the size of the polymerised sections increases with increasing pressure.[122] The solid-phase polymerisation takes place along the entire surface of the crystal and breaks arise as a result of contraction in the direction of the chain. In the non-irradiated regions of the crystal, secondary chain initiation by the primary growing chains has been observed.

5. The Joint Crystallisation of Diacetylenes and Their Polymerisation

The photoinitiated polymerisation of DA take place when the single crystals are irradiated with light having a wavelength within the absorption band of the monomer. The photosensitised polymerisation of 2,4-diynoic acids $R^1-C\equiv C-C\equiv C-R^2$ [$R^1 = COOH$, $R^2 = (CH_2)_nCH_3$, $n = 11$, 13, or 15], cocrystallised with phenazine, has been reported.[174,212] Mixed crystals of DA and phenazine having the dimensions 10 × 2 × 0.5 mm have been obtained from an alcoholic solution

containing both substances by slow evaporation of the solvent. The crystals have the stoichiometric composition of a complex comprising two molecules of the diynoic acid and one phenazine molecule and exhibit the fluorescence observed for pure phenazine crystals. According to infrared spectroscopic data, there is no formation of a salt (?complex) of any kind between the diynoic acid and phenazine. Polymerisation takes place readily in the mixed crystals under the influence of visible light ($\lambda \leqslant 450$ nm), while the pure diynoic acid is not polymerised by light with $\lambda > 300$ nm. It has been noted that, when $\lambda = 400$–430 nm, the quantum yield ϕ of the sensitised photopolymerisation of the cocrystallised material is approximately 10 times smaller than the ϕ observed on direct irradiation of the acetylenic chromophore.[212] The rate of polymerisation of the pure acid is initially higher than that of the cocrystallised compound, but a lower limiting degree of conversion has been noted in the former case.[174]

The crystal structures of the acids and their cocrystallised mixtures with phenazine have been studied (Table 3), which has led to a model capable of explaining the characteristic features of the topochemical polymerisation of the acid and its complex. According to the model, the acid molecules are packed in the single crystals in layers of the "head–head–tail–tail" type (Fig.10). The authors[174] regard the crystal structure of the complex as intermediate between the structures of the pure compounds and explain thereby why acridine and pyrazine do not form analogous complexes. On the other hand, the 4,6- and 10,12-diynoic acids do not cocrystallise with phenazine, unlike the 2,4-diynoic acids, probably because the latter have a higher pK_a owing to the strong electron-accepting character of the $C\equiv C-C\equiv C$ group, which means that they have a greater capacity for the formation of complexes with phenazine. Phenazine is removed by extraction from the coloured polymeric crystals obtained by topochemical polymerisation, after which the latter assume a fibrous form. Other substances can be introduced into the space produced by the removal of phenazine.[174] In the PDA chains the monomer units are linked "head to tail".[174]

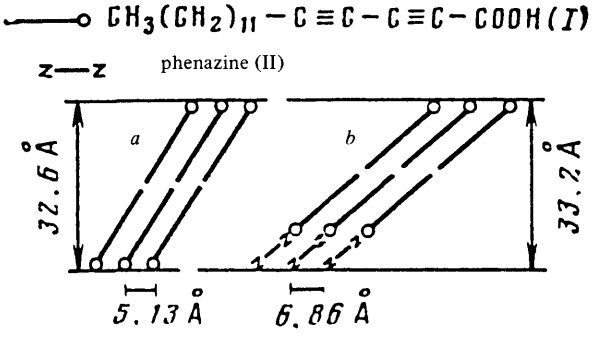


Figure 10. Structural models of DA (*a*) and of the cocrystallised DA–phenazine mixture (*b*) in the (100) projection i.e. at right angles to the direction of the PDA chains.[174]

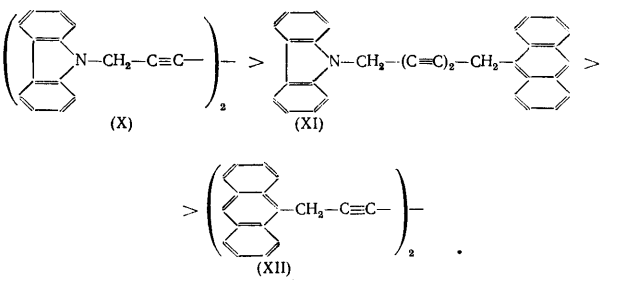
The study of the photoinduced topochemical polymerisation using the light corresponding to the optical excitation band of phenazine ($\lambda = 420$ nm) or DA ($\lambda = 280$ nm) revealed differences between the corresponding quantum yields ($\phi_{420} = 0.1$ and $\phi_{280} = 0.5$) and activation energies ($E_{420} = 0.21$ eV and $E_{280} = 0.17$ eV). It is believed that there is no electron transfer from the excited phenazine molecule to DA.[213]

Another aspect of the use of the mixed crystals is the solid-phase copolymerisation of various cocrystallising diacetylenic monomers, for example, those containing the urethane groups $R = CH_2OCONCH_6H_4X$, where X = H, *p*-Cl, or *p*-Br.[214] The relatively unreactive HD bis(*m*-trifluoromethylbenzenesulphonate) cocrystallises with the isomorphous TS. Thermal polymerisation of DA takes place in the jointly crystallised material, the duration of the induction period, which is also observed in the topochemical polymerisation of pure TS, depending on the ratio of the comonomers.[47,48]

It has been observed that the monomers (III) with R = *p*-Cl or *p*-CH_3 give rise to a series of mixed single crystals owing to the similarity of the van der Waals radii of the substituents Cl and CH_3.[215,216] The formation of solid solutions has been observed also for the symmetrical diacetylenes with $R = CH_2OCONHC_6H_5$ or CH_2OCONH-2-thienyl.[216] The diacetylene (III) with R = *p*-OCH_3 (there is no induction period[44,46,134,169,170]) and DA with R = naphthalene-2-sulphonyloxy (inactive in topochemical polymerisation[51]) also cocrystallise with TS, the composition of the crystals having been determined from the absorption spectra. Ideal solid solutions are formed when the content of the naphthalenesulphonates is 0–50%. The induction period in the topochemical polymerisation in the mixed crystals of TS with compound (III) (R = *p*-OCH_3) or DA with R = naphthalene-2-sulphonyloxy diminishes with decreasing fraction of TS in the crystal.[215]

It has been shown that the crystals produced by the cocrystallisation of TS and the inactive compounds (III) (where R = *p*-Cl[217,218] or R = *p*-Br[218]) form both reactive and unreactive modifications. A significant rearrangement of the TS crystal lattice does not occur when the content of the chloro-derivative is up to 20%, while in the mixed crystals of the bromo-derivative perturbations of the lattice are observed at lower concentrations of the latter as a consequence of the greater bulk of the bromine atom. The parameter *b* of the cocrystallised material diminishes monotonically with increasing content of the chloro- or bromo-derivative in the mixture with TS with a simultaneous decrease of the melting point. The copolymerisation of TS with compound (III) (R = *p*-Cl or *p*-Br) proceeds up to total conversion and is characterised by an induction period whose duration increases with increasing fraction of the inactive halogen-containing DA. However, in the case of the chloro-derivative an initial decrease of the induction period with increasing mole fraction of the chlorine-containing DA and the cocrystallised material in the range 0–0.05% has been observed, which is difficult to explain. The activation energy E_a for the copolymerisation reaction is identical with E_a for the homopolymerisation of TS, but the rate of topochemical polymerisation is lower than that for the pure TS.[218] Phase separation has never been observed in the course of topochemical polymerisation regardless of the composition of the cocrystallised material.[217,218] The comonomer units are distributed statistically.[218]

The capacity of DA with polynuclear aromatic substituents for polymerisation diminishes in the sequence[69,216]



The diacetylene (XI) undergoes thermal polymerisation (with decomposition) only near the melting point of the monomer and does not undergo radiation-induced polymerisation. The monomers (XI) and (XII) and certain DA derivatives of quinoline, phenothiazine, and acridine in various proportions cocrystallise with DCHD (X) (Fig.11), the mixed crystals polymerising not only thermally but also under the influence of γ-radiation. The ratio of the monomers in the non-polymerised cocrystallised material differs from that in the solution from which the crystal of the cocrystallised material has been grown. Compounds (XI) and (XII) have an inhibiting effect on the photoinitiated copolymerisation of compound (X) using light with $\lambda = 250$ and 350 nm, the wavelength corresponding to the absorption bands of the diacetylenic and carbazolyl fragments. When the crystals obtained by cocrystallising compound (X) with compound (XI) or (XII) are illuminated with light corresponding to the absorption band of the anthryl group ($\lambda = 400$ nm), the process is sensitised. This has been explained by the effective transfer of the excitation energy to the active centres in the crystals obtained by cocrystallisation.[99] As in the case of other types of cocrystallised crystals, the decrease of the fraction of the relatively inactive DA in the crystal obtained by crystallisation with an active DA [compound (X)][25,71] increases the rate of topochemical polymerisation with a simultaneous decrease of the induction period (Fig.12). This finding can be accounted for by the gradual approach by the parameter *b* of the crystal, along which the topochemical polymerisation takes place, to the optimum values characteristic of the pure compound (X) (Fig.11 and Table 2). Chemical and spectroscopic analysis of single crystals of the copolymers have shown that their composition is analogous to that of the initial comonomeric crystals.[99]

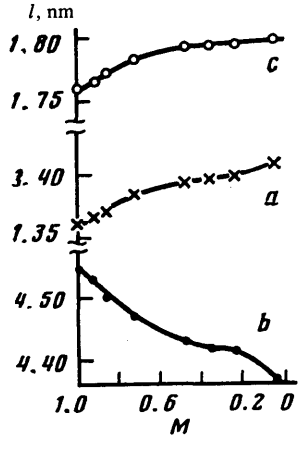
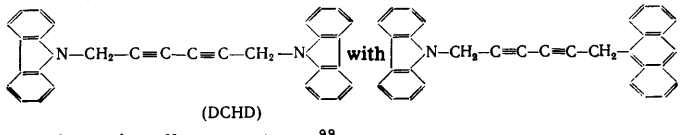


