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The Mechanism and Kinetics of the Polymerisation of Conjugated Diacetylenes. The Physical Properties of Polydiacetylenes

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The mechanisms of the polymerisation of disubstituted conjugated diacetylenes initiated in different ways are examined as are the factors influencing the polymerisation kinetics, the yield of the polymer, and the molecular weight distribution and the structure of the final product. Various physical properties of the most highly investigated polydiacetylenes are discussed: optical (including thermo- and solvato-chromism), non-linear optical, paramagnetic, electro-physicalm mechanical, etc. properties. The possible practical applications of polydiacetylenes are indicated.
The bibliography includes 289 references.

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I. INTRODUCTION

In polymer chemistry, the preparation of polymeric single crystals of macroscopic size has been of interest for a long time. It has been shown[1] that at the present time this problem can be solved for polymers with conjugated bonds only in the case of polydiacetylenes—polymers based on disubstituted diacetylenes (DA) with conjugated triple bonds having the structure $R-C\equiv C-C\equiv C-R'$ (in the present review DA will be understood only as diacetylenes having this structure).

During the comparatively short time that has elapsed since the publication by Wegner in 1969 of the first communication on this topic, it has been possible to synthesise several hundreds of DA with substituents of various types, and in many cases polymerise them with the formation of crystals and multilayers having different kinds of morphology. The materials obtained have many interesting properties which determine their possible practical applications (for example, non-linear optical properties, thermo- and solvato-chromism, high mobility of current carriers, high mechanical strength, thermal stability, etc.). Furthermore, the study of DA, of the mechanism and kinetics of their polymerisation, and of the relation between the electronic and molecular structures and the properties of the polymer help in the solution of many general problems of the chemistry and physics of polyconjugated systems whose investigation has been in most cases complicated by their structural and molecular inhomogeneity. In this sense polydiacetylenes (PDA) provide a unique opportunity, as model objects, for the investigation of the general characteristics of polyconjugated systems, since the specimen always represents a set of fairly long macromolecules having the same conformation. Certain PDA are soluble which makes it possible to study their equilibrium properties under conditions independent of external molecular stresses.

Only those DA which in the monomeric phase give rise to single crystals or mono- or multi-layers and polymerise subsequently with retention of the topological correspondence between the molecular structures of the monomeric and polymeric phases will be considered in the present review. The review is devoted mainly to questions of the kinetics and mechanism of the polymerisation of DA, the relation between the structure of PDA and their physical properties (optical, mechanical, and electrophysical) and their practical applications; the methods of synthesis of the initial DA will not be considered. In the foreign literature there are a number of reviews devoted to various questions of the synthesis and physical properties of DA and PDA[2-12]†. This review reflects the latest advances in the study of the physical properties of PDA. In those cases where there is no unanimous view concerning some problems, the alternative approaches are described.

II. PRINCIPLES OF TOPOCHEMICAL POLYMERISATION

The solid-phase polymerisation of DA belongs to the class of topochemical reactions. According to Wegner's definition[2,11], topochemical polymerisation is understood as a non-diffusional conversion of a monomer single crystal into the corresponding polymer single crystal in which the mass centres of the monomeric units retain their initial crystallographic positions and the symmetry of the monomeric units in the monomer and polymer single crystals remains the same. The polymerisation reaction of DA, which is in essence a 1,4-*trans*-addition reaction, is achieved as a result of specific rotations of the monomeric units relative to the positions of their centres of mass, is determined by

† In addition, during the preparation of this article for the press, the following reviews were published: D.Bloor, Mol. Cryst.Liq.Cryst., 1983, **93**, 183; D.Bloor, in "Developments in Crystalline Polymers - 1", (Edited by D.C.Bassett), Applied Sci.Publ., London, 1982, p.151.

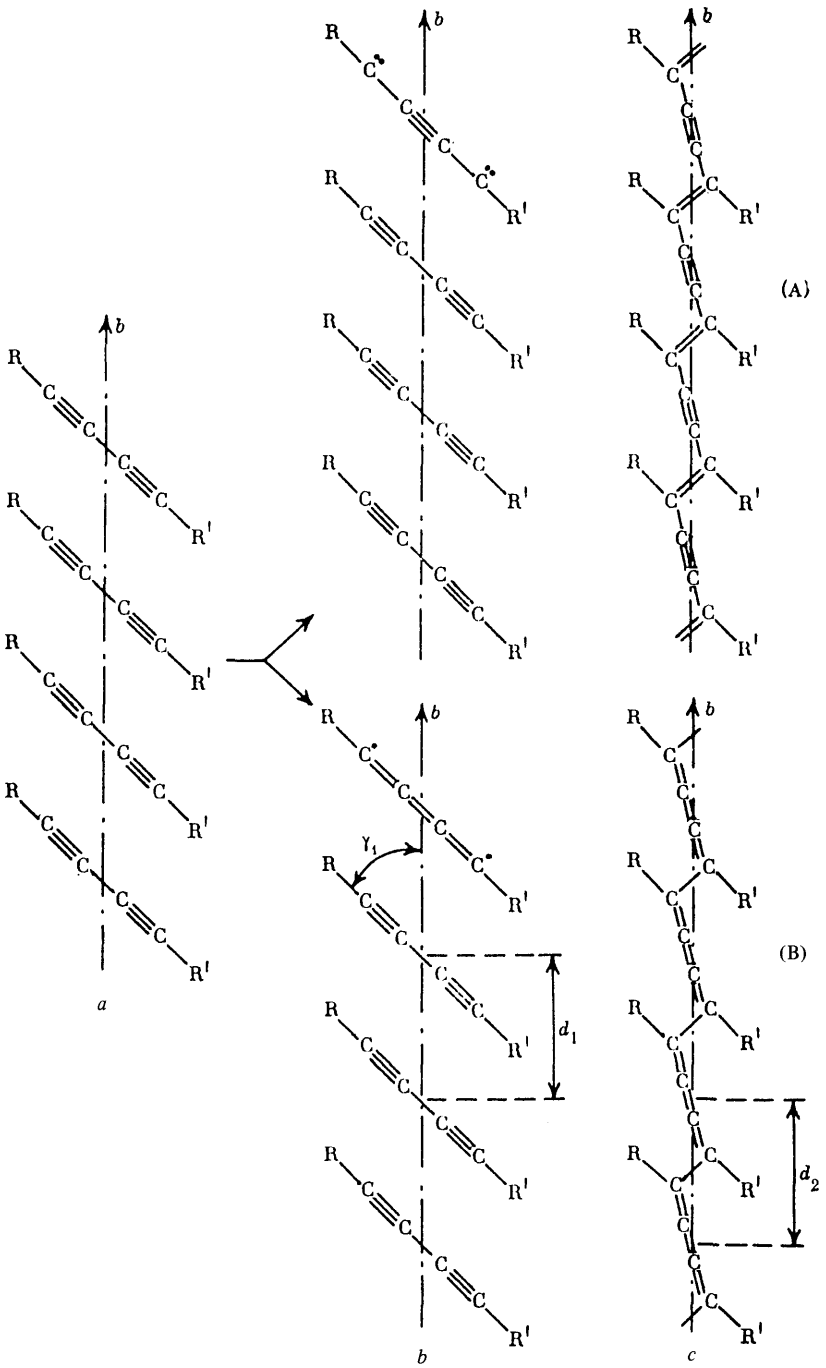


Figure 1. Schematic illustration of the topochemical polymerisation of DA: [2] *a*) arrangement of DA monomers in the single crystal; *b*) the structure of the initiating species in the carbene (above) and radical (below) initiation; *c*) PDA can exist as a function of type of initiation and structure factors in the enyne (A) or butatriene (B) mesomeric forms; *d*) axis of polymer chain.

the packing of the monomer in the crystal lattice, and proceeds without the formation of side products (Fig.1). Such stereospecific polymerisation results in the formation of a stereoregular polymer with a linear disposition of the macromolecules and with a small number of defects; in a number of instances the length of the polymer chain is comparable to the dimensions of the single crystal.

It has been shown by the topographic method using synchrotron radiation# that the solid phase polymerisation of diacetylenes is a true topochemical polymerisation, which takes place in the undeformed lattice of the monomer single

See M.Dudley, J.N.Sherwood, D.J.Ando, and D.Bloor, Mol.Cryst.Liq.Cryst., 1983, **93**, 223.

crystal in the absence of defects, in contrast to the other known solid-phase reactions, which can occur only in the vicinity of defects, dislocations, and admixtures.

The specific requirements which must be met for the occurrence of a topochemical reaction have been formulated by Baughman[10,13,14], who proposed several criteria whose fulfilment is necessary for the occurrence of such polymerisation reactions.

1. The criterion of minimum displacements states that the actual reaction pathway must be one in which the smallest mean square displacements of atoms take place. If this criterion for the four carbon atoms of the monomeric DA unit involved in the transition from the monomer to the polymeric phase is defined by the expression

$$R = \left\{\sum_{i=1}^{4} [(x_i, y_i) - (x_i', y_i')]^2\right\}^{1/2},$$

where x_i, y_i, x_i', and y_i' are the coordinates of the atoms in the monomeric and polymeric phases, then, according to Baughman, only those DA for which R is less than ~ 1.08 Å on passing from the monomer to the polymer are reactive.

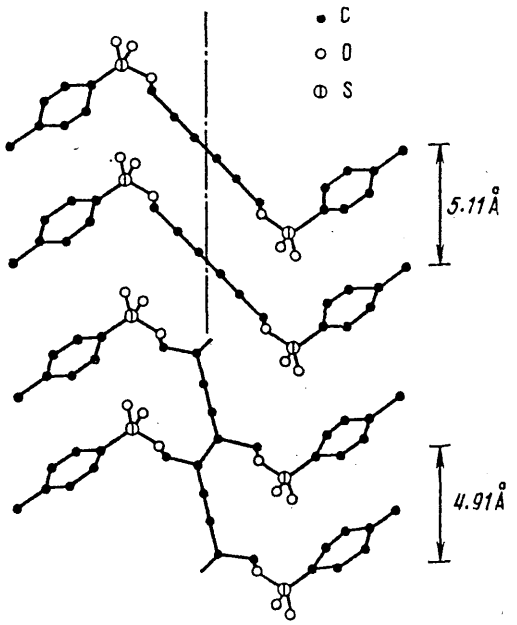


Figure 2. Projection of the crystal structure of TS (above) and poly-TS (below) onto the plane coinciding with the polymer skeleton[2].

As a rule the angle $\gamma_1 \cong 45°$ for the reactive DA and the relative lattice contraction $(d_1 - d_2)/d_2$ in the polymerisation reaction should not exceed approximately 0.1 (Fig.1), although there are exceptions to this empirical rule[2]. Fig.2 illustrates the changes in the geometrical disposition of the atoms of the monomeric TS unit (see Table 1 below) on passing from the monomer to the polymer. Evidently these changes are indeed small and reflect the rotation of the diacetylene group and the slight displacement and rotation of the benzene rings[2]. According to the minimum displacements criterion, the contribution of the lattice to the activation energy for the polymerisation reaction increases monotonically with increase of the mean square displacement of the atoms necessary for the occurrence of the reaction.

2. The group-theoretical criterion according to which the following conditions must be fulfilled for the reaction pathway to be unique: (a) the symmetry point group of the monomer must be a possible symmetry point group of the monomeric unit in the polymer and (b) the symmetry space group linking the reacting monomers must be a possible symmetry element between the corresponding monomeric units in the polymer chain. In other words, on passing from the monomer to the polymer, the degree of symmetry (point and space symmetry) must not decrease, i.e. during the reaction time all the crystallographic symmetry elements of the monomeric phase must be retained.

3. The criterion of the uniqueness of the phase transformation, which states that the polymer formed must be incorporated in the monomer matrix in the form of a solid solution for all degrees of conversion of the monomer. According to the last requirement, the monomeric and polymeric phases must be in equilibrium whatever the degree of conversion of the monomer[15].

The available literature data concerning unsuccessful attempts to polymerise a particular DA or the reported impossibility to attain 100% conversion of the monomer in the polymerisation reaction indicate the failure of at least one of the above criteria. Evidently the requirements enumerated impose very severe limitations on the size and interaction of the substituents. The role of the latter in topochemical polymerisation is great and reduces to the following[16]: the substituents control the packing of the monomer; they exert a steric influence on the reactivity, determining the unique reaction pathway; the interaction of the substituents controls the changes in the geometrical dimensions of the crystal lattice during polymerisation; they "soften" the mechanical stresses arising in the course of polymerisation owing to the incompatibility of the crystal lattice parameters of the monomer and the polymer. The specific requirements imposed on the substituents in the DA molecule are that as a rule they must have either a high dipole moment or the capacity to form intramolecular or intermolecular hydrogen bonds[17]. An obligatory condition is the presence in the substituent of one or several methylene groups, which separate the triple bonds and the functional groups of the substituents and whose purpose is to ensure the necessary flexibility in the rotation of the diacetylene groups during polymerisation with retention at the same time of the necessary interaction of the substituents.

Of the several hundred DA synthesised at the present time, only several tens proved capable of topochemical polymerisation. However, a polymer single crystal of large size and with a high degree of perfection cannot be obtained from all these monomers either. In certain cases the reaction does not lead to 100% conversion whatever the conditions. Furthermore, DA are known which are capable of existing in various crystalline modifications of which some are reactive, while others cannot be polymerised under any conditions[1,18-21]. Sometimes the monomer gives rise to up to 5 crystalline modifications on crystallisation[15,22]. All this shows that the geometrical packing of the molecules in the monomer single crystal, which specifies the distances between the reacting centres, and also the direction and the extent of the migrations of the atoms required for the reaction to occur are some of the decisive factors determining the reactivity.

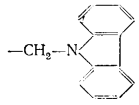
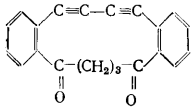
Table 1 presents the structural formulae and the abbreviations for the diacetylenes which polymerise quantitatively to give rise to polymers for which the greatest number of kinetic and physical investigations have been carried out.

III. THE MECHANISM AND KINETICS OF THE POLYMERISATION OF DIACETYLENES

The following features are characteristic of the polymerisation of the majority of DA:

(1) The polymerisation is initiated thermally, with the aid of ultraviolet light or X-rays, as a result of the application of hydrostatic pressure, and also under the influence of active gases, for example, halogens, nitrogen dioxide, ozone, etc.

Table 1. The structural formulae and abbreviations of the names of some of the most thoroughly investigated DA of the type R—C≡C—C≡C—R'.