Figure 11. The influence of the DCHD mole fraction *M* in the crystal obtained by cocrystallising



(DCHD)

on the unit cell parameters.[99]

It has been observed that mixtures of different DA show a greater contrast in colour changes on heating or irradiation than the individual DA. The cocrystallised crystals of two and more linear or cyclic monomers of different structure have therefore been suggested as thermal indicators or γ-radiation dose indicators on the basis of changes over their colour range.[219]

The cocrystallised crystallisation and copolymerisation of symmetrical monomers of similar structure, namely DA with $R = CH_2OCONH(CH_2)_3CH_3$ and $CH_2OCONHCH_2CH_3$ as well as DA with $R = (CH_2)_2OH$ and $C(CH_3)_2OH$, have been investigated with the aid of optical spectroscopy and DSC.[220]

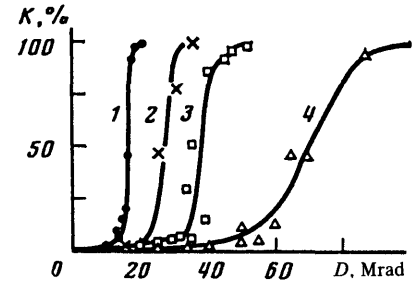
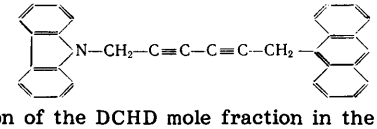


Figure 12. Dependence of the degree of conversion *K* on the dose *D* in the γ-initiated topochemical polymerisation of the cocrystallised mixture of DCHD and



as a function of the DCHD mole fraction in the cocrystallised material: 1) 1.000; 2) 0.989; 3) 0.978; 4) 0.945.[99]

IV. SOLUBLE DIACETYLENE POLYMERS AND THEIR PROPERTIES

The polymers obtained by the topochemical polymerisation of DA are as a rule insoluble in the usual organic solvents. However, it has been noted that many polymers based on the urethane derivatives of HD [2] and substituted DPB [5] dissolve in hexamethylphosphoramide (HMP). The polymers of 2,2-bis(acetamido)- and 3,3-bis(phenylureido)-diphenyldiacetylene dissolve in addition in concentrated sulphuric acid.[5]

Poly-TS dissolves in hot nitrobenzene, dimethylformamide (DMF), HMP, and butyrolactone, crystallising anew after the solutions have been allowed to stand.[37] The same polymer synthesised up to 12% conversion dissolves in DMF.[221] The yellow colour of the solution remains unchanged after reducing the temperature and adding the solvent. The electronic absorption spectrum of the solution has a broad maximum with $\lambda_{max} \cong 450$ nm and the extinction coefficient $\varepsilon = 5.6 \times 10^3$ litre mol^{-1} cm^{-1}, as well as a long-wavelength low-intensity downward slope. A gel permeation chromatogram demonstrated a broad molecular weight distribution (MWD) of poly-TS ($\bar{M}_n = 0.98 \times 10^5$, $\bar{M}_w = 4.80 \times 10^5$), it does not change as the degree of conversion increases to 12%, which demonstrates an increase in the number of oligomeric chains while their length remains unaltered. The average degree of

polymerisation of the soluble oligomer is $\bar{n} \cong 20$, while the chains with $\bar{n} \cong 100-200$, present in a small amount, are slowly precipitated at room temperature.[221] With increased degree of conversion of TS, the polymer chain length increases markedly. However, it is not clear whether this is a consequence of the growth of the chains formed during the induction period or whether it occurs as a result of the initiation of longer chains in the autocatalytic stage.

The results of a theoretical study of the thermal topochemical polymerisation of TS, which showed[157] that the growth of strained PDA chains is greatly hindered during the induction period (the rate constant is $k = 7.8 \times 10^{-7}$ s^{-1}), is in good agreement with experiment. Short chains [~100 Å ($\bar{n} = 20$)] are formed. After the attainment of a degree of conversion of ~15%, the chain length reaches 200 Å, In the autocatalytic stage ($k = 1.6 \times 10^{-4}$ s^{-1}) the length of the chains formed is greater than 700 Å.[222] An indirect estimate of the size of the poly-TS chains at high conversions of the monomer yielded the following values: $\bar{n} \cong 4200$ and a chain length $L \cong 2$ μm were found in a study of the kinetics of thermal topochemical polymerisation;[111] $100 < \bar{n} < 10000$ was found in a Brillouin scattering study;[116] $L \cong 5$ μm was found in an electron microscopic investigation of the etching profile of photopolymerised TS.[222]

Polydiacetylene with R = $(CH_2)_4OSO_2C_6H_4CH_3$-*p*, obtained by the γ-radiation-induced polymerisation of the monomer (42% conversion—1 Mrad; 68% conversion—3 Mrad) dissolves at room temperature in many polar solvents (chloroform, dichloroethane, DHF, DMF, acetone, nitrobenzene, and nitromethane).[43] The yellow-orange solution has λ_{max} = 466 nm and $\varepsilon_{max} = 16.7 \times 10^3$ litre mol^{-1} cm^{-1}. The addition of a precipitant alters the colour to red with formation of a deposit. The study of PDA solutions by the light scattering and gel permeation chromatographic (GPC) methods has been shown that the macromolecules in solution have a helical conformation and that $\bar{M}_w = 7.4 \times 10^5$ and $\bar{M}_w/\bar{M}_n = 2$.[43] A broadening and shift of the MWD maximum towards higher values of $\bar{M}_n$ ($\bar{n} = 60-2000$) with increase in the degree of conversion from 2 to 10% has been observed for this PDA. Subsequently the position of the MWD curve hardly changes.[136] According to light scattering and osmometric data,[223] the shape of rigid rodlike helices, consisting of linear segments, is also characteristic of the molecules of PDA with R = $(CH_2)_2$. .OCOR′ (R′ = isopropyl, benzyl, or 1-naphthyl) in solution in $CHCl_3$, for which $\bar{M}_w = (8-13.4) \times 10^5$, $\bar{M}_n = (2.4-3.4) \times 10^5$, and $\bar{M}_w/\bar{M}_n = 3.33-3.94$.

It has been observed that soluble oligomers of hepta-2,4-diynoic acid[133] and the DA (IX) ($m = n = 4$) have the cumulene structure (II) according to infrared spectroscopic data.

The readily soluble PDA with R′ = $(CH_2)_{11}CH_3$ and $R^2 = CH_2OH$ (decalin, 100 °C) and also with $R^1 = (CH_2)_{11}CH_3$ and R^2 = COOH (nitrobenzene, DMF, HMP, 100 °C; pyridine, 20 °C) have $\lambda_{max} \cong 460$ nm in solution and $\lambda_{max} \cong 550$ nm in the single crystal, which can be explained by the altered conformation of the macromolecular skeleton.[224]

In order to investigate the conformational transitions of the polymer chains in solutions, polymers of symmetrical DA, containing in the long side substituents a large number of polar (−CO−, −NH−) and flexible (−O−, $-CH_2-$) groups have been specially synthesised.[65] The degree of interaction of the side substituents with the solvent via such groups increases and hence also the solubility of the PDA molecules. Diacetylenes with R = $(CH_2)_nOCONHCH_2COO(CH_2)_mCH_3$ are relatively inactive for $n = 2$ and are totally inactive for $n = 1$ in topochemical polymerisation. The crystals of the 3BCMU, 3ECMU, and 4ECMU monomers became coloured on heating and γ-irradiation. According to X-ray diffraction data, the specimens of poly-3BCMU, obtained with a low degree of conversion, are in the main amorphous, which has been explained[66] by the existence of only a small number of the polymer chains which determine the crystallinity of the specimen. With increase in the degree of conversion, the degree of crystallinity also increases, because an increasing number of the polmer chains become parallel to one another. The PDA of this type, obtained with degrees of conversion up to 50–92% on γ-irradiation are readily soluble in chloroform, THF, and DMF.[65] According to the GPC data (solvent—DMF), all the polymers obtained are characterised by the following features: (a) there are no intermediate oligomeric compounds, (b) the MWD is wide for all degrees of conversion, and (c) there is almost no increase in the molecular weight in the range of degrees of conversion 7–68%.[225] For example, $\bar{M}_n = 0.98 \times 10^5$, $\bar{M}_w = 4.9 \times 10^5$, and $\bar{M}_w/\bar{M}_n = 5$ for the poly-3BCMU obtained by the γ-irradiation (50 Mrad) of the monomer. The study of the viscosity of its 0.05% solutions in variable-composition solvent–precipitant mixtures (chloroform–hexane, DMF–*o*-dichlorobenzene) demonstrated the absence of an influence by the fraction of the solvent in the mixture on the viscosity of the solution, which indicated the existence of an extended conformation of the rigid polymer chains in all the solutions investigated. The extended conformation of the macromolecule is also retained on extraction of the monomer which failed to react from the partly polymerised PDA single crystal or on fusion of the single crystal.[225] Since the number of units in the polymeric 3BCMU and 4BCMU molecules is known, amounting to 10^3 and 2.4×10^3 respectively,[225-227] the length of such rigid chains was determined and was found to be ~5×10^3 and 12×10^3 Å. The same number of units in poly-4BCMU has been found by the actinometric method.[120] The electronic absorption spectra of solutions of poly-BCMU in DMF have λ_{max} = 470–475 nm and $\varepsilon \cong 17.5 \times 10^3$ litre mol^{-1} cm^{-1}.[221]