R=R'	Abbreviation*
$-CH_2OH$	HD
$-CH_2OSO_2-C_6H_4-X$, X=CH_3	TS
X=OCH_3	MBS
X=F	PFBS
	DCHD
$-CH_2OCONHC_6H_5$	HDU
$-(CH_2)_4OCONHC_6H_5$	TCDU
$-(CH_2)_4OCONHC_2H_5$	ETCD
$-(CH_2)_nOCONHCH_2COOA$:	*n*ACMU
n=3, A=C_2H_5	3ECMU
n=3, A=C_4H_9	3BCMU
n=4, A=C_2H_5	4ESMU
n=4, A=C_4H_9	4BCMU
	BPG**

* To make it easier to become acquainted with the original literature, the abbreviations quoted for the DA are based on the most widely used English transcription.
** Cyclic monomer.

(2) On the basis of the kinetic curves, it is possible to distinguish autocatalytic (TS) and asymptotic (MBS) polymerisations§ (Fig.3). A fairly long induction period (up to 60 days at room temperature for TS) is observed in autocatalytic polymerisation during which an approximately 10% degree of conversion is attained, after which an autocatalytic stage is observed during which the latest polymerisation increases by a factor of several hundreds[24–27]; this stage is usually completed after the attainment of 100% conversion of the monomer.

(3) The range of variation of the activation energy in thermal polymerisation is fairly narrow, amounting to 80–105 kJ $mole^{-1}$.[25] For example, an activation energy of 94.3 kJ $mole^{-1}$ describes superbly the kinetics of the thermal polymerisation of TS in the temperature range 291–364 K, where the rates of polymerisation differ by a factor of 2400.[28]

§ The terms "autocatalytic" and "asymptotic" polymerisation are used for brevity in defining two different types of kinetics on the basis of the form of their kinetic curves. In fact the nature of the polymerisation is not autocatalytic[23].

(4) The polymerisation initiated by X-rays or ultraviolet light proceeds with an activation energy of approximately 10 kJ $mole^{-1}$.

(5) The activation energy for thermal polymerisation is constant over a wide range of conversions (up to 95%)[29].

(6) In the same range of degrees of conversion, the reaction is of first order with respect to the monomer.

(7) The pre-exponential factor in the expression for the first-order rate constant for thermal polymerisation in the autocatalytic stage is 10^{-8}–10^{-7} s^{-1}.[27,28]

(8) The capacity of the monomer crystal for polymerisation is determined by its previous history, in particular its crystallisation conditions[1,30] and purity[25].

(9) The polymerisation reaction is not initiated by radical initiators. Thus dicumenyl peroxide inhibits rather than initiates polymerisation[131].

(10) In many instances DA have two and more crystalline modifications differing sharply in their reactivity[15,22].

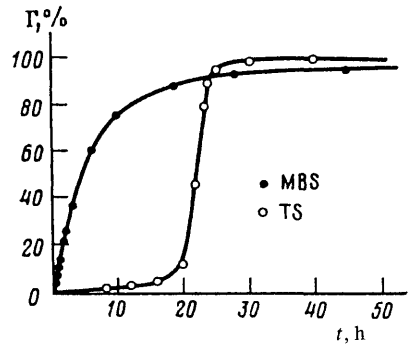


Figure 3. Kinetic curves for the polymerisation of TS and MBS at 333 K.[19] The degree of conversion of the monomer and the polymerisation time are plotted along the ordinate and abscissa axes respectively.

It is noteworthy that in the polymerisation of certain DA there may be deviations from the above rules. For example, the reaction sometimes ceases at a degree of conversion of 50–70%[16,32–34].

A kinetic mechanism of the solid-phase polymerisation of DA has been proposed by Baughman[35]. For autocatalytic polymerisation, the mechanism can be described qualitatively as follows. In the induction period stage of the polymerisation, oligomeric molecules with chain lengths corresponding to several tens of monomeric units are formed[28,36–38]. Since the transition from the monomer to the polymer crystal usually entails a decrease of the distance between the monomer units by 5–8%, the oligomeric molecules formed and the monomeric matrix are in a strained state: the bonds in the oligomeric molecules are extended relative to their equilibrium dimensions, while those in the monomer matrix are actually compressed. The elimination of these strains is accompanied by rapid polymerisation. At this instant the entire crystal decreases fairly rapidly in size in the direction of the growing chains (the *b* axis of the crystal lattice) and favourable energetic conditions are created for the occurrence of polymerisation.

The theory of topochemical polymerisation of DA was developed further in a study[39] where account was taken of a series of published comments and amendments. The observed

relation between the contraction along the *b* axis and the degree of conversion of the monomer (Fig.4) can serve as confirmation of this theory[40]. Analogous results have been obtained in dilatometric studies of the thermal TS polymerisation[41]. It has been established by dilatometric[40,41] and X-ray diffraction[38] methods that the lattice parameter along the *b* direction varies continuously with increasing degree of conversion. On the other hand, it has been found by the neutron scattering method[42] that this parameter changes abruptly. In contrast to γ-rays, a stream of neutrons does not initiate polymerisation and in this sense the neutron scattering method is more reliable; however, the experimental errors associated with this method are greater than in the case of the previous methods. At any rate, a correlation is always observed between the crystal lattice parameter along the *b* direction and the degree of conversion of the monomer. The interaction of the monomeric molecules during polymerisation is not accompanied by a change of the conditions along the *a* and *c* crystallographic directions. These results are fully consistent with the theory[35]. Generally speaking, the small change in the crystal lattice parameters on passing from the monomer to the polymer does not influence the feasibility of the polymerisation reaction and determines merely its kinetics and the quality of the final polymeric products.

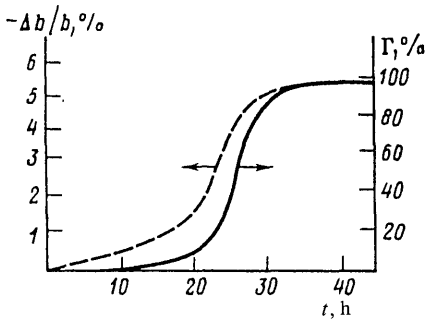


Figure 4. Kinetic polymerisation curve and the relative linear contraction of a TS single crystal along the *b* axis during thermal polymerisation at 323.2 K.[40]

The following postulates were made in the analysis of the kinetic polymerisation mechanism[35]: (1) the active centres are formed at a rate (calculated in terms of the concentration of the monomer which has not reacted) which is independent of the degree of conversion of the monomer; (2) the rate of deactivation of the active centres is independent of the degree of conversion of the monomer and is much greater than the rate of the competing chain initiation reaction; (3) the lifetime of the active centre propagating polymerisation is independent of the degree of conversion. In this mechanism the quantities which depend on the degree of conversion are the enthalpy components of the free energy for the initiation and chain propagation. This influence is due to the energetic strains in the reaction mixture matrix which is in the solid state.

Apart from the activation energy, the heat of polymerisation of various diacetylenes has also been determined. Over a wide temperature range, this quantity is −(120–150) kJ mole^{-1} for the majority of DA[24,43]. Furthermore, the heat of polymerisation has been calculated[25] with the aid of Dewar's "bond length–bond strength" relation and $\Delta H_p = -132$ kJ mole^{-1} for structure (B) of the polymer chain and $\Delta H_p = -123$ kJ mole^{-1} for structure (A) were obtained (Fig.1). The exothermic heat change is attributed to the addition of the monomer to the reactive end of the polymer chain.

It was later established in relation to 4BCMU¶ that the heat of polymerisation of the DA which polymerise predominantly only under the influence of illumination and γ-irradiation is much smaller than the usual values and amounts to approximately 100 kJ mole^{-1} (approximately 0.95 eV). Owing to the low heat of polymerisation, 4BCMU hardly undergoes thermal polymerisation. The low heat of polymerisation is attributed to the energetically unfavourable interaction of the side groups in the polymer compared with the monomer.

In discussing the mechanism of the thermal polymerisation, two structures are generally considered as the possible initiating species; the bicarbene structure $R\ddot{C}-C\equiv C-CR=RC-C\equiv C-C\ddot{R}$, first proposed by Wegner[22], and the biradical structure $R\dot{C}=C=C=CR-RC=C=C-\dot{C}R$. From the energetic standpoint, the formation of biradicals is more favourable than that of bicarbenes and there is a greater number of data showing that the biradical dimer is responsible for the initiation step[24,25,44,45]. Thus estimates of the energies of formation of bicarbenes and biradicals from the Dewar relations yielded 235 and 85 kJ mole^{-1} respectively[25]. However, EPR signals due to the bicarbene structure have been observed in the autocatalytic stage of thermal polymerisation[46–48]. It may be that a biradical is formed initially and then isomerises to a bicarbene[49].

The comparatively low ΔH_p constitutes indirect confirmation of the biradical mechanism of initiation[29]. Generally speaking, the initiation process and the structure of the final product are not related, since during polymerisation there are apparently transitions between the intermediate oligomeric molecules involving a decrease of multiplicity. The type of structure is then determined mainly by energetic factors, the electron energy, and the crystal strain energy. Virtually only the substituents determine the sequence of the bonds in the polymer chain.

Theoretical study of the unimolecular polymerisation initiation reaction using the Woodward–Hoffman rules[50] established that the formation of the monomeric bicarbene initiating species is photochemically allowed but thermally prohibited and, conversely, that the formation of a biradical is thermally allowed but photochemically prohibited. If there were no changes in multiplicity in the subsequent transformation, then thermal initiation would lead exclusively to form (B) of the polymers, while photochemical initiation would lead exclusively to form (A). In the study of initiation via the dimer, the conclusions concerning the formation of a biradical or a bicarbene being allowed in different types of initiation would apparently be the opposite to those established for the monomer.

Studies have been recently published whose authors note that the polymerisation model proposed[35] does not always make it possible to describe certain experimental results. For example, in the study of the thermal TS polymerisation under pressures[40,51], it was established that the reduction of the induction period of the reaction with increasing pressure is greater than predicted by the theory. Furthermore, in the investigation of the thermal polymerisation of the same monomer deuteriated in various positions[52], unusually large isotope effects were observed in the induction period stage of the polymerisation, which is difficult to explain in

¶ See H.Eckhardt, T.Prusik, and R.R.Chance, Macromolecules, 1983, **16**, 732.

terms of the theory[35]. A normal isotope effect is observed in the autocatalytic state.

An alternative model of the thermal polymerisation has been proposed[52], according to which excited states are constantly created in the monomer matrix. It has been suggested that the migration of the excitation energy in the lattice is a random process with considerable scattering[53]. In their diffusion pathway the excited states encounter randomly distributed but localised defects and are captured by them. If the lifetime of the excited state in such a trap is fairly long, then the state can serve as an initiator of chain polymerisation. Here there is a possibility of the following variants: (a) in the pure monomer matrix the concentration of defects is low and the rate of initiation is therefore also low; (b) for the average degree of conversion, the concentration of defects is large and many chain initiators are therefore formed, which leads to an increase of the overall rate of polymerisation. This approach explains the isotope effect and is consistent with the observed form of the kinetic polymerisation curve and with the earlier hypothesis that thermal polymerisation is initiated by the crystal defects[49,54]. The correctness of the choice of this type of polymerisation mechanism is confirmed by data concerning the influence of the previous history of the specimen, in particular its purity, on the duration of the induction period and the polymerisation rate constants[29]. Attempts have also been made to incorporate the influence of the anharmonicity of the bond vibrations and of the electron–phonon interaction in the explanation of the mechanism and kinetics of the polymerisation reaction[55].

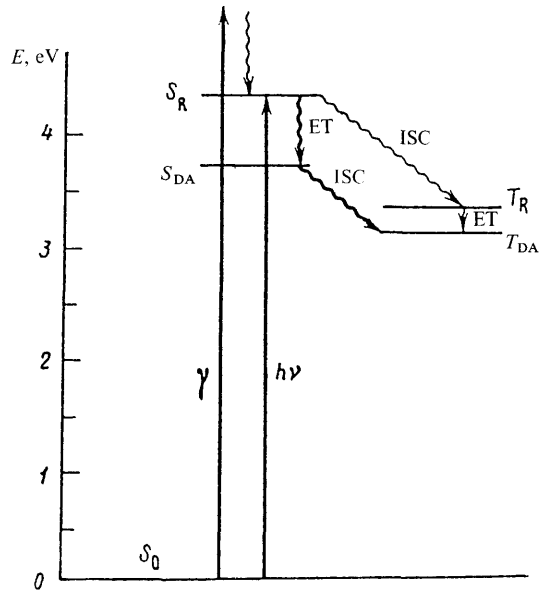


Figure 5. Diagram of the electronic levels of DA and the substituent R.[49] The possible pathways followed in the energy transfer are designated by thin wavy lines; the most probable pathway is shown by a bold wavy line.

Despite certain advances in the understanding of the mechanism and kinetics of thermal polymerisation, many problems remain unsolved. In particular it is not clear how energy is transferred to the reaction centre and is captured by it and the detailed mechanism of the initiation and the nature of the molecular excitation in thermal polymerisation are not understood. Indeed, the activation energy for thermal polymerisation $\Delta E_a \simeq 1.0$ eV,[49] while the energy of the lowest known triplet state in DA is approximately 3.1 eV[56]. The situation was actually made somewhat more complicated when it was established that certain DA are photopolymerised on sensitisation by phenazine[57,58] and by cyanine dyes[59,60]. Compared with DA, phenazine has a lower energy of the excited state[58] and therefore should inhibit rather than initiate the photopolymerisation of DA.

The influence of strain in the crystal on the polymerisation kinetics has not been ultimately elucidated either. In the study of the polymerisation of two monomers, MBS and TS, which have very similar molecular structures, it was established that MBS polymerises asymptotically[19,61], while a distinct autocatalytic stage is characteristic of the polymerisation of TS (Fig.3). Optical and Raman spectroscopic data have shown that during polymerisation the changes in the MBS and TS crystal lattices are the same[62], but the strain in the MBS crystal was greater than in the TS crystal[61,63]. Consequently the autocatalytic stage in the polymerisation of MBS should be more pronounced than for TS. Mixed crystals of the same monomers have been polymerised in different proportions[64]. With increase of the MBS content, the inductive period shortens. Since the crystal structures of these monomers are virtually identical, the differences between the polymerisation kinetics are hardly likely to be associated with the differences in the molecular packing and between the strains of these crystals. Analogous results have been obtained in the study of the polymerisation of mixed crystals of TS and diacetylenes with $R = R' = CH_2OSO_2C_6H_4X$, where X = Cl or Br[20,65]. This apparent contradiction can be obviated if it is supposed that the differences between the kinetics of the polymerisation of TS and MBS are associated with the longer lifetime of the active centre in MBS and hence with the larger pre-exponential factor[63]. Generally speaking, the two factors—the crystal strain and the lifetime of the active centre—are inter-related. Thus in the TS polymerisation it was observed by differential scanning calorimetry that the kinetics of the polymerisation reaction in the inductive period stage are virtually indistinguishable for single crystals of different qualities, whereas the rates of polymerisation in the autocatalytic stage can differ almost by an order of magnitude while the activation energy remains constant (93.4 ± 3.8 kJ mole^{-1}), which has been attributed to the difference between the pre-exponential factors due to the different strains in the single crystals[66].

The model of the polymerisation process involving the rotation of rigid diacetylene bonds in the plane of the polymer skeleton does not apparently fully correspond to reality and can describe the polymerisation process only in broad outline. It may be that the details of the topochemical polymerisation of diacetylenes can be understood when account is taken of the influence of low-energy phonons and also when one considers a reaction involving the rotation of non-rigid diacetylenic linkages with displacement of the carbon atoms from the plane of the skeleton†.

It is also incomprehensible why the kinetics obey the first-order law with respect to the monomer up to such high degrees of conversion.

A characteristic feature of the polymerisation induced by ultraviolet light and radiation is that it occurs regardless of whether an electronic state of the DA molecule is excited or whether the electronic excitation is initially localised at a

† See D.Bloor, Mol.Cryst.Liq.Cryst., 1983, **93**, 183.

substituent[22,67]. An electronic level scheme has been published[49] for substituted DA (Fig.5). The authors suggest the following scheme for the formation of active centres

$$S_0 + h\nu \rightarrow S_R \xrightarrow{ET} S_{DA} \xrightarrow{ISC} T_{DA} \rightarrow \text{polymer},$$

where S and T are the corresponding spin states of the DA and the substituent R, ET is the energy transfer, and ISC is intersystem crossing. All the energies of the electronic states of DA and the substituent, with the exception of the energy of the triplet state of DA, have been determined[49]. The only assumption made on the basis of the scheme is that T_{DA} lies below T_R. Later this hypothesis was confirmed and it was established that $T_{DA} = 3.1-3.2$ eV[56]. In this connection it is of interest to note that the polymerisation of the DCHD monomer is not initiated by ultraviolet light[68,69]. This can apparently be explained by the fact that the lowest excited energy state of the DCHD monomer is the triplet state of the carbazole group, i.e. the sequence in which the T_R and T_{DA} levels alternate changes (Fig.5) and the final stage of the energy degradation process is the triplet state of carbazole, which is incapable of initiating polymerisation. It can be assumed that the DA for which $T_R > 3.1$ eV will undergo photopolymerisation (provided, of course, that topological correspondence is observed).

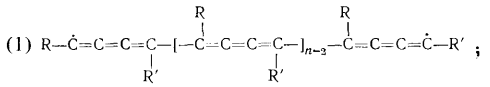
The kinetics of the polymerisation induced by ultraviolet light and radiation have been examined[49]. Both polymerisation stages are as a rule observed for these types of initiation: the induction period and the autocatalytic stage[49,70]. The study of the low-temperature photopolymerisation of DA led to a detailed determination of the initiation and chain propagation mechanisms, the chemical structure of the intermediate oligomeric chains, and also the multiplicity and the interconversions of various radical states of the growing ends of the oligomeric chains.

Biradicals[45,71] and symmetrical and asymmetric carbenes[45,46,71-76] have been detected by the EPR and optical absorption spectroscopic methods at 4.2 and 77 K in photoinitiated polymerisation. These states were identified as intermediate triplet states. For dimers and short oligomers, the interacting carbenes at the ends of the chains give rise to quintet[72,74,77,78] and singlet[74] states. Various types of intermediate species as well as the kinetics of their formation and destruction have been examined[67].

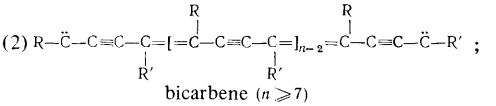
The polymerisation initiation process and the initial stage of the polymerisation have been thoroughly investigated at low temperatures, where the lifetimes of the excited initiating species and active polymerisation centres are sufficiently long to be determined experimentally. At low temperatures ($T < 200$ K) the initiation process is a two-quantum process[67,78], which follows from the experimentally observed quadratic dependence of the rate of formation of the active centres on the intensity of the irradiating light. The first absorbed quantum ($\lambda \lesssim 310$ nm) results in a transition of the monomer to an electronically excited state, which is converted into a monomeric biradical as a result of intersystem crossing[78]. The absorption of the second quantum results in the transition of the adjoining monomer molecule to a vibrationally excited state as a result of internal conversion. The combination of these molecules into a biradical dimer, capable of further chain propagation, actually constitutes the polymerisation initiation step. The subsequent photoreactions, consisting in the growth of the polymer chain by one monomer unit following the absorption of each quantum, is possible on irradiation with light at longer wavelengths, for example, 446 or 498 nm.[67]

At high temperatures ($T > 200$ K) there is a linear dependence of the rate of formation of dimers on the light intensity#, so that monomer molecules in vibrationally excited states are produced thermally.

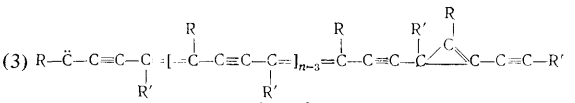
It has been possible to identify by the EPR method numerous intermediate triplet states of the oligomers in a low-temperature photoinitiated topochemical polymerisation[74]. It was found that there are only four types of products with different chain lengths§



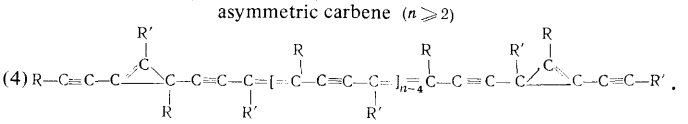
(1) biradical ($2 \leqslant n \leqslant 6$)



(2) bicarbene ($n \geqslant 7$)



(3) asymmetric carbene ($n \geqslant 2$)



(4) stable oligomer ($n \geqslant 3$)

Among all the details of the structures represented, only the existence of the pseudocyclopropene ring is hypothetical and is based on the assumption of the intramolecular deactivation of the active centres. It has been postulated that the pseudocyclopropene structures are stabilised by the molecular field of the crystal.

Analogous studies designed to discover the intermediate photopolymerisation products and to determine their nature have been carried out in connection with the photopolymerisation of TS at high temperatures[79]. A specially devised method was used to record the optical absorption spectra of short-lived (< 50 μs) intermediate species. The essential feature of the method was that it involved the recording of differential absorption spectra representing the difference between the absorption spectra after irradiation with a laser pulse ($\tau = 15$ ns, $\lambda = 308$ nm) and before irradiation. Several similar spectra have been recorded over a period of approximately 10^{-5} s. This method makes it possible, firstly, to isolate the spectra of the newly formed photoproducts and their measurement is not interfered with by traces of the polymer present in the specimen and, secondly, one can detect extremely short-lived species and investigate the kinetics of their formation, their interconversions, and destruction.

At least five intermediate species were detected, of which only one, having the maximum at the shortest wavelength in the absorption spectra, is a direct consequence of irradiation with light and was identified as a dimer. The remaining four products arise from the consecutive addition of monomer molecules, which takes place as thermal processes. The activation energy for the addition of the monomer is 0.25–0.30 eV and the pre-exponential factor is approximately 10^{11} s^{-1}. At low temperatures the quantum yield in

See H.Gross, W.Neumann, and H.Sixl, Chem.Phys. Letters, 1983, **95**, 584.

§ H.Gross and H.Sixl, Chem.Phys.Letters, 1982, **91**, 262.

the formation of dimers $\Phi \cong 10^{-2}$, diminishing to 10^{-3}–10^{-4} s with increase of temperature. The quantum yield Φ is highest for the defect-free monomer single crystal, but there are no channels for the transfer of energy to defects and the growing polymer chain.

The overall quantum yield (the number of polymerised monomeric units per absorbed light quantum) varies within wide limits: from 0.06 for TS (Bhattacharjee and Patel[80]) to 50 (Bhattacharjee and Patel[80]) and 90 (Shand and Chance[81]) for 4BCMU. Here one can trace a kind of compensation effect: the DA which have a high ($\gg 1$) polymerisation quantum yield do not undergo effective thermal polymerisation, while the DA which do undergo effective thermal polymerisation have a low ($\ll 1$) photopolymerisation quantum yield. Chemical actinometry[80] and photoacoustic spectroscopy[81,82] were used to determine the quantum yield. It was found that the rate of the photoinitiated polymerisation of DA greatly diminishes with increasing degree of conversion[83], which can be explained by energy transfer from the excited state of the monomer to the polymer chain. Such transfer is an important rate-limiting factor in photopolymerisation and must be taken into account in the determination of the quantum yield.

The kinetic polymerisation chain length depends on the stress applied to the monomer lattice[53]. The chain character of the photopolymerisation process has been demonstrated by photoacoustic spectroscopy[82]. Estimation of the lifetimes of the excited states yielded values differing by several orders of magnitude, from 10^{-3} s in the studies of Wegner and co-workers[52,53] to approximately 10^{-6} s in the study of Chance and Shand[82].

The photoinitiated polymerisation has been studied with irradiation of TS crystals by light through a dense grid under normal conditions[84] and with application of hydrostatic pressure[85]. Subsequently the reaction front profile in the shadow zone was investigated by scanning electron microscopy. The spatially isotropic growth of the polymer chains in the shadow zone and not only along the directions of the chain indicates the initiation in the primary step. Indeed, when one monomer molecule adds on, the energy liberated is 1.6 eV,[24] which exceeds the activation energy for the reaction ($\Delta E_a \cong 1.0$ eV). The excess energy liberated spreads isotropically from the reaction zone and gives rise to the vibrational excitation of the adjoining DA molecule, initiating thereby secondary polymerisation.

The photosensitised polymerisation of diynoic acid mixed with phenazine[57,58] and the autosensitised photopolymerisation of multilayers[86] can be explained analogously. The application of an electric field does not alter the rate of reaction or the profile of the reaction front; consequently the hypothesis[86] of the secondary initiation with the aid of the free carriers generated on deactivation of the electronically excited state is unfounded. A number of features of the photopolymerisation sensitised by cyanine dyes[59], in particular the independence of the maximum degree of conversion and the dye concentration and the high (approximately 90 Å) sensitisation radius[60] can be explained within the framework of the model postulating thermal initiation by the excess thermal energy liberated in the course of the u.v.-initiated polymerisation.

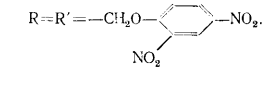
Similar results were obtained on sensitisation of the photopolymerisation by acridine and anthraquinone dyes¶, which are electron donors, in contrast to cyanine dyes. The authors of the above study nevertheless hold the view that charge transfer plays a decisive role in the photoinitiated polymerisation sensitised by electron-donating and electron-accepting dyes. The quantum yield of the photopolymerisation sensitised by cyanine dyes is in the range $0.7 \times 10^{-3} < \Phi < 17 \times 10^{-3}$: the corresponding values for the acridine and anthraquinone dyes are 2×10^{-3} and 7×10^{-3} respectively.

The radiation-initiated polymerisation of the various DA is characterised by a greater difference in the number of polymerised monomeric units per 100 eV of the irradiation energy [$G(-m)$]. Thus $G(-m) \cong 2 \times 10^5$ for 4BMCU[87] and $G(-m) = 66$ for TS[37,87]. When the substituents are altered, the sensitivity of the DA to ionising radiation on polymerisation can change by 6–7 orders of magnitude[87]. It has been suggested that the initiating species in the γ-initiated polymerisation is a biradical dimer[44,71]. The difference between the types of initiating species in photopolymerisation and γ-polymerisation is apparently associated with different selection rules for electronic transitions in various types of initiation.

In the study of polymerisation under the conditions of hydrostatic pressure, it was established[40,51] that, as in polymerisation under normal conditions, the reaction is first order with respect to the monomer up to 90% conversion and that pressure does not alter the activation energy for initiation and chain propagation. However, with increase of pressure, there is a decrease in the induction period, which disappears at $p > 3$ kbar; the polymerisation rate constant increases exponentially with increase of pressure. The increased rate constant for the reaction is attributed mainly to the component of the hydrostatic pressure acting at right angles to the direction of the growing chains and inducing the mutual approach of the hydrocarbon atoms of neighbouring monomeric units, which promotes the reaction. The decrease and even the disappearance of the induction period with increase of pressure is apparently associated with the fact that, under these conditions, the crystal lattice parameters in the monomeric and polymeric phases are equalised.

In the initial stage of polymerisation fairly long oligomeric chains are formed rapidly for all types of initiation[88]. The degree of polymerisation changes from $n \cong 20$ at the beginning of the induction period to $n \cong 40$ at the end of this period and reaches $n \cong 140$ in the autocatalytic stage[28]. At the instant of the completion of the polymerisation, n increases still further.

The molecular weight distribution in the initial stage of the polymerisation has been investigated† by an independent method—with the aid of X-ray diffraction for DA and TS with substituents:



The latter monomer polymerises fairly slowly under the influence of γ-rays and the molecular weight distribution curves and the average degrees of polymerisation could be determined for this monomer during the polymerisation reaction. Their values, which are close to those determined previously, are following values for different degrees of conversion Γ: $n = 22$ ($\Gamma = 0.65\%$), $n = 38$ ($\Gamma = 4.5\%$), and $n = 47$ ($\Gamma = 16\%$). Analogous results were obtained for the polymerisation of TS.

The molecular weight distributions for soluble PDA [poly-(3)4BCMU] have been determined by gel permeation chromatography[89,90] and $M_n = 49 \times 10^5$ g mol^{-1} (poly-3BCMU, $n \cong$

¶ See C.Bubeck, K.Weiss, and B.Tieke, Thin Solid Films, 1983, **99**, 103.

† See P.A.Albony, J.N.Patillon, and J.P.Pouget, Mol. Cryst.Liq.Cryst., 1983, **93**, 239.

10^3)[90] and $M_n = 1.2 \times 10^6$ g mol^{-1} (poly-4BCMU, $n \cong 2.4 \times 10^3$)[89] were obtained; the polydispersity index is $M_w/M_n \cong 5$.