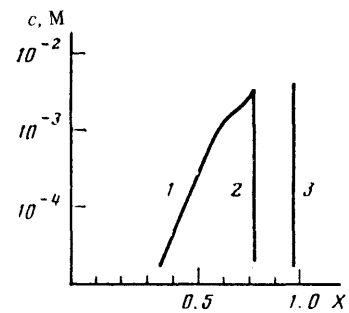


Figure 13. The phase diagram of poly-3BCMU in the chloroform–hecane system; the regions of the blue deposit (curve *1*), the blue solution (curve *2*), and the yellow solution (curve *3*) are designated as a function of the molar concentration of PDA (c) and the mole fraction of $CHCl_3$ (X).[228]

It has been observed that the addition of hexane (a precipitant) to yellow solutions of BCMU and ECMU in chloroform leads to a sharp reversible change of the colour of the solution to blue (3BCMU) or red (4BCMU). The coloured solutions are stable and do not give rise to a precipitate on standing after ultracentrifugation. An increase of the

fraction of hexane leads to the precipitation of the polymers.[105,225,227-230] The precipitation point of the deposit is strongly dependent on the polymer concentration, while the colour transition point is independent of the polymer concentration but is specific to each polymer of the series considered (Fig. 13 and Table 6).[228] Direct titration and back titration lead to different values of the $CHCl_3$ fraction (X and X') at the colour transition point. The quantity X (titration of the chloroform solution with hexane) is then always smaller than X' (titration of the blue solution with chloroform) (Table 7).[229] The solvatochromic phenomenon observed had been explained by conformational transitions of the polyconjugated PDA molecules whose optical spectrum is determined by the length of the continuous conjugation and not the chain length. In the yellow solutions the planarity of the polymer chains is perturbed by the rupture of the intermolecular hydrogen bonds, the interactions of the side substituents with the solvent ($CHCl_3$), and the rotation of the molecules about the C–C bond. The addition of a precipitant (hexane) weakens the PDA–solvent interaction and leads to a conformational transition in the macromolecules with the formation of a planar zig-zag structure of the polymer chains, fixed by hydrogen bonds, with a high effective conjugation length.[105,228-231]

Table 6. Solvatochromic and thermochromic properties of a PDA solution.[228,233,234]

PDA	K, %	X	Q, kJ mol^{-1}	T_p		
				o-dichlorobenzene	nitromethane	ethyl methyl ketone
Poly-4BCMU	92	0.55	35±2	49, 58*	52, 60	42, 47
Poly-4ECMU	75	0.65	25±2	85, 97	60, 71	72, 85
Poly-3BCMU	53	0.71	27±2	93, 102	—, 92	—
Poly-3ECMU	50	0.91	—	**	**	**

Notation: K is the degree of conversion, X the mole fraction of $CHCl_3$ at the solvatochromic transition point, Q the heat of solution, and T_r the temperature of the rupture of the hydrogen bonds of PDA in various solvents.

*The first figure denotes the dissociation of the intermolecular bonds and the second the dissociation of the intramolecular bonds.

**Poly-3ECMU dissolves only in highly polar solvents (DMF) to form a yellow solution immediately.

The effectiveness of the formation of hydrogen bonds in the 3BCMU polymers is greater than in the 4BCMU polymers owing to the difference between the lengths of the side substituents (the values of n in the side substituents).[228] Indeed construction of models taking into account the hydrogen bonds showed that the capacity of 4BCMU for polymerisation is higher, which has been reflected in the kinetics of the polymerisation of these two monomers.[105,227,228] The difference between the absorption band shifts of the 3BCMU and 4BCMU polymers in the course of conformational transitions has been accounted for by the difference between the densities of the hydrogen bond networks.[227] The strong influence of hydrogen bonds on the physicochemical processes in PDA has been demonstrated by adding small amounts of trifluoroacetic acid (acetic acid is ineffective) to the blue or red solution of poly-BGMU, which resulted in an instantaneous alteration of the colour to yellow. This colour transition is associated with the rupture of the intramolecular hydrogen bonds in the PDA network, the formation of hydrogen bonds between the added acid and the ether and urethane groups of PDA, and finally the subsequent conformational transition of the polyconjugated macromolecules.[227,228,231]

The solvatochromism of solutions of sparingly soluble (~10^{-4} mol litre^{-1} in DMF) PDA with R = $(CH_2)_nOCONHC_6H_5$ (n = 3, 4) when a precipitant is added to them can be accounted for by a similar intramolecular hydrogen bond formation process.[232]

Table 7. Solvatochromic transition points for solutions of poly-3BCMU.[229]

Dose, Mrad	K, %	Molecular weight			T_t, °C	Mole fraction of $CHCl_3$ at the colour transition points	
		$10^{-6}\bar{M}_n$	$10^{-6}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$		X	X'
0.09	20.9	1.33	3.90	2.93	20	0.66	0.80
0.09	20.9	1.33	3.90	2.93	0	0.68	0.84
45	57.5	0.0802	3.18	39.7	22	0.70	0.89
45	57.5	0.0802	3.18	39.7	0	0.73	0.96

Notation: K is the degree of conversion, T_t the transition temperature, X the mole fraction obtained by titrating the yellow chloroform solution with hexane, and X' the mole fraction obtained by titrating the blue solution with chloroform.

Poly-BCMU and poly-ECMU are sparingly soluble in xylene, *o*-dichlorobenzene, ethyl methyl ketone, and certain other solvents. However, with increase of temperature, they dissolve and this is accompanied by sharp and reversible (hysteresis) colour changes. For example, the yellow solution of poly-3BCMU in *o*-dichlorobenzene (t = 106 °C) becomes blue at t < 80 °C, while the yellow solution of poly-4-BCMU (t > 68 °C) becomes red at t < 40 °C.[233] Heating PDA in a poor solvent leads to the reverse process. Thus, when red fibrillar particles of poly-4BCMU are stirred for 0.5 h at 49 °C, a red solution is formed in *o*-dichlorobenzene. Rapid heating (for less than a minute) at 58 °C gives rise to a yellow solution of PDA. Regardless of the solvent employed, the crystals of poly-4BCMU and poly-4ECMU initially form a red solution and then, on raising the temperature, a yellow solution (Table 6).[234] The heat of solution of each PDA is almost independent of the solvent.[233,234] A study of solutions and gels of these PDA by infrared spectroscopy, ^{13}C NMR, and DSC made it possible to explain the colour transitions occurring on raising the temperature by the successive dissociation of initially intermolecular and then intramolecular hydrogen bonds with formation of a non-planar conformational structure in yellow solutions at a higher temperature.[226,232-235] A decrease of temperature is accompanied by the reverse processes. The narrow temperature ranges of the thermochromic transitions indicate the cooperative character of the processes. The presence of isobestic points in the electronic spectra at 510 and 490 nm indicates the presence of a conformational equilibrium planar structure (red or blue solution or gel)–non-planar structure (yellow solution).[233]

The latest studies on poly-3(4)BCMU have shown§ that coloured solutions (blue or red) in a poor solvent are not true solutions. Thus the explanation of the colour change in the PDA solution by a conformational transition in individual rod-like conjugated macromolecules, leading to a change in the effective conjugation block is not correct and final¶.[225]

The thermochromic transition in solution has also been observed for PDA with R = $(CH_2)_4OCONHCH_2CH_3$. Its solution in DMF at 100 °C has the yellow colour characteristic of a non-planar conformation of the macrochains (λ_{max} = 470 nm), while at room temperature it has the orange colour of the planar conformation (λ_{max} = 520 nm). However, this phenomenon was not observed for the phenyl-containing DA with a similar structure [R = $(CH_2)_m$. .$OCONHC_6H_5$, where m = 3, 4] even in the presence of a precipitant.[232]

It has been reported that, on treatment with ultrasound in water, DA with R = $(CH_2)_8CH_2OP(O)(OH)_2$ dissolves and polymerises (irradiation with ultraviolet light) with formation of a dark-blue thermochromic solution.[236] However, in this case a true solution is apparently not formed, since the topochemical polymerisation of DA cannot take place in it.

A visible conformational transition has been observed in aqueous solutions of PDA with the symmetrical substituents $(CH_2)_nCOO^-K^+$ (n = 2, 3) and $(CH_2)_3OCONHCH_2COO^-K^+$.[67,68] The solution of the first polymer has a yellow colour at pH ≥ 7. The maximum in its absorption spectrum shifts from 462 to 535 nm when the pH is reduced from 9.5 to 3,, while at low pH (after the addition of HCl) an absorption band with λ_{max} = 575 nm appears in addition. The change in the colour of the solution to red or purple takes place because the planar conformation of the macrochain, which obtains for polymers with the COO^-K^+ groups at pH < 7, is perturbed with increase of the pH by virtue of the formation of the ionic groups COO^-, between which there is a powerful electrostatic repulsion. At pH < 2 a blue-black polymer is precipitated. The introduction of an electrolyte (LiCl, NaCl, KCl) into the solution, leading to a suppression of the dissociation of the ionogenic COO^-K^+ groups and the subsequent decrease of the repulsion between then, has a lesser influence on the conformation. It is of interest that, when the concentration of the electrolyte was altered, the existence of an isosbestic point was noted but the latter vanished when the pH of the medium was altered.[68] The character of the influence of the pH and the electrolyte on solutions of two other polymers is analogous and the difference observed in the shift of the maxima of the absorption spectra of the solutions has been explained by the different distances of the terminal COO^-K^+ groups from the main chain.[68] The salt-like PDA of this class can be synthesised only via the corresponding polymeric acids with subsequent formation of their salts in

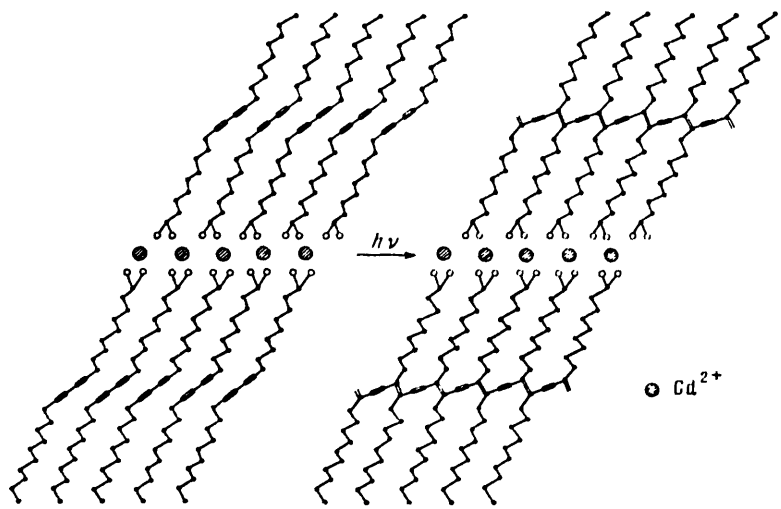


Figure 14. The structure of the cadmium salt of poly-DA in the monolayer.[192]

§ G.Wenz, M.A.Müller, M.Schmidt, and G.Wegner, Macromolecules, 1984, **17**, 837; M.A.Müller, M.Schmidt, and G.Wegner, Macromol.Chem.Rapid.Comm., 1984, **5**, 83.