Later more detailed studies were made[91] of the molecular weight distribution (MWD) for poly-3BCMU in γ-initiated polymerisation with various irradiation doses in the range from 0.09 to 45 Mrad and fairly high molecular weights and narrow MWD were obtained for small doses ($M_n = 1.33 \times 10^6$ g mol^{-1}, $M_w = 3.9 \times 10^6$ g mol^{-1}, $M_w/M_n = 2.93$, dose = 0.09 Mrad). The values of M_n and M_w diminish significantly with increase dose of radiation and the polydispersity index increases very strongly; for example, $M_n = 1.79 \times 10^5$ g mol^{-1}, $M_w = 2.31 \times 10^6$ g mol^{-1}, and $M_w/M_n = 12.8$ have been obtained for a dose of 15 Mrad. As the irradiation dose is increased from 0.09 to 45 Mrad, the degree of conversion of the monomer rises from 21% to 49%. The decrease of the molecular weight of the polymer is attributed to degradation during irradiation. High molecular weights have been obtained for PDA with R = R′ = $(CH_2)_9OC(O)X$ in a study by Plachetta and Schulz[92]: $M_n = 2.4 \times 10^5$, 3.4×10^5, and 3.2×10^5 g mol^{-1} and $M_w/M_n = 3.33$, 3.94, 3.75 for X = $CH(CH_3)_2$, $CH_2C_6H_5$, and CH_2-α-naphthyl respectively.

Analogous studies have been carried out for poly-TS at conversions from 0 to 12%, at which the polymer is still soluble[37]. In this range of degrees of conversion the MWD is fairly broad and does not change with the degree of conversion and $n \cong 20$. It may be that this low value of n is due to the degradation of the polymer in the strong solvent (dimethylformamide, chloroform) used in the determination of the MWD[93], since $\bar{M}_n$ determined by other methods is much greater[24,38].

IV. THE ELECTRONIC STRUCTURE OF POLYDIACETYLENES

Polydiacetylenes constitute a convenient and unique object for the theoretical description and investigation of the electronic structures of polyconjugated systems. There are exhaustive data on the structures, bond lengths, and valence angles of certain PDA. There are also extensive experimental data for the optical properties of these polymers[4,5]. The energies and polarisations of the electronic transitions have been determined on the basis of these results and the vibrational energies of the excitation of various bonds have been found from infrared and Raman spectroscopic data[6]. The polymers considered are of interest also because they constitute in essence a model one-dimensional system of virtually infinite length made up of rigorously repeating monomeric units without defects in the structure and conformation of the chains. This simplicity of the structure is, however, only apparent. Calculation of the electronic structure and ultimately the understanding of the physical properties are complicated by the interaction of the side groups of a single chain and also by the intermolecular interaction between chains.

The studies which have been made on the electronic structure of PDA were devoted mainly to the elucidation of the nature of the long-wavelength optical absorption with an energy of approximately 2 eV, the influence of the substituents and external conditions on the electronic structure of PDA, and also certain electrophysical properties.

In the study of the electronic structure of PDA many unsolved problems are common to all types of conjugated systems, for example, the question of the nature of the forbidden energy gap in the spectrum for one-electron excitations. So far there is no unanimous view concerning the origin of this gap even for polyene systems. The extreme views are that the gap can be attributed either to the alternation of the bond lengths (the Peierls instability of the one-dimensional metal relative to the doubling of the crystal lattice period) or that its nature is of the correlation type (the Mott–Hubbard electronic phase transition due to the electron interaction). For conjugated systems, this problem has been investigated in detail[94] and the hypothesis that the nature of the energy gap is of the correlation type appears to be supported by the soundest arguments.

The question of the nature of the energy gap in PDA is masked by the fact that the alternation of bond lengths is a permanent property of these systems, which can be readily adopted as the cause of the appearance of the energy gap. In describing the electronic structure of PDA, one must bear in mind all the theoretical data which have accumulated on conjugated systems and studies must be made taking into account the electron interaction. The question of the nature of the gap in PDA was specially studied[95] with the aid of a modified Hubbard Hamiltonian; it has been shown that the contribution of the Coulombic correlations to the energy gap is approximately 1.9 eV and that the exciton band is split off from the conductivity band only when account is taken of the electron interaction at the neighbouring atoms.

Table 2. Results of the calculations of the width of the forbidden gap ΔE for PDA.

Method of calculation	Free electron[a]	Hückel	Extended Hückel[b]	X_α^c	PPP + CI[d]	LCAO-MO SCF[e]	LCAO-MO + CI[f]	CNDO/S + CI	STO-3G basis	7s/3p basis	Effective Hamiltonian	ΔE_{exp}, eV
ΔE, eV	2.0	1.36	1.0; 1.22	2.21	1.31–1.42[g]	0.25–0.51	2.0–4.0[g]	4.09–4.38	4–11	—	2.1	1.9–2.6[h]
R=R′	—	—	C≡C–H; H	—	H	NH_2; CH_2OH	—	H	H; F	H	H	i
Refs.	[96]	[97]	[98, 99]	[100, 101]	[102]	[103]	[104, 105]	[106]	[107–109]	[110]	[111, 112]	

Remarks: [a] A modified method of free electrons with sinusoidal modulation of the potential was used; [b] the numerical values quoted in accordance with Parry's data[98]; [c] the calculation was performed for the model compound 1,5,9-tridehydro(12)annulene; [d] Ono's parametrisation; [e] the gap width for seven substituents was calculated by Parry[103]; here the minimum and maximum values are quoted; [f] Yarkony[104] used the experimental geometry corresponding to poly-TS and poly-TCDU; [g] the scatter of the values is associated with the different geometries chosen for the molecule for which the calculations were made; [h] the gap widths determined from the positions of the optical absorption maxima are quoted; the width of the forbidden gap is greater by several tens of electron-volts; [i] the literature data are quoted in Section V of this review.

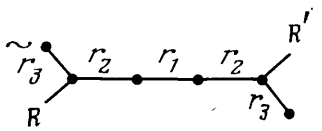
The range of suitable methods for the study of the electronic structure of PDA is fairly broad: from the simple free electron in a potential box and Hückel methods to non-empirical calculations. Attention has been concentrated in the calculations on the correct description of the energy of the longest-wavelength optical transition. A satisfactory description of this quantity is usually regarded as one of the principal criteria of the applicability of a particular computational method. The results of the calculations of the width of the forbidden gap are presented in Table 2. Evidently

satisfactory optical excitation energies are obtained, as was to be expected, only in calculations which include the configurational interaction, which takes into account partly the electron interaction. Much attention has also been devoted to questions of the relative stabilities of structures (A) and (B) and a correct description of the behaviour of the energy gap in the excitation spectrum in the transition (A) → (B). The ground state of the PDA chain is structure (A). A non-empirical calculation[110] with the optimisation of bond lengths and angles in terms of the 7s/3p basis set showed that structure (A) is more stable by approximately 50 kJ mol^{-1} per C_4H_2 unit than structure (B). In order to understand the nature of this transition, it is necessary to go beyond the limits of the Hartree–Fock approximation.

As an illustration of the relative nature of the concepts concerning structures (A) and (B) of the PDA chain which have been introduced, Table 3 presents the experimental and calculated bond lengths in real and model PDA. It is evident that, although poly-PTS, poly-DCHD, and poly-HDU have been arbitrarily assigned to the (A) type while poly-TCDU and poly-BPG have been assigned to the (B) type, nevertheless the bond lengths in polymers of both types are fairly remote from the theoretical values calculated for the model compounds.

Theoretical studies have led to certain general conclusions. The long-wavelength optical absorption has an exciton character. The difficulties associated with the correct description of the behaviour of the energy gap in the (A) → (B) transition indicate a number of factors which have not been taken into account, such as the influence of the intramolecular and intermolecular forces in the interaction between chains and also the influence of substituents. If the overall energy of the crystal is divided arbitrarily into two components—the electronic energy and the crystal field energy, then the above effects can in fact be attributed to the crystal field energy.

Table 3. The carbon–carbon bond lengths in the main chains of various PDA determined by X-ray diffraction (in accordance with Karpfen's data[110]) and calculated by the *ab initio* method in terms of the STO-3G basis set for the "ideal" structures (A) and (B)[108]



Polymer	r_1, Å	r_2, Å	r_3, Å
Poly-PTS	1.19	1.43	1.36
Poly-DCHD	1.21	1.44	1.33
Poly-HDU	1.21	1.41	1.36
Poly-TCDU	1.24	1.37	1.44
Poly-BPG	1.29	1.38	1.42
Structure (A)	1.20	1.45	1.34
Structure (B)	1.26	1.35	1.48

At the present time there are no theoretical methods whereby one could calculate simultaneously and with self-consistency both energy components. It is therefore necessary to justify model concepts which makes it possible to take into account in the first place the intermolecular interactions and their influence on the electronic structure of PDA. Numerous experimental results have shown that the forces governing these interactions are fairly large.

V. THE OPTICAL PROPERTIES OF POLYDIACETYLENES

The intense optical absorption of photons with an energy of approximately 2 eV ($\lambda_{max} \cong 620$ nm) is due to the presence of the conjugation system in PDA and in this sense the latter resemble polyenes[96]. However, in contrast to the optical spectra of the known polymers with conjugated bonds, having a broad structureless maximum and a long-wavelength absorption "tail",[113] the PDA spectra have characteristic features whose broad outline can be seen from Fig. 6.[114] The anisotropy of the crystal structure of PDA is responsible for the anisotropy of virtually all the physical properties including optical properties. The optical absorption therefore depends on the polarisation of light relative to the crystallographic axes. For light polarised parallel to the plane of the conjugation chain, a sharp absorption edge is observed in the region of approximately 2 eV, where a fairly narrow maximum is observed in reflection spectra. The smallest energy of the optical transition in solid PDA (approximately 1.89 eV) has been obtained for poly-DCHD.[115] The degree of dichroism of PDA single crystals is fairly large; thus in the case of poly-TS, for light polarised approximately parallel to each of the three principal crystallographic axes, the absorption coefficients at $h\nu \cong 2$ eV are respectively 9×10^5, 2×10^3, and 5 cm^{-1}.[5] Analogous results have been obtained for other PDA[89,115,118]. For partly polymerised specimens, the edge of the absorption band and the reflection maximum are more diffuse[114], but their positions are related to the kinetic polymerisation curve: at the instant when the autocatalytic stage begins, there is also a sharp bathochromic shift of the absorption edge and reflection maximum frequencies[119].

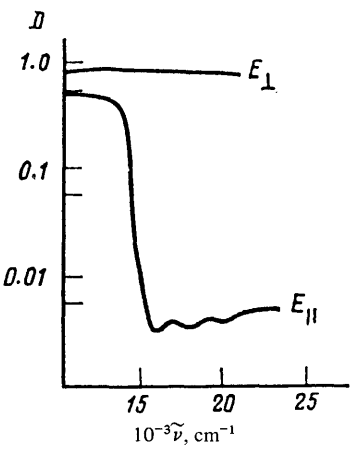


Figure 6. Optical transmission spectrum of a single crystal of poly-TS for light polarised parallel ($E_\parallel$) and at right angles ($E_\perp$) to the *b* axis.[114]

The initial DA are usually colourless or only slightly coloured. Changes in the colour of the partially polymerised DA are already observed for a monomer conversion of approximately 0.01%, since the molar absorption coefficient of

PDA is very high ($\varepsilon \geq 1.7 \times 10^4$ dm^3 mol^{-1} cm^{-1}).[120,121] As polymerisation proceeds, the colour deepens and at the end of the polymerisation reaction the PDA usually has a metallic lustre with various colour tints. In terms of colour and other optical characteristics, PDA can be divided into two categories. The first includes PDA coloured reddish-gold and the second PDA coloured green and blue. PDA with sulphonate substituents (poly-TS, poly-MBS) belong to the first category and those with urethane substituents (poly-TCDU, poly-ETCD, etc.) belong to the second[122]. The number of methylene groups in the diacetylene $X-(CH_2)_n-C\equiv C-C\equiv C-(CH_2)_n-X$, separating the functional groups X (urethane, sulphonate etc.) and the triple bond, is apparently more important for the colour of PDA than the type of substituent[8]. Thus the majority of partly polymerised DA with $n = 1$ and 2 are red and those with $n = 3$ and 4 are blue.

In order to extend the range of the colour changes, DA with the chromophoric azobenzene groups $-C_6H_4N=NC_6H_5$ in the side chains have been synthesised[43]. At a low degree of conversion, the colour of the DA is determined by the chromophores. The partly polymerised DA has a colour which is determined both by the chromophores and by the absorption due to the conjugation chain. At a degree of conversion $\gtrsim 10\%$, the colour is determined mainly by the absorption due to the conjugation chain in the macromolecule formed.

Various optical methods, mainly transmission or reflection spectroscopy, have been used to investigate PDA. For a fully polymerised specimen, the depth of penetration of light in the most interesting spectral region is approximately only 100 Å,[16] which imposes definite limitations on the applicability of the technique of transmission spectroscopy. With the aid of this method, the greatest reliability of the results is achieved in the study of specimens with low (approximately 1%) degrees of conversion. Parameters such as the absorption band shape, the absorption coefficient, and others are then measured directly.

On the other hand, the possibilities of reflection spectroscopy are manifested most effectively in the study of specimens with a high degree of conversion. The determination of the spectroscopic parameters involves in this instance the application of the Kramers–Kronig dispersion relation between the real and imaginary components of the complex dielectric constant. The procedure whereby the absorption spectrum is deduced from the reflection spectrum with the aid of the dispersion relation is not unambiguous, since there is an uncertainty associated with the necessity for extrapolations. However, the results obtained with the aid of transmission and reflection spectroscopy agree[116].

The long-wavelength optical absorption was initially attributed to the direct interband electron transition from the valence to the conductivity band, which was seemingly confirmed by the analysis of the optical absorption line forms of certain PDA.[114,123–126] This analysis indicated the existence of a one-dimensional Van Hove singularity, which arises in a vertical interband transition when there is a plateau on the dispersion curve relating the energy to the wave vector.

On the other hand, there exists much evidence supporting the view that the long-wavelength edge of the optical absorption band is associated with exciton absorption. One of the most important indirect arguments in support of this view is the absence of photoconductivity at the optical absorption edge of PDA[127,128] and the hypsochromic shift of the maximum in the photoconductivity spectra relative to the maximum in the absorption spectrum. The magnitude of this shift is 3000 cm^{-1} for poly-TS[127] and is anomalously large (approximately 15000 cm^{-1}) for poly-CDU.[117] Consequently the long-wavelength optical absorption gives rise to an excited state. This excited state is most probably an exciton. The evidence in support of the exciton nature of the absorption is also provided by the lateral phonon bands in the optical absorption spectra and by the resonance Raman scattering[114]. Apart from indirect data, there exists also direct experimental evidence that the long-wavelength optical absorption in PDA has an exciton character. Surface exciton states have been observed for poly-TS[129,130] and the method of electric field-modulated reflection spectroscopy yielded analogous results: the width of the forbidden gap is $\Delta E = 2.44$ eV for poly-TS[131,132] and $\Delta E = 2.335$ eV for poly-DCHD[133]. The reflection spectra of both polymers showed a signal due to the exciton absorption for an energy smaller by 0.48 eV than the width of the forbidden gap[134]. Identical results have been obtained in the study of poly-TS in polarised thermo-reflection#. In this method the temperature of the specimen is modulated (frequency ~ 1 Hz, amplitude ~ 1 K) and derivatives of the absorption spectrum in polarised light are recorded. This method is extremely sensitive, particularly in relation to the temperature-dependent regions of the TS spectrum. The following data have been obtained with its aid: the exciton absorption begins with an energy of 2.00 eV and the width of the forbidden gap is 2.44 eV. The results of the analysis of the optical absorption line form near its absorption edge have also been revised recently. It has been found that the asymmetric Lorentz form, corresponding to the exciton model, provides the best description of the experimental line[5,116,135]. A similar ambiguity in the treatment of the line form also arose in connection with the narrow energy range in which linearisation was carried out and with the errors associated with this factor.

An interesting feature of the TS monomer and of its partly and fully polymerised specimens is that at low temperatures all the lines observed in the optical absorption and reflection spectra[123,126,136–138], the piezomodulated absorption spectra[136], the Raman spectra[138], and the EPR spectra[76] are divided into doublets. The splitting is observed down to the very lowest degrees of conversion (1%)[138] and even for the pure monomer[38]. The splitting in the optical spectra at 300 K is almost zero, but increases monotonically with decrease of temperature, amounting to 30 meV at the helium temperatures. Line splittings are not observed in the optical spectra of other PDA[115,117,124,125]. In order to explain this phenomenon, it is necessary to answer two fundamental questions: firstly what is the nature of the splitting of the bands and secondly why is it observed only for TS and its polymer.

The first attempts to account for the band splitting were made on the basis of X-ray diffraction data. It was established that the size of the unit cells of TS and its polymer is doubled in the low-temperature phase along the *a* crystallographic direction[135,140,141]; the number of monomeric units in the unit cell of the crystal is also doubled, which can be explained by the changes in the distances between the monomeric units in pairs owing to the reorientation of the substituents[141,142]. As a result, each of two types of molecules has a different environment and in such a situation it is logical to expect the splitting of all the observed lines to give doublets.

It has been suggested that the observed transition is a second-order phase transition[142,144]. In the study of this phase transition by spectroscopic methods[142,143], the critical

See S.Stizza, I.Davoli, V.Prantera, A.Bianconi, J.Glinski, and J.Kalinowski, J.Phys.C., Solid State Phys., 1983, **16**, 2165.

parameters were determined and an attempt was made to determine the order parameters. Comparison with the available exact results based on the theory of critical phenomena established that the two-dimensional phase transition apparently takes place at low temperatures, acquiring a three-dimensional character in the vicinity of the critical temperature. The broad temperature range of the transition indicates the important role of fluctuations. Regions with an altered orientation of the groups arise at random throughout the bulk of the specimen and are of the fluctuation type, so that reorientation is hardly likely to occur simultaneously. The character of the temperature dependence of the line splitting of the spectra (the logarithm of the splitting energy varies linearly with the lattice parameter along the *c* crystallographic direction) shows that the splitting is two- or three-dimensional[145].

In order to identify the nature of the band splitting in the spectrum of poly-TS, the PFBS monomer, isomorphous with TS, in which the intermolecular interaction is stronger owing to the presence of the fluorine atom which also has a van der Waals radius close to that of the methyl group, was synthesised[146]. However, it was found that, although the optical and Raman spectra of poly-TS and poly-PFBS are virtually identical at 300 K, there is no band splitting in the spectrum of poly-PFBS even at low temperatures[139]. Clearly the band splitting is not associated with the intermolecular interaction of the polymer chains[147,148] and is due to the existence of two types of polymer chains having different environments.

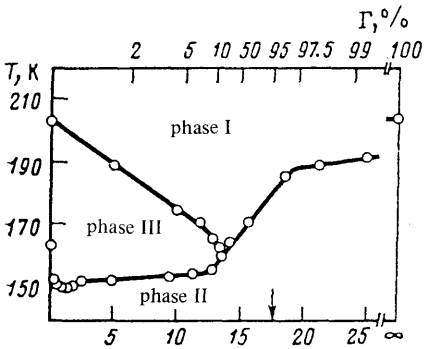


Figure 7, Phase diagram of partly polymerised TS.[154] The arrow denotes the instant of the maximum rate of polymerisation (at 60 °C) during the autocatalytic stage; phase I—single crystal with two monomeric units ($z = 2$) in the unit cell; phase II—$z = 4$; phase III—incommensurable phase.

The situation became more complex and more difficult to explain when yet another, third stable phase, corresponding to an incommensurable modulated structure, was observed in the spectrum of TS for a degree of conversion < 50%[150-152] (Fig.7). The temperature range corresponding to the existence of this phase is a maximum for a low degree of conversion (~ 1%) and is between 163 and 206 K, becoming gradually narrower with increase of the degree of conversion and disappearing in the autocatalytic stage. According to X-ray diffraction data, the incommensurable phase is modulated with a wave vector $\mathbf{q} = \frac{1}{2}\mathbf{a}^* + (T)\mathbf{b}^*$,[153,154] where the lattice period along the *b* direction depends on temperature. The intensities of the corresponding satellite lines in X-ray diffraction vary in accordance with the law $(T_c - T)^{2\beta}$, where $\beta = 0.43$ and $T_c = 199.2$ K. The critical exponent for the specific heat is approximately 0.7, which is too large for any simple model[150].

Two features of the incommensurable phase were observed by low-frequency polarised Raman scattering: (1) at temperatures approximately 15 K below the critical temperature, the existence of a soft mode (amplitone) was observed, the mode becoming softer as T_c is approached from the low-temperature side; (2) the line observed at 13 cm^{-1} is characteristic only of the incommensurable phase[153]. The first feature shows that for $T < T_c$, there is a mutual displacement of the monomeric units or parts from the latter relative to one another. When static shifts of this kind become commensurable with the average phonon vibration amplitude, the multiphonon scattering process is transformed into first-order Raman scattering, which is the reason for the appearance of the line at 13 cm^{-1}.[153]

In the study of the pyroelectric effect for TS along the *b* direction over a wide range of degrees of conversion, it was found that, when the temperature is altered, the pyroelectric coefficient has maximum values near the phase transition temperatures[155]. The phase transition temperatures agree well with those obtained previously[154]. The existence of the pyroelectric effect shows that the crystal loses its centre of symmetry and that the extent to which central symmetry is lost is a maximum near the critical temperatures, possibly owing to the occurrence of macroscopic fluctuations.

Anomalies have also been observed in the rate of propagation of sound§, showing that the phase transitions in the monomeric TS single crystal occur at 159 and 192 K and those in the polymer occur at 196 K.

Sharp phase transitions were detected with the aid of the methods enumerated above as the temperature was varied; however, the optical splitting varies smoothly with temperature. The causes of such behaviour are still obscure. Nor is the detailed nature of the formation of the incommensurable structure itself in TS and its partly polymerised crystal clear. It may be that the identity of the modulation wavelength of the incommensurable structure (b^*/δ) with the chain length of the polymer during the inductive period is not fortuitous[28].

(a) Thermochromism and Solvatochromism

The phenomenon of thermochromism, i.e. the change in colour with temperature, is normally confined to the bisurethane polymeric derivatives of diacetylene; poly-TCDU[117,156,157], poly-ETCD[158,159], and others. For example, the crystal of poly-ETCD is green in reflected light at a temperature below that of the colour transition, while above the transition temperature it acquires reversibly a red colour[158]. Changes in the reflection spectrum appear at 115 °C and cease at 130 °C. Subsequently on heating to 180 °C, no changes take place in the spectra. The shift of the maximum in the reflection spectra of poly-ETCD is hypsochromic and amounts to approximately 2750 cm^{-1}. With decrease of temperature the reverse colour change occurs at a temperature (approximately 70 °C) differing greatly from that of the forward transition. Such marked hysteresis is typical for thermochromism in PDA and is evidence for the occurrence of a first-order phase transition. The observed thermochromic transition is multiply reversible. Thermochromism is observed not only for single crystals[33,160] but also for amorphous film and solutions[89,161-163].

§ See W.Rehwald, A.Vonlanthen, and W.Meyer, Phys. Stat.Solidi, 1983, **B.A75**, 219.

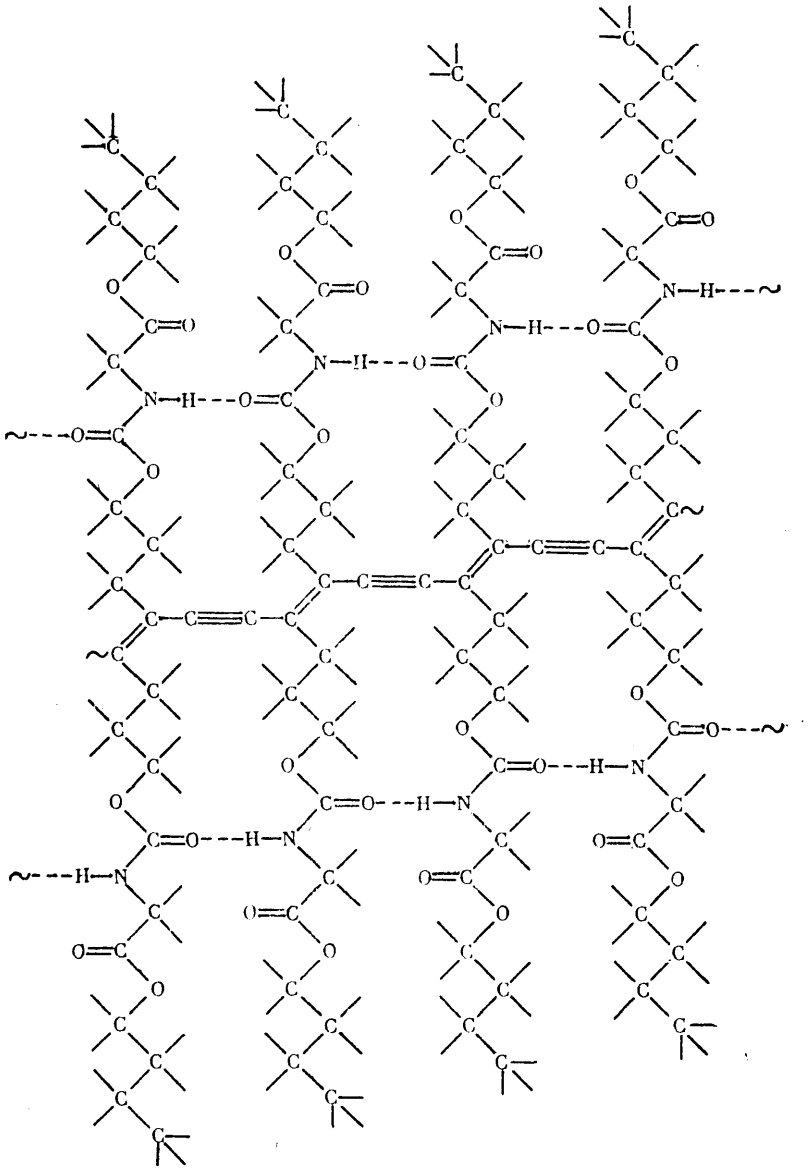


Figure 8. A fragment of the chain of poly-3BCMU in the planar conformation; the intramolecular hydrogen bonds are shown dashed[121].

For partially polymerised nACMU (n = 3,4; A = E,B) and a degree of conversion of approximately 5%, the changes in colour from dark-blue to red with increase of temperature to the melting point take place smoothly. For fully polymerised specimens, the colour changes take place abruptly, over a range of approximately 5 K, and only two colour transitions are observed (Table 4). Two endothermic peaks at the temperatures corresponding to the colour change have also been observed by differential scanning calorimetry[164]. The first endothermic peak is associated with the fusion of the polymer, which remains oriented due to hydrogen bonding. The second endothermic peak is associated with the rupture of the hydrogen bonds and the complete fusion of PDA[165]. Fig. 8 presents as an example a fragment of the chain of poly-3BCMU with intramolecular hydrogen bonds. The shift of the maxima in the reflection spectra of substituted bisurethane PDA in thermochromic transitions is approximately 3000 cm^{-1} and with increase of temperature the position of the maximum changes from 15500 to 18500 cm^{-1}.[89,117,158] Sometimes the shift of the maximum can approach 5000 cm^{-1}.[121]

The temperature range in which thermochromic transitions are observed for PDA is fairly broad and is not limited to positive temperatures. Changes in colour are observed for a series of PDA down to approximately −200 °C.[8] For example, the majority of the red PDA gradually change colour to blue on cooling to the temperature of liquid nitrogen. However, these transitions are not phase transitions, in contrast to those in the high-temperature range.

It is noteworthy that there is one exception here. The DCHD single crystal undergoes a first-order phase transition

at atmospheric pressure and a temperature of 142 K with a sharp colour change[167]. At this temperature the crystal contracts along the *b* axis by approximately 8% and its density increases by approximately 5%¶. Owing to the large change in density at the phase transition point, the transition is very sensitive to pressure: its temperature increases by approximately 300 K at a pressure of 300 MPa.

Table 4. The thermochromism of poly-*n*ACMU with the substituents R = R′ = $(CH_2)_nOCONHCOO(CH_2)_mH$.[33]

Polymer	*m*	*n*	Temperature of colour transition, °C	
			gold-green → red	red → yellow
Poly-4BCMU	4	4	112	136
Poly-3BCMU	4	3	160	183
Poly-4ECMU	2	4	118	137
Poly-3ECMU	2	3	192	—

[11] См. *Rehwald W., Vonlanthen A., Meyer W.* Phys. Stat. Solidi 1983, B. A75, S. 219.

Soluble PDA have been obtained from DA with urethane substituents. Depending on the changes in the external conditions (temperature, solvent, pH of the medium), numerous phase transitions, called a "transition tree", have been obtained for solutions of these polymers[166]. The total number of transitions involving a colour change is approximately 15. In the series of soluble PDA, the colour transitions have been most thoroughly investigated for poly-*n*ACMU[33, 120,167].

The solvatochromism of solutions of these polymers has been investigated under the conditions of changes in the solvent/non-solvent volume ratio, for example, the chloroform/hexane ratio[33,89,120,121,162,167]. The colour of a solution of poly-3BCMU in pure chloroform is yellow. When hexane is added in an amount sufficient to give a composition with 75 vol.% of chloroform, the colour remains unaltered. On further decrease of the relative content of chloroform to below 75 vol.%, there is a sharp colour change to blue and a blue precipitate is deposited (the colour changes are sharp, so that the titration method can be used). The maximum in the absorption spectrum of poly-3BCMU shifts from 21300 cm^{-1} (yellow solution) to 15900 cm^{-1} (blue solution)[167]. The absorption maximum of the blue solution (15900 cm^{-1}) constitutes the absorption limit for a polyene and PDA of infinite length[96]. Analogous colour changes have been observed for a solution of poly-TCDU[168]. Detailed studies of the solvatochromic transitions of poly-3BCMU in a chloroform/hexane mixture showed[91] that the solvent/non-solvent ratios at which colour changes occur differ in the forward and reverse titrations.