¶ K.C.Lim, L.A.Fincher, and A.Heeger, Phys.Rev.Letters, 1983, **50**, 1934.

the presence of alkalis. The monomeric potassium and sodium salts of the DA acids are incapable of topochemical polymerisation.[67]

V. MONOMOLECULAR AND POLYMOLECULAR LAYERS BASED ON DIACETYLENES

The principles of the topochemical polymerisation of diacetylenes in single crystals examined earlier are also valid in the solid-phase polymerisation of DA packed into thin layers. Studies in this field have been vigorously prosecuted[237] in connection with the extensive possibilities for the practical application of such layers.

Monomeric monolayers were first obtained using tricosa-10,12-diynoic acid $C_{10}H_{21}C\equiv C-C\equiv C(CH_2)_8COOH$.[192] It was noted that, from the standpoint of the solubility of the layers, the cadmium salt of this acid, forming in the mono-layer a polymer whose structure is illustrated in Fig.14, is more suitable as regards the stability of the layers. The method of preparation of the monomolecular and polymolecular layers has been described†.[238] the monomolecular or polymolecular layers of the monomers satisfied the criteria for topochemical polymerisation and polymerised under ultraviolet irradiation via 1,4-addition without breakdown of the layer structure and with formation of ultrathin films, which are stable under laboratory storage conditions (oxygen, light, etc.).[192,239] The polymerisation of the macromolecular and polymolecular layers, like that of single crystals, can proceed thermally (below the melting point) and under the influence of high-energy radiation.[224]

Subsequently layers based on a whole series of asymmetrically substituted DA (XIII) were obtained similarly and then investigated:

$$CH_3(CH_2)_m-C\equiv C-C\equiv C-(CH_2)_nCOOH\ ;$$
(XIII)

m = 4, 7, 9, 11, 13, or 15, n = 8;[190,191,240,241] m = 2–15, n = 0, 2, 3, or 8:[242] DA with $R^1 = (CH_2)_{11}CH_2$ and R^2 = CH_2OH or COOH.[224] The monomers synthesised exhibit different capacities for the formation of monolayers and for polymerisation in the latter (Table 8).[216,239] It has been observed that the polymerisation of DA in monolayers, initiated by ultraviolet radiation, must be carried out in an inert atmosphere, since the reaction in oxygen leads to the formation of ozone under the influence of which the polymer chains are ruptured.[190,243] As a result of this, the side chains replace the main chains and thereby expand the monolayer, disrupting it.[190] It has been noted that the stability of layers increases with increase in the m/n ratio in compound (XIII). The layers are stronger when the aqueous phase on which the film is formed contains the Cd^{2+}, Ba^{2+}, Ca^{2+}, Fe^{3+}, or Al^{3+} ions.[242]

Polymerisation results in contraction, the extent of which makes it possible to infer the degree of conversion. The change in the degree of conversion was compared with the change in the optical density in the electronic spectra and with the position of the maximum in the absorption spectra.[190,191,240] It has been shown[190,191] that diacetylenes having the general formula (XIII) (m = 11, 13, 15; n = 8) polymerise rapidly in a monolayer at 20 °C (ultraviolet radiation). For m = 9, the polymerisation proceeds only at 2 °C, while acids with still shorter chains (m = 4.7) do not polymerise under such conditions. With increase in the pH of the aqueous phase, the rate of polymerisation increases when the lithium, sodium, and potassium salts of the acid are employed. The use of the Be^{2+}, Cd^{2+}, and Ba^{2+} ions[190,191] and Ca^{2+} and Mg^{2+} ions[190,243] perturbs the packing of the monomer molecules in the layer and suppresses the polymerisation process at high pH. With decrease of pH to below 6 (by adding HCl), the polymerisation proceeds to completion also in the presence of bivalent ions.[191]

†L.M.Blinov, Uspekhi Khim., 1983, 52, 1263.

Table 8. The capacity of DA acids for the formation of monomolecular and polymolecular layers and for polymerisation in the latter.[239]

DA	M.p., °C	Capacity for formation of monomolecular layers		Formation of polymolecular layers	Photopolymerisation at $\lambda < 300$ nm[1]	
		on water	on 10^{-3} M $CdCl_2$ soln.		in the crystal	in polymolecular layers
n-C_9H_{19}—C≡C—C≡C—$(CH_2)_8$—COOH	48	yes	yes	—	++	—
n-$C_{10}H_{21}$—C≡C—C≡C—$(CH_2)_8$—COOH	57	yes	yes	yes	++	+
n-$C_{12}H_{25}$—C≡C—C≡C—$(CH_2)_8$—COOH	61	yes	yes	yes	++	+
n-$C_{14}H_{29}$—C≡C—C≡C—$(CH_2)_8$—COOH	46/59[2]	yes	yes	yes	++	+
n-$C_{12}H_{25}$—C≡C—C≡C—$(CH_2)_8$—COOH	57	yes	yes	no	++, +[3]	—
n-$C_{16}H_{33}$—C≡C—C≡C—$(CH_2)_2$—COOH	93	yes	yes	yes	++	—
n-$C_{16}H_{33}$—C≡C—C≡C—COOH	75	yes	yes	yes	+++	+
n-$C_{12}H_{25}$—C≡C—C≡C—COOH	58	no	no	no	+++	—
n-$C_{10}H_{21}$—C≡C—C≡C—$(CH_2)_9$—OH	49	yes	yes	no	+	—

Remarks: [1]+++ = dark-blue after less than 10 s; ++ = dark-blue after 10–30 s; + = dark-red after more than 2 min; − = no reaction. [2]Phase transition at 46 °C. [3]There are two modifications with different reactivities.

The study of the acid $CH_3(CH_2)_{17}C\equiv C-C\equiv C-COOH$ and of a series of its salts (NH_4^+, Ag^+, Na^+, Cd^{2+}, Cu^{2+}, Hg^{2+}, and Mn^{2+}) with the aid of optical and infrared spectroscopy and EPR showed that the acid itself and its silver and ammonium salts polymerise in the polymolecular layers (the PDA have respectively λ_{max} = 670 and 635 nm), the topochemical polymerisation of the cadmium, sodium, and manganese salts does not occur, while the polymerisation of the copper and mercury salts is accompanied by the decarboxylation of the DA.[244,245] The non-linear optical susceptibility of the blue polymeric ammonium salt is the same as that of the PDA with a $-(C\equiv C)_2-$ group in the centre of the aliphatic chain.[245]

In the polymolecular layers the alkyl side substituents of the monomers (XIII) (m = 2–15, n = 0, 2, 3, 8) are inclined at an angle of 48–63° relative to the support in each monolayer. During polymerisation, the substituents become almost perpendicular to the surface of the support, which results in the observation of the phase transition accompanied by a hypsochromic shift of the maximum in the absorption spectrum.[242]

According to X-ray diffraction and electron microscope data, the PDA chains are extended in the monolayer parallel to the support, while the layers have the crystalline domain structure and are made up of a mosaic of blocks or crystallites. The average size of the domain in which there is a homogeneous orientation of the main PDA chains depends on the conditions of the preparation of the layers and is of the order of several μm.[190,200,239,246,247] In a two-layer and multilayer membrane both monolayers retain the individual morphology of the crystallites.[248,249] Various modifications of the monomeric and blue polymeric layers as well as the transitions between these modifications have been investigated by electron microscopy (Fig.15).[250]

A crystalline dichroic fibre with a thickness of the order of several micrometers has been obtained by withdrawing from the surface of water a PDA acid monolayer. In these fibres the long lateral paraffinic chains, deviating from the polymer units, are oriented at right angles to the fibre axis and form crystallites which are packed at random across the fibre.[190] The tensile stress in the PDA fibres is comparable to that for the usual non-oriented polymers and the modulus of extension is high, due to the high degree of crystallinity. An increase in the size of the crystallites is then accompanied by an increase of the modulus.[251]

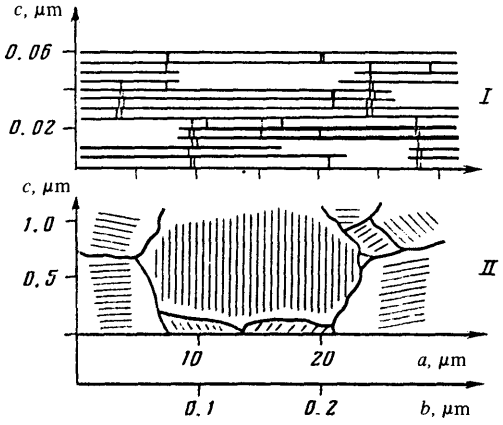


Figure 15. A model of the polymolecular layers based on $CH_3(CH_2)_nC{\equiv}C{-}C{\equiv}C(CH_2)_8COOH$ at right angles (I) and parallel (II) to the specimen; *A*) and *B*) DA; *A'*) and *B'*) PDA; *A*) and *A'*) the low-temperature phase; *B*) and *B'*) the high-temperature phase ($t > 60$ °C). The dimensions of the low-temperature (*A* and *A'*) phase (*a*) and the high-temperature (*B* and *B'*) phase (*b*) are indicated along the horizontal axes. Sections with parallel cross-hatching represent identically oriented planes.[250]

Polymolecular layers have been used to determine the quantum yield ϕ of the photochemical polymerisation of DA. The specimens used were films deposited on quartz plates and consisting of 32 monolayers of the diynoic acids (XIII) ($m = 9$, 11, 13; $n = 8$). The initial value of ϕ (the number of DA molecules which have reacted for each absorbed light quantum) is 10–14, so the polymerisation has the character of a chain reaction. With increased degree of conversion, ϕ falls rapidly for all the monomers investigated.[252]

On the basis of the results of the study of the processes involving the photochemical topochemical polymerisation of diacetylenic acids in polymolecular layers, sensitised by the surface-active cyanine,[246,253] acrydine, and anthraquinone[255] dyes, models have been proposed for the sensitised photochemical polymerisation of DA.[246,253–255] The quantum yield ϕ depends on the amount of sensitiser, depends only slightly on temperature, and is independent of the light intensity.[246] The photochemical topochemical polymerisation is initiated solely by ultraviolet light with $\lambda \leq 313$ nm. After the formation of small amounts of PDA, the polymerisation occurred in the range $400 < \lambda < 500$ nm.[256] The observed effect of the self-sensitisation of the photochemical topochemical polymerisation of the polymolecular layers has been explained by the generation of the PDA chains of highly mobile charge carriers, which activate the centre capable of polymerisation present at the end of the chain, ensuring further chain propagation.[256]

For the polymerised polymolecular layers of the cadmium salts of the DA acid $CH_3(CH_2)_{11}{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_8COOH$, a thermochromic transition has been observed (Fig.16).[247]

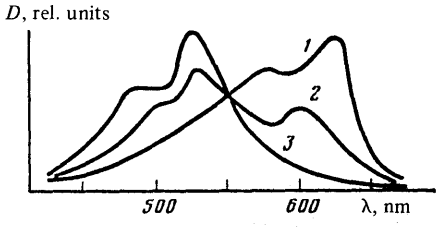


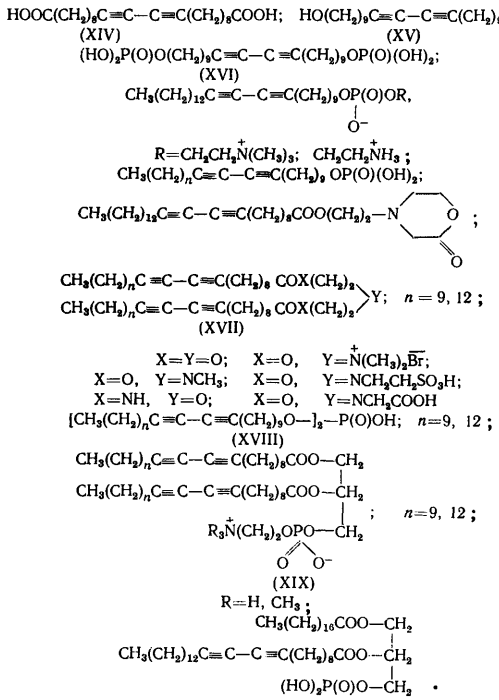
Figure 16. The thermochromic transition in polymolecular layers of the cadmium salts of the PDA acid $CH_3(CH_2)_{11}{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_8COOH$; temperature (°C): 1) 23; 2) 52; 3) 91.[247]

Apart from the monomolecular and polymolecular layers based on individual acids and their salts, polymolecular layers made up of mixtures of different acids and their cadmium salts have been investigated. An increase in the stability of mixed polymolecular layers based on the cadium salts of pentacosa-10,12-diynoic and arachidic acids (the latter is inactive in topochemical polymerisation) has been observed relative to the stability of polymolecular layers of the pure diynoic acid. In mixed layers the components form individual domains whose structure resembles that of the monolayers of the corresponding pure components. At a low concentration pentacosa-10,12-diynoic acid forms domains whose size is <0.1 μm, while the second component forms large domains whose size extends to several μm. It is of interest that, with increase of the concentration of the diynoic acid, the dimensions of its domains also increase but the degree of conversion nevertheless falls.[257] Polymolecular layers of the cadmium salts of tricosa-10,12-diynoic and tricosa-4,6-diynoic (less reactive) acids also separate into phases, but, in contrast to the previous pair of acids, another picture is observed: when the concentration of one of the components exceeds 50%, the polymolecular layer consists of a mixture of domains of this pure component and of domains of a crystalline complex of the acid components in 1 : 1 proportions.[257]

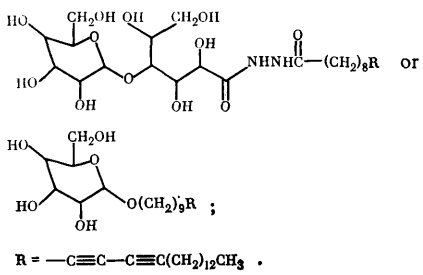
It has been suggested that the thickness of the polymolecular layers based on DA acids could be determined from the standard bond lengths and valence angles. However, the lack of validity of this approach owing to the ambiguity in the conformations of the individual CH_2 groups of the paraffinic moieties of the diacetylenic acids has been demonstrated.[250]

The chiral $DA{-}CH_3(CH_2)_{11}{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_8CONH{-}\overset{*}{C}H{-}C_6H_5$ polymerises rapidly in polymolecular layers on
CH_3
irradiation with ultraviolet light and X-rays. Even under the influence of scattered laboratory light, the topochemical polymerisation of layers of this monomer at the air/water interface takes place in seconds.[198]

The development of the principles governing the preparation of strong monomolecular and polymolecular layers based on diacetylenic acids and their salts and the study of the topochemical polymerisation of diacetylenes made it possible to obtain a whole series of polymeric membranes and DA-based liposomes modelling the natural lipids and certain functional compounds:[258-264]



The polymerisation of the diacetylenic phosphorylcholine (XIX) (R = CH_3, n = 12) initiated by ultraviolet light (argon) in a monolayer leads to the formation of a polymeric phospholipid coloured red and exhibiting optical activity.[265-267] The topochemical polymerisation of phospholipids containing one of two residues of tricosa-10,12-diynoic acid has been investigated on the basis of the contraction of the layers and various types of structures corresponding to phospholipid polymers have been examined taking into account the intra- and intermolecular cross-links involving both one and two acyl groups containing the C≡C–C≡C bond.[266,267] Spherical multilayer lipsomes 4000 Å in diameter have been obtained by hydrolysing suspensions of diacetylenic phospholipids.[266] Structures modelling liposomes have been obtained also by treating the DA (XVI) with ultrasound in water in the presence of cholesterol with subsequent ultraviolet irradiation.[236] On the other hand, on treatment with ultrasound, the symmetrical DA (XIV) and (XV) form crystalline suspensions in water, which do not model liposomes.[236]



The phototopochemical polymerisations of the lipid DA (XVII) [n = 9, X = O, Y = $\overset{+}{N}(CH_3)_2Cl^-$], (XVIII) ($n$ = 9), and (XIX) (n = 9, R = CH_3) have been compared. It has been shown that the capacity of compound (XIX) for polymerisation is appreciably lower than that of the other two DA. The quantum yield of the phototopochemical polymerisation of compound (XVII) is ~6500 times higher than for compound (XIX).[268]

Naturally non-polymerising lipids {distearyl- and dioleylphosphatidylcholine and cholesterol combined with lipids having DA groups in the chain, for example (XIX) (n = 9, R = CH_3) and (XVII) (n = 9, X = O, Y = $\overset{+}{N}(CH_3)_2Cl^-$; n = 12, X = O, Y = $\overset{+}{N}(CH_3)_2Br^-$; n = 12, X = O, Y = $-(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2-$)} form mixed monomolecular and bimolecular layers, consisting of domains, or homogeneous membranes, depending on the type of the monomeric and natural lipid.[269-272] It has been observed that, when systems of this kind are acted upon by the enzyme phospholipase A_2, only the natural lipids are hydrolysed and in layers with separated phases the rate of cleavage is the same as in layers comprising one of the natural lipids; the rate is much lower in homogeneous layers.[270]

The biological models of two-layer lipid membranes synthesised in this way have been investigated by electronic spectroscopy for chemical analysis (ESCA). The presence on the surface of the layers of the elements (P, N, Br, and C) which enter into the composition of the functional group has been demonstrated. The angle of wetting by water θ, which decreases when the monolayers with a hydrophobic surface are kept in air, has been determined. It has been observed that for hydrophilic polymers the nature of the functional groups has less influence on θ for the monolayer than in the case of a hydrophobic polymer.[273]

The preparation of thin films based on PDA with the aid of other methods without employing the principles governing the formation of Langmuir–Blodgett monolayers has been described. These films also demonstrate the specific character of the properties of the polymers.