Another possible way of influencing the colour of the solutions is by altering the pH of the medium for water-soluble PDA with the substituents $(CH_2)_nOCONHCH_2COO^-K^+$ (n = 3,4) and $(CH_2)_nCOO^-K^+$ (n = 1,2).[169,170] When the pH changes from 9 to 3, the colour of the solution changes from yellow to red or purple.

¶ See D.Bloor, I.F.Chalmers, R.J.Kennedy, and M.Motevalli, Mol.Cryst.Liq.Cryst., 1983, **93**, 215.

An isosbestic point is frequently observed for the thermochromic and solvatochromic transitions, indicating the absence of intermediate products in transitions between two forms of different colour[161,162,169].

It has been suggested that the solvatochromic transitions in PDA solutions have the following cause. In a "poor" solvent or a weak electrolyte, the macromolecules have a planar arrangement of their skeleton, which is additionally stabilised by intramolecular hydrogen bonds (see Fig.8). When a "good" solvent is added or with increase of the concentration of ions in solution, these bonds are ruptured and the planar conformation breaks down, which leads to an alteration of the optical properties[120,121,161,167]. The hypothesis of the existence of planar PDA chain conformations has been confirmed experimentally by viscometric[91] and light scattering[92] methods. The conformational changes lead to statistically distributed breaks in the conjugation chain when the polymer skeleton rotates relative to single bonds and a distribution with respect to effective conjugation lengths l_{eff} arises[121]. Comparison with the spectra of model conjugated molecules has led to the estimate $l_{eff} \gtrsim 30$ repeat units for blue PDA (600 nm < λ_{max} < 700 nm), 20 < l_{eff} < 30 for red PDA (500 nm $\lesssim \lambda_{max} \lesssim$ 600 nm), and l_{eff} < 6 for yellow PDA (400 nm $\lesssim \lambda_{max} \lesssim$ 500 nm)[8].

The method of photoselection with the aid of Raman scattering was used to justify this hypothesis experimentally[171,172]. It is assumed that one conformationally disordered polymer chain consists of a set of chromophores differing in l_{eff} and having as a result different vibrational spectra. The observed absorption band consists of an inhomogeneously broadened line with contributions due to different chromophores. Analysis of the line shape in different solvents where PDA has different colours made it possible to determine the distribution of l_{eff} for the same polymer having, however, different conformations.

Evidently the thermochromic transitions in the crystallised state of PDA cannot be explained by changes in the conformations of the macromolecules. The initial explanation of the thermochromism was based on the hypothesis that this phenomenon is associated with transitions between the mesomeric structures (A) and (B) in the polymer chain[117,118,158]. Indeed the optical absorption spectrum of poly-ETCD at a temperature below the transition point resembles the spectrum of poly-TS for which the structure (A) of the polymer chain has been established. Above the transition point, the spectrum of poly-ETCD resembles that of the poly-DCHD, which has a structure of type (B).

Another view on the cause of the changes in the optical properties of PDA involves the hypothesis that they are determined by the strain in the macromolecular chain and hence by its deformation[173]. Similar deviations from equilibrium bond lengths in a conjugated polymer chain arise owing to interactions of the substituents. The absorption energy of "free" PDA in solution in the equilibrium conformation is approximately 2.4 eV. The smaller value observed in films and crystals is due to the stress applied to the polymer chain as a result of intramolecular and (or) intermolecular interactions of the side groups[4]. The most important causes responsible for the position and form of the optical absorption band are, firstly, the statistical (time-average) deformation of the polymer skeleton and, secondly, dynamic deformation. Whereas the first cause determines the position of the band and its inhomogeneous broadening, the second determines the homogeneous (temperature-dependent) band width. A large inhomogeneous band width can be observed in highly strained or disordered systems[173] and the change in optical absorption takes place owing to the homogeneous band broadening[93]. In other words, it is assumed that the

conjugated PDA chain is rigid and does not undergo conformational changes, while alteration in external conditions leads to the appearance of only a gradual deformation of the bond lengths in the chain. It may be that the thermochromic transitions in the solid PDA are associated with the trans-orientation or a change in the packing of the substituents, which leads to the deformation of the conjugation chain and changes in the electronic structure and colour.

Apart from the thermochromic and solvatochromic phenomena described above, there are a series of physical and chemical transformations of DA and their polymers accompanied by a change in colour[8]. These include the fusion of PDA, the extraction of the monomer from partly polymerised DA, and others. A correlation is almost always observed between the number of methylene groups N_{CH_2} joining the DA triple bond to the functional group and the observed colour transition. For example, in the extraction of the monomer from partly polymerised DA, red specimens with $N_{CH_2} = 1$ and 2 remain red, while blue specimens with $N_{CH_2} = 1,2,4$ become red ($\lambda_{max} = 530 \pm 10$ nm). Thus, regardless of the initial colour, the extraction of the monomer leads to the appearance of a red colour. On the other hand, the extraction of the solvent from partly polymerised DA with $N_{CH_2} = 3$ does not affect the colour. Apart from the colour changes, a correlation has been observed between the number of methylene groups and the solubility and fusibility of PDA[8]. Almost all PDA with $N_{CH_2} = 1$ are infusible and decompose on heating without melting; they are also insoluble in the usual organic solvents. An increase in the number of methylene groups leads to an improvement of fusibility and solubility. Almost all PDA with $N_{CH_2} = 4$ melt and the majority of them are soluble.

(b) Fluorescence

Like the model long polyenes, fully polymerised PDA specimens do not fluoresce. The exceptions are the radiation-polymerised BPG[125], PDA with defects[125,174,175], certain soluble PDA[169,170], and also PDA with chiral substituents in only one of the reactive phases[121].

The causes of the absence of fluorescence of the fully polymerised specimens are obscure, but they can be as follows[168]: (1) the high efficiency of the absorption of the emitted light quanta (reabsorption of light) owing to the small depth of penetration by light which is only 10–100 nm; (2) non-radiative processes in the deactivation of excitation; (3) the transmission of excitation to low-lying energy states from which emission takes place but which have not so far been detected experimentally; rapid intersystem crossing to a triplet level, whose energy is less than half the width of the forbidden gap, and subsequent non-radiative decomposition with emission of phonons may constitute this process.

Some of the monomeric DA are phosphorescent. For example, DCHD phosphoresces with a well-resolved spectrum corresponding to emission from four traps, whose depths are 2.8, 8.7, 27.8, and 45.7 meV.[68] It has been assumed[68] that these traps are populated and liberated via a triplet exciton band. Direct emission from this band cannot be detected for some reason. The arrangement and concentration of the traps are not random, since the ratio of the phosphorescence band intensities is the same for different specimens. The time of emission from the traps is less than 7 s. It has been suggested that the traps have a triplet spin polarisation.

Almost nothing is known about the nature of the broad fluorescence bands of the DCHD monomer. From the instant of the beginning of polymerisation, both the phosphorescence and fluorescence are fully absorbed by the conjugated polymer skeleton[176]. Certain partly polymerised PDA do fluoresce. Thus the partly polymerised TS specimen gives rise to a fairly satisfactory fluorescence spectrum[175]. On excitation with light (at 4.2 K), two emission bands were observed at 20486 and 20802 cm^{-1} accompanied by vibrational side bands. The emission band frequencies are displaced by approximately 4000 cm^{-1} towards shorter wavelengths relative to the optical absorption edge of the polymer. Furthermore, four additional emission bands are observed whose wavenumbers $\tilde{\nu}_{fl}$ are related to the wavenumber of the exciting light $\tilde{\nu}_{exc}$ by the simple expression $\tilde{\nu}_{fl} = \tilde{\nu}_{exc} - \tilde{\nu}_i$, where $\tilde{\nu}_1 = 988.7$, $\tilde{\nu}_2 = 1227$, $\tilde{\nu}_3 = 1513$, and $\tilde{\nu}_4 = 2085$ cm^{-1}. The ν_i were assigned to the vibrational energies of the excited state of the fluorescent centre. It is surprising that these quantities, which refer to an excited state, agree well with the vibrational energies of the ground state of the chain observed with the aid of Raman spectroscopy: 955, 1205, 1487, and 2088 cm^{-1}.[177]

The spectroscopic characteristics of the fluorescence of the partly polymerised poly-TS are independent of the type of specimen (single crystal, polycrystalline material, or powder). The observed fluorescence is attributed to the geometrically and energetically localised states. The concept of geometrical localisation arose owing to the dependence of the fluorescence intensity on the position of the laser spot of the exciting light on the surface of the crystal. On passing from one irradiated site to another, the fluorescence intensity can then change by a factor of 100 and the maximum intensity is observed when the boundaries between the crystals are irradiated. The energetic localisation is understood as the absence of an energy linkage between the fluorescence centres and the polymer chain[174].

In order to elucidate the role of defects in fluorescence, a study has been made[174] of a specially prepared poly-TS specimen with a large number of defects[174]. The absorption spectra recorded at 4.2 K showed new (relative to the defect-free specimen) bands; two narrow bands (at 20665 and 21050 cm^{-1}) and two broad bands (at 20500 and 20830 cm^{-1}). The positions of the last two bands coincide with those of the fluorescence bands. It is not clear why fluorescence is observed for only one of the pairs of bands observed in absorption.

As regards the nature of the fluorescent centres, it has been suggested that they may consist of triplets at the end of the polymer chain which have become frozen in the ground state. In this case the absorption and fluorescence are associated with the allowed $T-T$ transition[175]. The fluorescence of solutions is determined by sections of the polymer with disrupted chain conjugation[169].

(c) Non-linear Optical Properties

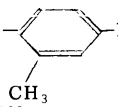
The tensor molecular polarisability $\mathbf{P}$ and the applied electric field $\mathbf{E}$ are linked by the relation $\mathbf{P} = \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}^2 + \chi^{(3)}\mathbf{E}^3$, where $\chi^{(1)}$ is the coefficient of the linear optical susceptibility and $\chi^{(2)}$ and $\chi^{(3)}$ are the coefficients of the non-linear second- and third-order optical susceptibilities respectively. For centrally symmetrical molecules, to which the vast majority of PDA belong, $\chi^{(2)} = 0$. In calculations based on the perturbation theory using the free electron model, $\chi^{(3)} \propto L^5$, where L is the length of the conjugation chain in the linear molecule[178], while in calculations based on the π-electron approximation $\chi^{(3)} \propto N_d^6$, where N_d is the electron localisation parameter[179]. It has been shown experimentally that $\chi^{(3)}$ does not increase with increasing conjugation chain length as rapidly as predicted by the theory. The

explanation is that the real electron potential is periodic, for example, owing to the alternation of the bond lengths, the degree of delocalisation of electrons is therefore smaller than in the free electron model[178].

The non-linear optical susceptibility coefficient is fairly high for PDA single crystals. Thus $\chi^{(3)} = 7 \times 10^{-11}$ CGS units for poly-TCDU and $\chi^{(3)} = 8.3 \times 10^{-10}$ CGS units ($\lambda = 1.89$ μm) for poly-TS.[178,180] The electrical breakdown parameter for PDA is very high. For poly-TCDU it is 50 GW cm^{-2} in the picosecond range, which is higher by a factor of 20 than for germanium. If one considers the quality parameter defined as $\chi^{(3)}/n^2$ (n is the refractive index), the latter is found to be 1.1×10^{-11} for poly-TCDU and 4.5×10^{-10} for poly-TS, compared with, for example, 2.5×10^{-11} for germanium and 0.45×10^{-11} for gallium arsenide (all the values are expressed in CGS units). Multilayers based on DA also possess non-linear optical susceptibility†. $\chi^{(3)} = (0.67 \pm 0.20) \times 10^{-12}$ CGS units for the ammonium salt $CH_3-(CH_2)_{17}-C\equiv C-C\equiv C-COO^-NH_4^+$, which yields $\chi^{(3)} \cong 1.34 \times 10^{-11}$ CGS units when account is taken of the degree of conversion.

The non-linear optical properties of solutions of poly-3(4)BCMU have been investigated by the method of three-wave mixing, in which two light beams from laser sources with frequencies ω_1 and ω_2 were directed onto the specimen and the generation of light with the frequency $\omega_3 = 2\omega_1 - \omega_2$ was observed[181-184]. It was found that there is a large contribution by the direct two-photon absorption with a cross-section β to the third-order non-linear optical susceptibility coefficient. The value obtained for a solution of poly-4-BCMU is $5 \times 10^{48} \lesssim \beta \lesssim 10^{-46}$ cm^4 s photon^{-1} (chain unit)$^{-1}$, which is the highest known value, much greater than, for example, that for CS_2, where $\beta \cong 5 \times 10^{-49}$ cm^4 s photon^{-1} molecule^{-1}.

The occurrence of the two-photon absorption and its large cross-section can limit the application of PDA as active elements in non-linear optics. On the other hand, studies of poly-TS and poly-TCDU single crystals have led to the hypothesis that the observed absorption is not a two-photon process and is more likely to be a two-stage process: the absorption of the first photon creates a defect in the conjugation chain, for example, by transition of an electron to a localised orbital; the absorption of the second photon is associated with a transition whose initial or final state is a newly formed defect[185]. Subsequent experiments should provide an answer to the question of the role of the two-photon absorption and its nature and hence of the practical value of PDA from the standpoint of their application in non-linear optics.

In order to expand studies on the non-linear optical properties of PDA and of their possible applications, asymmetric DA[186,188] and DA with chiral substituents[21,189] have been synthesised. The generation of a second harmonic has been observed for DA with R = CH_2NH––NO_2 and R′ = $(CH_2)_8CONHC_2H_5$ and its polymer[188]. The possibility of using multilayers based on PDA in integrated non-linear optics and also in light guides has also been considered[190].

VI. ELECTRON PARAMAGNETIC RESONANCE IN POLYDIACETYLENES

During the polymerisation of diacetylenes, considerable changes take place in the EPR spectrum. In the initial polymerisation stage several lines are observed, many of which are characterised by the anisotropy of properties as a function of changes in the mutual orientations of the external magnetic field and the crystal[46]. As polymerisation reaches completion, the number of lines and the overall paramagnetic susceptibility diminish until a single weak signal, characteristic of all polyconjugated systems, remains when almost 100% conversion of the monomer is reached[48]. Such a change in the EPR spectrum on polymerisation is explained by the fact that in the initial polymerisation stage the main contribution to absorption comes from the active species at the end of the growing chains, while after the completion of polymerisation the EPR signal is determined by the paramagnetic species bound to the polymer chain. In conformity with such subdivision, the study of the EPR parameters in the initial polymerisation stage can yield information about the polymerisation kinetics and about the structure of the active centre propagating the chain, while the conformational structure of the polymer chain can be investigated by studying the EPR spectrum after the end of polymerisation.

The observed EPR spectrum in the initial polymerisation stage can be described by the spin Hamiltonian $H = \mu_B \mathbf{B} g \mathbf{S} + D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2)$.[46] The g-tensor is almost isotropic and its principal values hardly differ from the g-factor of the free electron. The splitting parameters at zero field on polymerisation of TS and BPG are very similar and amount to $D/hc \cong 0.26-0.27$ cm^{-1} and $E/hc \cong -0.05- -0.08$ cm^{-1}, which indicates the identical mechanism of initiation and the identity of the paramagnetic centres active in polymerisation. The smallness of the parameter E shows that the distributions of the spin density of the carbon atom in the sp-hybridised state along the x and y axes are approximately equally probable.

In the ultraviolet-initiated polymerisation a number of lines in the EPR spectra and the range of variation of the zero field splitting parameters increase. For example, lines due to nine non-equivalent triplet centres have been observed for TS and the following values have been obtained for them: 0.275 $cm^{-1} \leqslant D/hc \leqslant 0.367$ cm^{-1} and -0.008 $cm^{-1} \leqslant E/hc \leqslant -0.006$ cm^{-1}.[76] The study of the dependence of the line intensities in the EPR spectrum and of the zero field splitting parameters on the degree of polymerisation together with a parallel investigation of the optical properties made it possible to reach well-founded conclusions concerning the nature of the initiating species in the structure of the active polymerisation centres. During the ultraviolet polymerisation of BPG, optical spin polarisation is observed[191]. The proposed mechanism of this phenomenon consists in the absorption of light (280 nm $\leqslant \lambda \leqslant$ 370 nm) by the benzene ring of the substituent and the subsequent triplet energy transfer to the conjugated chain via intersystem crossing $S_1 \rightsquigarrow D_0$, where S_1 is the excited singlet state of the benzene ring of the substituent and D_0 the triplet state of the DA molecule. As a result, two new emission lines are observed in the EPR spectra. Optical electronic spin polarisation ($\lambda < 590$ nm) is observed also for the ground triplet state of the poly-TCDU chain having the structure ~CR–RC=C–C≡CR.[88] The authors explain this phenomenon with the aid of a Jablonski diagram.

As polymerisation proceeds, the intensity of the high field lines, characteristic of the triplet state, diminishes until the ultimate disappearance of the lines at the end of the rapid stage of the reaction. After the completion of polymerisation, a single line remains with a g-factor close to that of the free electron. As in the discussion of the mechanism of the formation of paramagnetic centres in polyconjugated systems, it has been suggested that the paramagnetic properties of PDA are determined mainly by the delocalised structural

† See F.Kajzar and J.Messier, Thin Solid Films, 1983, **99**, 109.

defects of the polymer chain[114] which can have, for example, the following structure:

$$\sim\!=\!RC\!-\!C\!\equiv\!C\!-\!\dot{C}R\!-\!RC\!=\!C\!=\!C\!=\!CR\!-\!RC\!=\!C\!=\!C\!=\!CR\!-\!R\dot{C}\!-\!C\!\equiv\!C\!-\!CR\!=\!\sim\ .$$

It is easy to represent different mesomeric forms of this biradical which correspond to the migration of the free spin along the chain. It is less likely that the paramagnetism is due to inactive radicals at the ends of the growing polymer chains[47].

The parameters of the EPR signal in the fully polymerised PDA specimens are very similar to the known characteristics of the EPR signals for other polyconjugated systems. In particular the g-factor is $g = 2.0023 \pm 0.0002$,[46] the line form at the centre is Lorentzian, the wings have the Gaussian shape[16,46], and the line width, measured between the points of maximum slope, varies from 5 G for poly-TS[46] to approximately 10 G for poly-HD.[16] The concentration of the paramagnetic species depends on the nature of the monomer and amounts to 1.6×10^{17} spins g^{-1} for poly-HD[36] and 8×10^{15} spins g^{-1} for poly-TS.[48] As for other polyconjugated systems, the EPR signal of PDA is readily saturated for low UHF field powers and a relation is observed between the intensity of the EPR signal and the degree of crystallinity (the degree of packing in the case of polyconjugated systems): the greater the degree of crystallinity, the lower the concentration of paramagnetic centres[192].

As for polyconjugated systems, in the case of PDA the previous history of the specimen is found to influence the behaviour of the EPR parameters. This is apparently associated with the slow relaxation of the internal stresses in the crystal and the consequent change in the number of paramagnetic defects in the chain due to this process. A narrow EPR signal ($\Delta B = 0.9$–1.2 G) has been observed for poly-TS in addition to the usual EPR signal[192]. Irradiation of a PDA specimen having R = CH_2OH and R′ = CH_3 by light at a wavelength $\lambda \cong 700$ nm results in the observation of a narrow signal (< 3 G) in the "tail" of the optical absorption. This signal is of unknown origin, appearing and disappearing reversibly at all temperatures from liquid helium temperature to room temperature. Its lifetime amounts to hours at 4.2 K and seconds at 30 K.[5]

The study of the temperature variation of the EPR signal intensity in poly-TS led to the following results[193]. In the range 90–220 K the paramagnetic susceptibility obeys the Curie law, which indicates a constant density of defects in this temperature range, provided that the PDA paramagnetism is attributed to structural defects. Activated processes, leading to an increase of the number of paramagnetic species, begin above 220 K. In the temperature range 233–353 K the EPR signal intensity is given by the expression $\chi'' = \chi_0''[\exp(-\Delta E/kT)]h\omega/2kT$, where $\Delta E = 75 \pm 25$ meV; this quantity is thought to be related to the activation energy for the formation of mobile paramagnetic defects[46]. The product of the spin–spin and spin–lattice relaxation times T_1T_2 was measured in the same temperature range and it was established that at 250 K there is a fairly sharp change in the law governing the temperature variation of the product of the reciprocals of the relaxation times: $1/T_1T_2 \propto T^{1.8}$ at temperatures below 250 K and $1/T_1T_2 \propto T^{9.3}$ above 250 K, i.e. there is apparently a change in the relaxation mechanism from the direct mechanism at low temperatures (the theoretical power exponent of the temperature is $n = 2$) to a two-phonon Raman mechanism ($n = 9$). Below the transition temperature, the molecular movements of the chains are "frozen", whereupon their densest packing is attained and the number of chain defects is constant. Above this temperature the mobility is "unfrozen" and the number of defects is determined by the temperature. It is apparently not fortuitous that a phase transition associated with the reorientation of the substituents is in fact observed in this temperature range[126,135,138,140,141].

The overall experimental results indicate the dependence of the EPR signal parameters on the nature of the initial monomer, the method used to isolate the polymer, and the previous thermal and morphological history of the specimen[194]. Thus the EPR signal intensity during polymerisation at conversions > 10% can either decrease (TS)[114] or increase (HD)[16]. Such behaviour is attributed to the different degrees of strain in the polymer chains formed, which is greater in the case of HD[16]. This is also indicated by the greater width of the absorption line for HD. It has likewise been suggested that only a small proportion of all the chain defects are paramagnetic while the majority are non-paramagnetic and the chain defects are attributed to the transition from the non-paramagnetic strained state of the polymer chain to a state having a lower energy with breakdown of the conformation and the formation of paramagnetic defects[192]. Different defects, allowed by the topology and symmetry, have been considered theoretically[195].

VII. ELECTROPHYSICAL PROPERTIES OF POLYDIACETYLENES

In terms of their absolute dark conductivity, the PDA are dielectrics. The dark conductivities of polymers obtained from different initial monomers vary from 10^{-16} to 10^{-10} Ω^{-1} cm^{-1}.[69,127,128,196] According to the kinetic analysis of the carriers, the dark conductivity of PDA is due to the ionisation of impurities.[197] Indeed, the dark current is determined by the quality of the crystal and the time for which it is maintained *in vacuo* before the measurements and varies from specimen to specimen. For example, the decrease of the dark conductivity on passing from measurements in air to measurements *in vacuo* amounts to several orders of magnitude[10].

It was later established that the dark conductivity, which obeys Ohm's law like the dark current limited by the space charge, is determined by the localised levels at distances of 0.80 ± 0.02 eV from the edge of the band and their concentration, which corresponds to $\lesssim 1$ centre per meter of the length of the polymer chain[198]. The level with an energy of 0.80 eV functions as the donor for the Ohmic dark conductivity and as a trap for the injected carriers. For all the orientations of the polymer single crystal relative to the external electric field and under all conditions of study, the dark current obeys the law $i \propto \exp(-\Delta E/kT)$, where $\Delta E = 0.80$ eV. The sign of the carrier could not be determined.

By analogy with the familiar results obtained for the doping of polyacetylene, the PDA specimens were also treated with halogen vapours[199]. Thus polyhexa-2,4-diyn-1-ol absorbed iodine vapour in an amount up to 1.2 atoms per unit, forming a lustrous black material. The dark conductivity increased by 6–7 orders of magnitude and in terms of its increment the effect proved almost the same as for $(CH)_x$. The colour of polyocta-3,5-diyne-1,8-diol did not change and its weight did not increase on treatment with iodine vapour or solution, which can be explained by the dense molecular packing of the hydrogen-bonded macromolecules. The diffusion of the large iodine molecules between such macromolecules is greatly hindered. The doping with iodine was carried out for two-layer poly(diacetylenecarboxylic acid) films. In this case the increase of the dark conductivity is not so great and σ increases from 10^{-10} to 10^{-7} Ω^{-1} cm^{-1}. The increase of the conductivity is reversible: after the removal of iodine, the conductivity returns to its initial value[200]. Somewhat better

results were obtained when the doping was carried out before polymerisation. For example, the specific conductance $\sigma = 10^{-4}\ \Omega^{-1}\ cm^{-1}$ was obtained for the TS crystal doped with iodine and polymerised at room temperature[201]. Analogous investigations have been carried out for other DA and the influence of various factors on the specific conductances of the doped polymers was studied.

Numerous studies have been devoted to the photoconductivity of PDA. It was established as a general rule that the maximum on the spectral photoconductivity curve is always displaced towards higher energies relative to the maximum in the optical absorption spectrum. The absolute photocurrent in PDA depends greatly on the nature of the monomer and can vary by several orders of magnitude[2,10,117]. The yields of the photocurrent carriers of both signs are the same, which indicates their dipolar generation[202]. An approximately linear dependence of the photocurrent on the exciting light intensity has been observed[127]. Like other physical properties, the photoconductivity is found to be anisotropic: for light polarised parallel to the chain, the photocurrent is approximately 10 times[158] and the quantum yield in the formation of the carrier is approximately 100 times[203] greater than for the light polarised at right angles to the chain. The ratio of the photocurrent to the dark current at 300 K is approximately 300; it increases with decrease of temperature to approximately 600 at 120 K for an electric field strength of 1300 V cm^{-1}.[127]

The mobility of the carriers, one of the most important characteristics of photoconductors, is unusually high for organic materials and, according to data obtained by different methods for different specimens, varies within wide limits: from 1–5 $cm^2\ V^{-1}\ s^{-1}$ [202–206] to 10^2,[207] 2.8×10^3,[133] 6×10^3,[208] and even $2 \times 10^5\ cm^2\ V^{-1}\ s^{-1}$.[209] The mobilities calculated by quantum-chemical methods are $10^3\ cm^2\ V^{-1}\ s^{-1}$ [97] and $1.7 \times 10^3\ cm^2\ V^{-1}\ s^{-1}$.[107] Other workers[206–210] continue to adopt for the mobilities values in the range 1–10 $cm^2\ V^{-1}\ s^{-1}$. More careful experiments and the theoretical consideration of the mechanism of the formation of the current carriers and the associated kinetics should indicate the true mobility and the causes of such large discrepancies between the experimental values.

Like other physical properties, the mobility is anisotropic $\mu_\parallel / \mu_\perp = 10^2–10^3$.[128,198,203,204] An even greater anisotropy ($> 10^4$) has been found for the microscopic mobility#. The rate of drift of the carriers is in the range from 240 m s^{-1} [204] to 900 m s^{-1},[202] while another study[209] yielded an unexpected result, namely that the rate is constant at 2×10^3 m s^{-1} and is independent of the electric field strength down to the lowest values ($E < 1$ V cm^{-1}) and is comparable to the estimated velocity of sound (5×10^3 m s^{-1}).[42]

According to various estimates, the lifetime of the carriers ranges from $10^{-6}–10^{-8}$ s[128,202,205] to 10^{-13} s.[133] Owing to the differences between the estimated mobilities and lifetimes of the carriers, the estimated length of the free path varies within a wide range: from approximately 10 nm for monolayers and multilayers of cadmium polydiacetylenecarboxylate salts[211] to 1 mm in a single crystal of poly-TS.[207,209] The latter value is in surprisingly good agreement with the average length of the unaffected sections of the polymer conjugation chain (0.1–1 mm) obtained from the measured density of dislocations ($\sim 10^{13}$) m^{-2})[212] and, provided that this agreement is not fortuitous, the length of the free path is limited solely by the dislocations in the single crystal which serve as traps for the carriers. The average length of the carrier path between interactions with acoustic phonons has been estimated as 8 μm.[209] The effective mass of the carrier is surprisingly small ($m^* = 0.05m_0$) for organic crystals[133].

In the study of photoconductivity over a wide range of energies of the light quanta (from 0.62 to 3.1 eV), the principal qualitative characteristics of the behaviour of the spectral curve were elucidated.[207,213] One of the main features proved to be a rapid decrease of photoconductivity at $\hbar\omega < 0.8$ eV, which is consistent with data[198] indicating the existence in PDA of localised impurity levels with the same energy. The spectral photoconductivity curve can be divided into three regions: (1) in the region where $\hbar\omega < 2.0$ eV, photoconduction takes place as a result of the ionisation of impurities; (2) in the region where $2.0 < \hbar\omega < 2.4$ eV, it arises as a consequence of the exciton absorption with subsequent autoionisation of excitons; (3) in the region where $\hbar\omega > 2.4$ eV, direct generation of current carriers in an interband transition is observed. The quantum efficiency of the irradiation is high in the first and third regions and is small in the second region. The photoconductivity maximum in the first region at 1.64 eV[197] is fairly difficult to account for. Nor is it clear whether or not it is fortuitous that the energy of this maximum is approximately equal to twice the energy of the traps.