Thus a thermochromic colour change (at 455 K) from green to yellow has been observed in amorphous films of poly-3BCMU obtained by precipitation from dilute chloroform solutions of PDA with hexane and subsequent drying. The reverse colour change occurs at 435 K. It has been shown by DSC and infrared spectroscopy that the thermochromism is associated with a one-dimensional order ↔ disorder transition, which is determined by the disruption or formation of hydrogen bonds along the polydiacetylene chain containing the C(O)O and NH groups.[274] This explanation of the phenomenon is similar to that given when the thermochromism of single crystals of the same nature was considered.[65]

Thin PDA films with R = $(CH_2)_nOCONHC_6H_5$ (n = 1, 4) and R = CH_2OH have been obtained by an epitaxial mechanism on the surfaces of alkali metal halide single crystals. It has been shown by electron microscopy and electron diffraction that the films consist of highly oriented lamellar single crystals extended in the direction of their maximum dimension along the [110] crystallographic direction on the support.[275]

VI. MECHANICAL PROPERTIES OF POLYDIACETYLENES

A negative coefficient of thermal expansion α has been observed for a series of PDA single crystals along the direction of the polymer chains. Thus $\alpha = -(1.686 \pm 0.039) \times 10^{-5} - (1.35 \pm 0.18) \times 10^{-7}t$ (t in deg C) for a freshly prepared poly-HDDU specimen[53,276] in the temperature range

$t = -50-100$ °C, diminishing by an order of magnitude after evaporation of the dioxan occluded in the single crystal. The coefficient of thermal expansion of the same polymer in the direction of the chain has been determined in another study[277] as -2.0×10^{-5} K^{-1}. For poly-DCHD, $\alpha = (-2.38 \pm 0.07) \times 10^{-5}$ K^{-1}.[70] The coefficient α for poly-TS is negative below 70 K and positive above this temperature, the change in the coefficient within the range of hydrostatic pressures 0–3.43 kbar not exceeding the error of measurement.[278]

Negative values of α had been observed earlier for certain partly crystalline polymers, for example, polyethylene,[279] only with the aid of X-ray studies, since the negative value of α characteristic of the crystalline phase, is masked by the significantly more positive α for the amorphous component. Explanations of the anomalous behaviour of the coefficient α, involving the use of the principle that the amplitude of the torsional movement (torsional vibration) of the chain increases with temperature,[279] have been put forward.[53,277]

It has been concluded[276] that the sign of the coefficient α is not determined by the change in the delocalisation of π electrons arising owing to the thermal conformational fluctuations or the reversible formation of defects, since the theoretically possible calculated contribution to the coefficient should be much less than the value actually observed. Subsequently[278] the unusual behaviour of the coefficient α was analysed in terms of an equation including the Grueneisen parameter and it was postulated that this behaviour is caused by the characteristic properties of the PDA chain.

The positive value of the coefficient observed solely for the polymer based on compound (IX) ($m = n = 4$) in the temperature range $-50-40$ °C ($\alpha = 4.46 \times 10^{-6}$ K^{-1}) has been attributed[179] to the presence of $-(C\equiv C)_2-$ groups which failed to react, which leads to disordering of the chains and the conversion of the polymer into an amorphous form.

The mechanical properties of traditional polymers are determined to a large extent by the presence in them of structural and phase defects. For very perfect PDA crystals made up of extended macrochains, there is a possibility of particularly high strength properties of the polymer molecules within the macrovolume of the specimen with the simultaneous manifestation of a pronounced anisotropy: the modulus in the direction of chains is much higher than that for the direction at right angles to the chains.[280]

The dynamic and static moduli of extension of the crystalline fibres of poly-HDDU, obtained in the region of elastic deformations, are virtually identical (~4.5×10^4 N mm^{-2}).[52] The observed deviation from Hooke's law (the decrease of the modulus by ~3 and 6% on 3 and 4% deformation respectively) is analogous to the behaviour of other filamental crystals, for example, those of iron, quartz, etc. The tensile strength, reaching 1.7×10^3 N mm^{-2}, usually increases with decrease of the length of the fibre and is approximately proportional to the reciprocal of the fibre diameter. The latter factors can be accounted for by the existence on the surface of the fibre (or in its vicinity) of a small number of defects, which control the disruption process. Indeed photographs obtained with the aid of a scanning electron microscope demonstrated the formation of a crack on the surface of the crystal after the tensile strength has been exceeded, the crack spreading initially to a certain depth and then along the fibre. As a result of this, the crystal is partly cleaved and there is an irreversible slip of its two components relative to one another.[52]

The tensile strength of PDA with R = $CH_2OCONHC_2H_5$ (diameter 10–100 μm, length up to 5 cm) is also proportional to the reciprocal of the fibre diameter. The tensile strength, which increases with increase in the degree of conversion, amounted to $(0.6-1.4) \times 10^3$ N mm^{-2} for a relative elongation of 12–20%, but in a number of instances it reached 6.2×10^4 N mm^{-2}. Creep was not observed in the fibres.[281]

Poly-TS specimens increase in length by 4% before they are ruptured: the corresponding tensile strength is 2.0×10^3 N mm^{-2}.[282] The degree of conversion in the thermal polymerisation of TS (60 °C) has been followed by measuring the frequencies of phonons with wave vectors parallel to the *a*, *b*, and *c* axes of the crystal. It has been shown that the density varies from 1.404 to 1.483 g cm^{-2}, while the modulus of elasticity increases in the direction of the chains from 0.97×10^4 to 4.38×10^4 N mm^{-2} on passing from the monomer to the polymer.[58]

It has been observed that the Raman spectra of the deformed and undeformed regions of poly-TS are identical[280,283] and the *b* axis of the unit cell, which is the direction of the main PDA chain, should therefore remain unchanged. A transition from the monoclinic to the triclinic unit cell has been observed in the deformed regions of poly-TS.[280] Under these conditions, the *a* axis is unchanged, while the *b* axis and the angle β are altered, which diminishes the volume of the cell by ~7% and leads to closer packing of the polymer chains in the deformed regions.[36] The slip planes in the deformation of poly-TS crystals have been determined.[36,52]

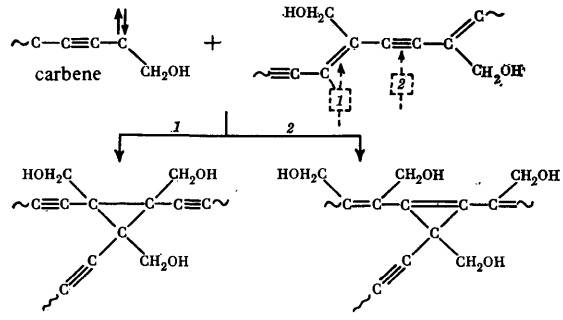
A ladder polymer based on compound (IX) ($m = n = 4$)[179,208] has a low modulus (5.5×10^3 N mm^{-2}) and tensile strength (2.2×10^2 N mm^{-2} (despite the existence of a dense cross-linked network. The reason for this is the disorder in the chains owing to the presence of $-(C\equiv C)_2-$ groups which have reacted incompletely (see Section III).[179] The tensile strength of DCHD is 0.6×10^3 N mm^{-2}.[70]

The morphology and mechanical properties of a fibre obtained from a polymerised DA layer have been investigated[271] (see Section V).

The high mechnical strength of many single-crystal PDA fibres enabled Young and Galiotis[284] to suggest that fibres of this type be used in thermoplastic and thermally hardening composite materials with high strengths and rigidities. A comparative study with the aid of resonance Raman spectroscopy (Kr laser, $\lambda = 676$ nm) of poly-DCHD fibres and fibre joints overed by an epoxy-resin (hardened with an amine) showed that the strength of the bond between the fibres and the epoxy-resin is fairly high and the tensile strength at the joint is comparable to that of a whole fibre.[285]

VII. CHEMICAL PROPERTIES OF POLYDIACETYLENES

According to mass-spectrometric data and elemental analysis, the CH_2OH side groups in the HD polymers obtained in air or in argon exhibit a high chemical stability in the course of polymerisation.[30] However, in the solid-phase polymerisation of HD crystals containing occluded oxygen, the reactive terminal carbene radicals, which propagate the polymerisation reaction, may be oxidised with formation of the ~=C(CH_2OH)–C≡C–C(CH_2OH)=O end groups. The polymerisation of HD in argon leads to a high conversion (>20%) in intermolecular interactions between the terminal carbene radicals and the multiple bonds in the polymer chains, which results in cross-linking of the polymer formed[30] in accordance with the scheme



--[ ]--→ possible direction of attack by the carbene and the corresponding reaction products.

A low chemical stability in thermal polymerisation has been observed for the R–(C≡C)$_3$–R polymers (R = CH_2OH or $CH_2OSO_2C_6H_4CH_3$-*p*) (Table 5).[193]

The thermal stabilities of various types of PDA have been investigated. It has been observed that, despite the polyconjugated main chain, the crystalline PDA do not possess a high thermal stability owing to the presence in the macromolecules of side substituents which are unstable at a high temperature. Their thermal decomposition begins as a rule at a temperature not exceeding 200–215 °C. For example, the PDA obtained by the thermal polymerisation of TS at 60 °C would not decompose on rapid heating to 210 °C; prolonged heating induces decomposition at a much lower temperature (110 °C). The thermal decomposition of poly-TS specimens obtained at 70° and 80 °C takes place immediately after the attainment of 110 °C.[36] Mass-spectrometric studies of the molecular structure of poly-TS as well as investigation of its degradation process suggested a mechanism for the low-temperature decomposition.[40] Gas-chromatographic and mass-spectrometric studies of the products of the pyrolysis of this polymer at 400–1000 °C have shown that the main pyrolysis products are triacetylene and toluene-*p*-sulphonic acid.[40]

The poly-BPG, whose polyconjugated main chain is doubled by the chain of the side substituent coiled around it, has a higher thermal stability. The polymer loses 2 wt.% at 350 °C, 13 wt.% at 400 °C, 30 wt.% at 450 °C, and 39 wt.% at 500 °C.[103] A cyclo-ladder polymer based on compound (IX) ($m = n = 4$), possessing a dense cross-linked network, has been synthesised.[179] However, an improvement in thermal stability was not achieved primarily because of additional weight loss due to the evolution at 150 °C of the solvent cocrystallised with the initial monomer. Apart from the weight loss mentioned above at 150 °C (9 wt.%), the thermogravimetric curve shows a sharp weight loss beginning at 400 °C and reaching a maximum (48 wt.%) at 470 °C.[179]

Poly-DCHD exhibits a higher thermal stability, probably owing to the aromatic carbazolyl nuclei, being stable to 300 °C and losing 6.5 wt.% at 400 °C. However, exothermic decomposition, leading to a weight loss of 62% at 475 °C, begins between 400° and 450 °C.[70]

As in the case of polyalkynes, obtained by liquid-phase polymerisation, the polyhexa-2,4-diyne synthesised by topochemical polymerisation is vigorously oxidised by oxygen.[24] Accoring to Chance et al.,[286] the hypsochromic shift in the optical spectrum of a solution of poly-3BCMU arises partly owing to chemical defects which perturb the conjugation and appear as a result of the slow (in the course of months) oxidation of the PDA chains.

In addition, like other polyacetylenes having multiple bonds within the chain, the PDA can combine with ozone. For example, it has been observed that ultraviolet radiation causes the disruption of PDA monolayers[190,243] and decolorisation of PDA solutions[287] owing to the interaction of the main polyconjugated chains of the polymers with the ozone formed and subsequent decomposition of the ozonides.

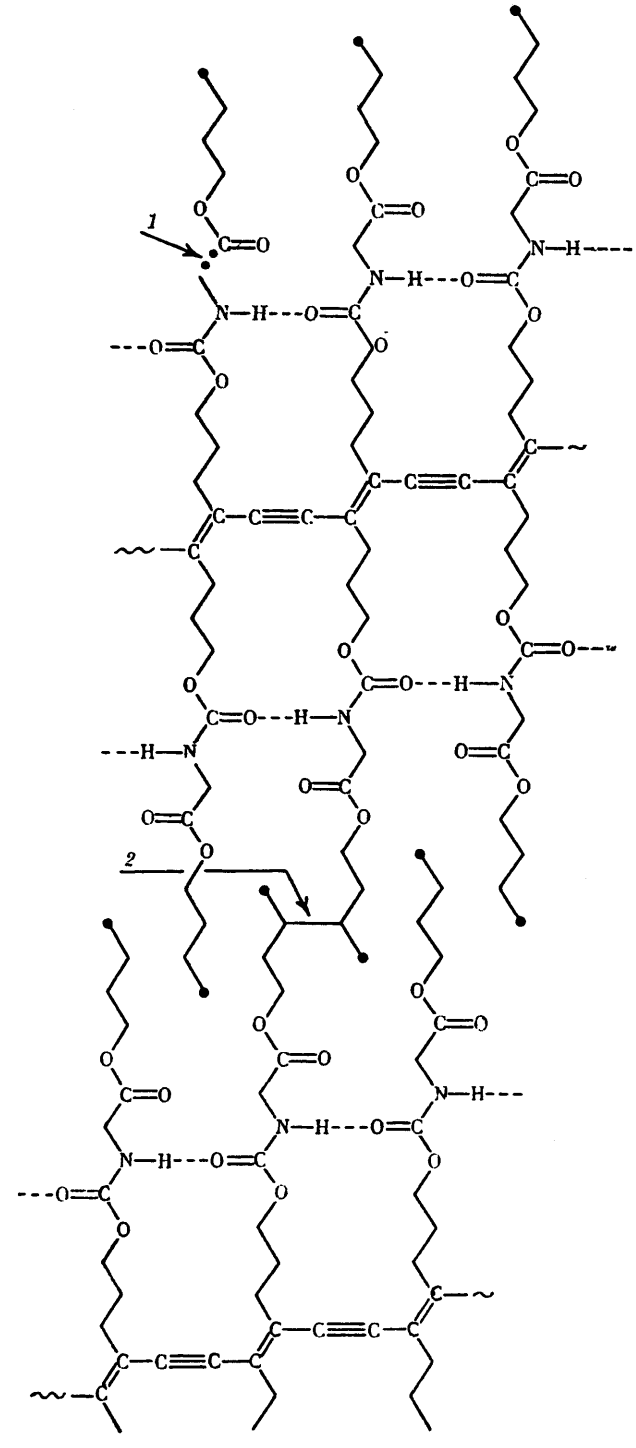


Figure 17. Schematic illustration of the decomposition of poly-3BCMU under the influence of γ-radiation: 1) disruption; 2) cross-linking.[290]

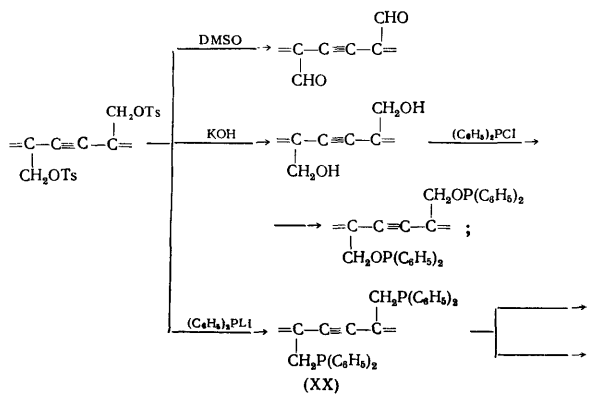
PDA washed free of monomers,[193] PDA double layers,[288] and a TS single crystal, subsequently polymerised via a topochemical polymerisation mechanism,[289] have been doped with iodine. The conductivity of the specimens then increases by several orders of magnitude but neither the mechanism of the doping process nor the structure of the products of the interaction of PDA with iodine have been studied in detail.

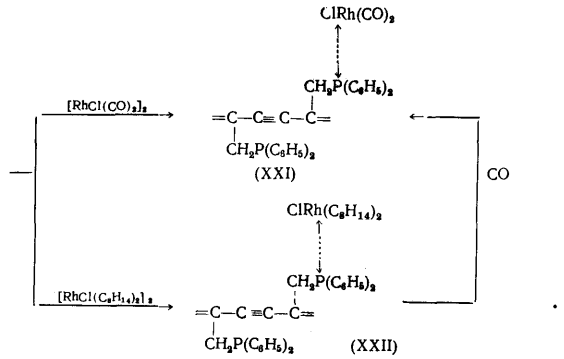
Investigation of the radiation stability of poly-3BCMU (^{60}Co γ-radiation, 20 °C, vacuum) showed that crystalline PDA remains soluble after irradiation with a dose of 50 Mrad. In amorphous PDA, obtained by dissolving and precipitating crystalline PDA, the gel fraction is formed at 3 Mrad, while for a dose of 200 Mrad the polymer loses its solubility completely.[290] It has been noted that the highly conjugated main chains do not undergo cross linking, while irradiation leads to the degradation of the side chains and their cross linking by intermolecular bonds (Fig.17). The marked decrease of $\bar{M}_n$ and the widening of the MWD with increase in the degree of conversion from 20.9 to 57.7% probably take place as a result of degradation in the course of polymerisation (Table 7).[229]

Using the chemical structure of the side substituents, PDA has been modified. Charge-transfer complexes between electron acceptors and the monomeric DA containing the anthryl or carbazolyl groups have been obtained.[69] However, it has been shown[64] that the monomeric charge-transfer complexes based on 1,6-bis(3-pyrenyloxy)hexa-2,4-diyne and electron acceptors (tetracyanoquinodimethane, tetracyanoethylene, trinitrofluorenone, etc.) do not polymerise in the solid phase. Nor are charge transfer complexes formed on treating a suspension of PDA in CH_2Cl_2 with a solution of tetracyanoquinodimethane. Only on mixing solutions of a pyrene-containing PDA and acceptors, diluted with HMP, are intensely coloured 1:1 or 1:2 complexes (depending on the type of acceptors) precipitated.[64] The equilibrium constants for the formation of the charge-transfer complexes investigated are higher than for the model charge-transfer complexes with the corresponding monofunctional compounds.

The presence of labile toluene-*p*-sulphonyl groups made it possible to carry out reactions between poly-TS and $LiP(C_6H_5)_2$ with formation of a fully phosphinated dark-brown amorphous polymer (XX) having $CH_2P(C_6H_5)_2$ side groups.[291, 292] The photomicrographs obtained with the aid of a scanning electron microscope showed a loose surface of the specimen with its area not quite so large as that of silica gel. The toluene-*p*-sulphonyloxymethyl groups have been replaced via polymer-analogue reactions by CHO, CH_2OH, and $CH_2OP(C_6H_5)_2$ groups.[292]

The study of the EPR spectra of a dry specimen of poly-TS with an attached spin label as well as specimens wetted with benzene and CCl_4 did not reveal a difference between the shapes of the spectra obtained.





Thus, in the given instance the nature of the solvent did not influence the behaviour of other molecules attached to the polymer chains.[277] The polymeric complexes $RhCl(CO)_2R'$ (XXI) and $RhCl(C_8H_{14})_2R'$ (XXII) (R' is one phosphine group in PDA)[291] have been obtained respectively by the reaction of compound (XX) with $[RhCl(CO)_2]_2$ and $[RhCl(C_8H_{14})_2]_2$ (C_8H_{14} is cyclo-octene).[291] In the presence of the complex (XXI) mono-olefins are hydrogenated by cyclohexa-1,3-diene is relatively inactive. In the presence of the complex (XXII) cyclohexa-1,3-diene is hydrogenated more rapidly to acrylonitrile than are α-olefins. Benzene is also hydrogenated at a measurable rate at atmospheric pressure. On the other hand, the "monomeric" complex $RhCl[P(C_6H_5)_3]_3$ does not catalyse the hydrogenation of conjugated olefins at atmospheric pressure. The high reactivity of the phosphinated polymeric complex is apparently associated with the increased rigidity of the polymer chains, which ensures the stabilisation of two coordination sites and prevents the formation of the chelate. Thus the possibility arises of activating both hydrogen atoms and the conjugated olefin.[291]

VIII. POLYMERISATION OF LINEAR COMPOUNDS WITH SEPARATED $-C\equiv C-C\equiv C-$ GROUPS

Linear DA of the types

$$R-C\equiv C-C\equiv C-(CH_2)_3-C\equiv C-C\equiv C-R,$$
$$R-C\equiv C-C\equiv C-(CH_2)_2-C\equiv C-C\equiv C-(CH_2)_2-C\equiv C-C\equiv C-R,$$
$$R-C\equiv C-C\equiv C-(CH_2)_2-C\equiv C-C\equiv C-C\equiv C-C\equiv C-(CH_2)_2-C\equiv C-C\equiv C-R,$$
$$R=CH_2OSO_2C_6H_4CH_3\text{-}p,\ CH_2OCONHR'(R'=CH_3,\ C_2H_5,\ C_6H_5),$$

have been proposed as temperature–time indicators.[219–293]

At 100–200 °C or under the influence of ultraviolet light, the crystalline $H_3C-C\equiv C-C\equiv C-Hg-C\equiv C-C\equiv C-CH_3$ polymerises up to 100% conversion (the yield has been determined gravimetrically) with formation of violet, blue, and even red-brown insoluble crystals. The S-shaped conversion curves show an induction period, as in the case of the solid-phase polymerisation of TS. The authors[294] believe that this involves the formation reaction of a ladder polymer (Fig.18).

The presence of the $C\equiv C-C\equiv C$ groups in the long polymer chains does not rule out the possibility of the reaction involving the 1,4-cleavage of the diacetylenic groups in such chains via the mechanism described above for low-molecular-weight DA. Indeed, the oxidative condensation of nona-1,7-diyne[176,295] and dodeca-1,11-diyne[176,177,296] yielded the corresponding crystalline macromers containing reactive groups in the chain.

$$HC\equiv C[(CH_2)_mC\equiv C-C\equiv C]_n(CH_2)_mC\equiv CH;$$
$$m=5,\ 8.$$

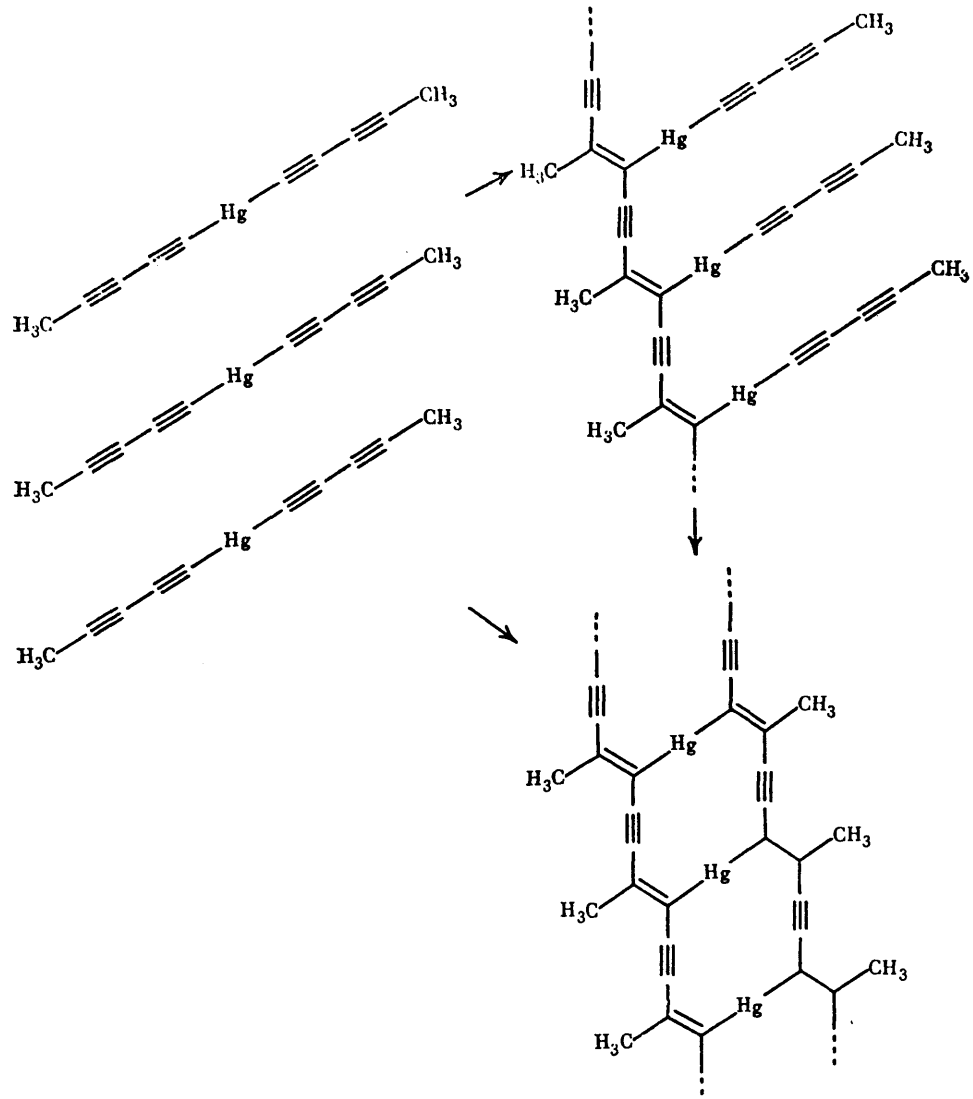


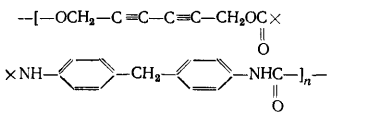
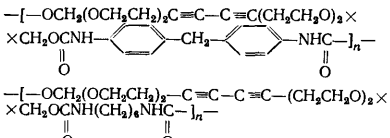
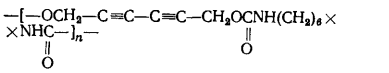
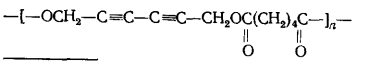
Figure 18.

A cross-linked polymer is formed under the influence of ^{60}Co γ-radiation in the crystals of these macromonomers via the topochemical polymerisation mechanism. The crystal unit cell parameters of the initial macromonomer and the cross-linked product have been determined (Table 3) and the possible polymer structure have been examined. It has been shown by ^{13}C NMR that the cross-linking is incomplete and that $=C-C\equiv C-C=$ bridges are formed during the reaction, since the signals characteristic of the butatrienes $C=C=C=C$ have not been observed in the range 200–220 p.p.m.[297]

An analogous reaction occurs also in less ordered polymeric systems. Thus the reactions of glycols containing DA groups with di-isocyanates or adipic acid dichloride gave rise to the corresponding soluble polyurethanes and a polyester (Table 9).[298,299] Owing to the presence of the reactive DA groups, the films made up of the heterochain polymer synthesised are coloured under the influence of ultraviolet light or heating to give red or orange tints with formation of a three-dimensional network. Polyurethanes based on hexamethylene di-isocyanate show the highest reactivity (Table 8), being coloured even when the specimens are merely pressed (at a pressure of 100–200 kg cm^{-2}).[299] Proof of the occurrence of the reaction in the more ordered regions is provided by the formation of a coloured gel from a precipitate of polyurethanes several seconds after the start of ultraviolet irradiation, while irradiation of solutions of these polymers leads to the appearance of only a weak brown colour after 30 min. It has been observed that the cross-linking of solid polymers is catalysed by radical initiators (benzoyl peroxide, azobisisobutyronitrile) and is inhibited by hydroquinone. Solutions of polymers do not exhibit this type of behaviour.[299]

The polyurethane $-[-NH(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-O-CH_2-(C\equiv C)_3-CH_2-O-\overset{\overset{O}{\|}}{C}-]_n-$, obtained from octa-2,4,6-triyne-1,8-diol and hexamethylene di-isocyanate, also gives rise to cross-linked products in yields of 75 and 13% respectively on heating (70 °C, 48 h) or ultraviolet irradiation (3 h).[300]

Table 9. The properties of heterochain polymers with the $-(C\equiv C)_2-$ groups in the main chain.[298,299]

Polymer	M.p., °C[1]	Appearance of colour	
		u.v. irradiation	heating
	~150	yellow	colourless
	~130	yellow	colourless
	138	purple	purple
	149	red	red
	~130	orange	yellow-red

[1]With decomposition; DSC, 32 K min^{-1}. [2]After 1 h at 110 °C.

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The data examined indicate a vigorous development of the research into the polymerisation of monomers with conjugated diacetylenic groups and also the wide-scale investigation of a whole set of specific properties of the polymers. The fact that the methods employed to obtain the polydiacetylenes are in essence the methods for the synthesis of polyconjugated polymers with small numbers of defects or no defects at all, which serve as effective models for the study of the physics of one-dimensional systems, is of special interest. The synthesis of tens of monomeric and oligomeric compounds of different classes, the study of their capacity for topochemical polymerisation, and the study of the structure of the polymerisation products formed revealed general rules obeyed by the polymerisation of compounds containing the $-(C\equiv C)_2-$ groups.

Nevertheless many problems, for example, the elucidation of the causes of the manifestiation of different reactivities of DA having similar electronic and steric structures, have remained unsolved. There is no doubt that further development of studies in the field of the solid-phase polymerisation of diacetylenes will lead to the creation of new types of oligomeric-polymeric materials with a specific structure and to a considerable expansion of their practical applications.

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