The one-dimensional conductivity model is valid for the current flowing along the polymer chain[213–217]. According to its electronic properties, PDA belong to the class of semiconductors with broad bands. The existence of bands with a width amounting to several electron-volts has been established for these substances with the aid of calculations and electronic spectroscopy for chemical analysis (ESCA) and electron injection[208] and photoemission[218] methods. However, it is not clear how these results can be reconciled with the high mobility of current carriers observed for PDA which is characteristic only of semiconductors with narrow bands.

Compared with many polymers having conjugated bonds, the PDA have fairly weak electrophysical characteristics. There are several reasons for this. Firstly, the structure of the chain in these polymers is significantly one-dimensional, which leads to the effective recombination of the carriers located on one chain and their consequent low concentration. Indeed not more than two carriers per polymer chain have been observed[209]. Secondly, a pure PDA single crystal contains a very small number of impurities and defects, so that the impurity conductivity is low. Thirdly, a characteristic feature of the optical absorption of PDA is that the probability of the transition to the exciton levels is much higher than that of the direct interband transition. The exciton states lie approximately 0.5 eV below the bottom of the conductivity band and their lifetime is very short. The probability of the thermal ionisation of excitons with formation of free carriers is therefore negligible. These factors create serious difficulties for the practical employment of PDA as photoconductors.

On the other hand, the mobility of the carriers in PDA is very high. Therefore, if it were possible to create a high concentration of carriers (one of the obstacles to this is the one-dimensional character of the polymer chain), one might hope to obtain high electrophysical characteristics of PDA. Another way of increasing the photoconductivity involves the sensitisation of the photoconduction either by means of chromophores constituting a component of the side substituents in the PDA chain or by introducing chromophores capable of cocrystallisation with the DA monomers and the subsequent formation of PDA. In both cases it is possible to achieve a location of the chromophores which is the closest possible to the polymer chain in order to ensure the

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See U.Seiferheld, B.Ries, and H.Bässler, J.Phys., C., Solid State Phys., 1983, **16**, 5189.

most effective charge transfer. Furthermore, the introduction of chromophores must not hinder the solid-phase polymerisation and the electronic structure must promote most effectively the sensitisation of the photoconduction in PDA. The first attempt of this kind was undertaken in a study of the photoconductivity of poly-DCHD containing carbazole side groups[219].

It may be that an improvement of the electrophysical properties can be attained by employing isostructural doping (i.e. doping which does not alter the structure of the PDA crystal or multilayers).

VIII. RAMAN SPECTROSCOPY OF POLYDIACETYLENES

The application of the Raman spectroscopic method to the study of PDA is one of the examples illustrating the extensive possibilities of this method[6]. In contrast to other procedures, Raman spectroscopy can yield direct information about the bond sequence in the polymer, about the degree of their strain, and about the influence of the surrounding monomer matrix on the growing polymer chain[4,5]. Despite the fact that, according to the results of analysis, the total number of vibrations active in the Raman spectrum of PDA is fairly large, only a small proportion of such vibrations are enhanced by resonance, which results in a considerable simplification of the Raman spectra. This can be explained by the fact that the intense optical absorption observed in the visible region owing to the excitation of the π-electron conjugation system in the polymer chain leads to the resonance enhancement of only those vibrations which induce the modulation of electron density along the chain. The resonance enhancement effect is so large that Raman spectra without noise can be recorded for only 20 DA monolayers[220] or for a degree of conversion of the monomer much less than 1%.[221] The normal vibrations of the main chain, which do not induce the modulation of the electron density along the chain, and the vibrations of the side groups are almost inactive in the Raman spectra.

Between four and nine bands in the range 600–2200 cm^{-1} have been observed in the Raman spectra of DA and PDA specimens[177]. The emission is highly polarised for all the bands and the electric field vector is parallel to the direction of the polymer chain[138]. The position and form of the bands depend on the nature of the substituents, the temperature, the mechanical stress applied to the specimen, and the wavelength of the exciting light.

The largest number of studies have been performed for TS and its partly and wholly polymerised specimens. For the fully polymerised poly-TS crystals, only four intense bands are observed in the Raman spectra: $\tilde{\nu}_1 = 2086$, $\tilde{\nu}_2 = 1485$, $\tilde{\nu}_3 = 1203$, and $\tilde{\nu}_4 = 952$ cm^{-1}. The changes in the positions of these lines during polymerisation have been investigated[221]. During the induction period of the polymerisation reaction (degree of conversion of the monomer < 10%), the frequencies in the Raman spectra are independent of the degree of polymerisation. During subsequent polymerisation, the frequencies increase: the shifts of $\tilde{\nu}_1$ and $\tilde{\nu}_2$ are much greater than those of $\tilde{\nu}_3$ and $\tilde{\nu}_4$ and amount, for example, to approximately 60 cm^{-1} for $\tilde{\nu}_1$. In addition it has been established that the polymerisation is spatially inhomogeneous. This is manifested particularly by the broadening of the line, the appearance of additional lines, and by the fact that the intensities and frequencies of the lines are sensitive to the position of the laser beam relative to the surface of the irradiated specimen[221].

The dependence of the frequency shift on the application of external mechanical stresses to poly-TS has been investigated[222,223]. The Raman bands are then displaced towards higher frequencies, while the optical absorption maximum at 2 eV is actually displaced towards lower energies "at a rate" of approximately 8 meV $kbar^{-1}$. Both these results are in satisfactory agreement with predictions based on the molecular orbital method. It has been suggested that the changes in the Raman frequencies during polymerisation and the frequency shift when external mechanical stresses are applied to the specimen have a common basis—namely they are due to the appearance of strain in the polymer chain and the change in the force constants of the bonds.

The thermal polymerisation of MBS, a monomer isomorphous with TS, has been investigated by the Raman method[19,63]. The positions of the lines in the Raman spectra of MBS virtually coincide with their positions in the spectrum of TS, although the initial molecular strain in the polymer chain of MBS is greater. This excess strain is, however, eliminated in the very early stages of the polymerisation of MBS because of the easier, compared with TS, reorientation of the side substituents, which leads to a longer lifetime of the active centre and to a higher pre-exponential factor, which determines the significant difference between the kinetic curves for the polymerisation of TS and MBS.

Other DA have also been investigated by the Raman method. The spectra of the partly and fully polymerised BPG have a greater number of bands than that of TS[125], which can be explained by the presence of structures without a centre of symmetry, by the Fermi resonance interactions, or, finally, by vibrations in the substituents linked to the polymer skeleton. The frequency shifts in the Raman spectra of BPG on passing from the monomer to the polymer are greater than for TS.[224]

In contrast to poly-TS, the frequencies of the Raman lines of poly-HDU subjected to stretching stresses decrease linearly with increase in the length of the specimen[225]. It has been demonstrated by Raman spectroscopy that the phase transition in DCHD is due to a rearrangement of the side groups, which leads to an alteration of the strain in the crystal[160]. The frequency shift following the introduction of phenazine into the cocrystallising composition with diacetylenemonocarboxylic acid is small, indicating an effective cocrystallisation which does not give rise to additional strains[34].

A very intense narrow line has been observed in the Raman spectrum following the absorption of O_2 molecules on the surface of the single crystals of certain PDA[226]. The resonance enhancement occurs in this instance owing to the considerable energy transfer from the conjugated skeleton to the O_2 molecule in the electronic transition in PDA with an energy of 2.39 eV. The Raman frequency $\tilde{\nu} = 1521$ cm^{-1} has been obtained for a poly-TS single crystal.

Because of the large number of observed bands due to the functional side groups in the infrared spectra of diacetylenes and their polymers and the difficulty of interpreting these lines, studies have been performed only in the near infrared ($\tilde{\nu} = 3500–12000$ cm^{-1})[227] and the far infrared ($\tilde{\nu} = 5–120$ cm^{-1})[143].

IX. OTHER EXPERIMENTAL METHODS FOR THE INVESTIGATION OF POLYDIACETYLENES

Polydiacetylenes have fairly good mechanical properties. For example, the tensile strength of poly-HDU is approximately 1.7×10^7 Pa, while the dynamic modulus is approximately 4.7×10^6 Pa.[228] If the modulus is calculated per PDA

molecule, its value is almost the same as for diamond. The maximum disruptive stress depends on the size of the specimen: it is greater, the smaller the crystal, which indicates the decisive role of dislocations or other defects in the breakdown of the specimen. The anisotropy of the mechanical properties of PDA is very pronounced[229]. The mechanical properties have been examined in greater detail by Young and Zachmann[230].

The temperature coefficient of the linear expansion α for the PDA investigated is negative over a wide temperature range 231–233, which have been attributed mainly to the increase of the amplitude of the torsional vibrations as the temperature increases and with decrease of the length of the polymer chain due to this effect. The typical values of α are -10^{-5}– -10^{-6} K^{-1}.

The specific heats of a poly-TS single crystal and their temperature variation have been determined in the temperature range from 3 to 300 K.[144] The experimental results are described satisfactorily by the long chain model involving the presence of acoustic and optical phonons.

A pyroelectric effect has been observed for poly-TS[155,234], which is extremely strange, since theory predicts its existence only for molecular crystals without central symmetry. The measurements are performed along the *b* axis, the pyroelectric constant changes sign several times as the temperature is varied, and its maximum value is approximately 10^{-10} CGS units. Pyroelectric properties have also been observed for other PDA.[235]

The ^{13}C NMR method has been used to study solutions of poly-3(4)BCMU[93,236] and it has been established that these polymers have the (A) structure of the chain and that in the gel state the chain has a rigid planar conformation.

The ESCA method has been used to determine the positions and widths of the valence and conductivity bands[237–240]. The ionisation potentials of several of the PDA investigated proved to be similar, amounting to 7 ± 1 eV. Unfortunately the application of the ESCA method is complicated by the considerable contribution of the photoelectrons emitted by the substituents, which precludes the determination of other parameters of the electronic structure of the polymer chain.

In contrast to the ESCA method, the electron photoemission method[218] does not suffer from problems associated with the movement of the charge within the material and the results obtained with its aid may be more reliable. Thus it has been found that the ionisation potential is 7 ± 1 eV, the electron affinity is 5 ± 1 eV, and the width of the forbidden gap is 2.1 ± 0.1 eV. According to the diamagnetic susceptibility measurements, the conjugation in PDA is significantly one-dimensional with a large electron delocalisation region[241].

X. THE POSSIBLE APPLICATIONS OF DIACETYLENES AND POLYDIACETYLENES

The specific features of the reactivity of DA, the characteristics of its structure, and the changes in its physical properties on passing from the monomer to the polymer as well as a number of the physical properties of DA-based polymers determine the possible applications of these compounds.

For example, DA with R = R′ = $CH_2OCONH(CH_2)_3CH_3$. .(HDDBU) and R = R′ = $CH_2OCONHC_2H_5$ accelerate the radiation-induced cross-linking of polyethylene (PE).[242] The dose in the irradiation of the PE + HDDBU mixture necessary to attain the gel point is smaller by a factor of 15 than for pure PE. The reason why the radiation-induced cross-linking of PE is accelerated only by the DA indicated above consists in the fact that these monomers cocrystallise homogeneously with PE, while others form their intrinsic phase on mixing.

It has been suggested that the numerous colour changes in PDA during its polymerisation be used for the direct visual indication of the previous radiation and thermal history of the specimens[87,243,244]. Both the individual DA and the numerous cocrystallising compositions are very sensitive and visually observable indicators of γ-irradiation doses in the range from 50 rad to 50 Mrad.

The reversible thermochromic transitions in various PDA at temperatures from −180° to 220 °C can be used as temperature indicators and also in indexing devices[245].

Diacetylenes and polymers based on them can be used as indicators of ozone[246], since even small amounts of this gas decolorise the materials by breaking the conjugation chain.

The solubilities of certain PDA as well as their ability to change colour when external conditions are altered made it possible to create on their basis one-component inks and dyes[247].

Cocrystallising compositions made up of HDU and a symmetrical DA with R = R′ = $CH_2OCONHC_6H_4Cl$ have been suggested for the recording of fingerprints[248]: polymerisation does not take place on a surface containing traces of fat, while on a clean surface thermal polymerisation occurs with a change in colour from red to violet over a period of approximately 10 min at room temperature or approximately 1 min at 120 °C.

The ability of DA to change colour on polymerisation under the influence of external sources (irradiation with ultraviolet light, γ-rays, and electrons) has led to numerous suggestions for their employment as carriers of information. One can achieve thereby a high density of the recording of information. For example, the resolution attained for a TS single crystal (> 1000 line mm^{-1}) is better than for highly resolving photographic films based on AgBr and photoresistors[249]. Amplitude and phase holograms[249,250], also with a high resolution, have apparently been obtained for the first time for organic crystals on the same TS single crystal. A disadvantage of the TS single crystal is its brittleness. The technology of the employment of DA for the recording of information can be improved by using multilayers[251]. An important advantage of the application of DA for this purpose is the fact that there is no need for a development process in order to obtain an image or information.

The use of DA, particularly of their multilayers, as photoresistors and electronic resistors in lithography is extremely promising. The general requirements which must be met by the materials used for this purpose are a high resolution, high contrast, a high sensitivity, uniformity of the coating, etc.[252] The first results obtained (resolution ~ 50 nm, sensitivity ~ 10^{-6} C cm^{-2}) showed that the employment of multilayer coatings in electronic lithography and photolithography is promising[252–254].

Yet another possibility for the recording and storage of information is provided by the suggestion that multilayers each of which carries an electric charge be used[255]; the charge is photoinjected into a film in a time sequence corresponding to the information introduced, after which it is distributed in space and arranged in order with the aid of a controlling electric field.

The prospects for the application of DA and their polymers in non-linear optics are no less promising. Apart from the high non-linear third-order optical susceptibility coefficient examined above, which is itself important for practical applications, it has been reported[188,256] that a second harmonic of the emission can be generated on the basis of DA and their polymers and that the characteristics are greatly improved compared with those known for inorganic materials,

such as, for example, lithium niobate. It has been suggested that DA and their polymers be used as planar waveguides and other non-linear optical elements[190]; the losses in such waveguides are very small, amounting to 0.01–0.1 dB km^{-1}.[256]

However, one should note that despite the promising predictions as regards the application of DA and their polymers for practical purposes, there exist a number of obstacles to their extensive use. The point is that monomeric diacetylenes can frequently be obtained only as a result of fairly complex multistage syntheses; they must be stored under special conditions (in solution or at low temperatures in the dark); the single crystals must be grown by special methods; it is also difficult to obtain their multilayers. However, the prospects for the employment of DA and PDA are so great and promise so much that these temporary difficulties will undoubtedly be overcome.

XI. MONOLAYERS AND MULTILAYERS BASED ON DIACETYLENES

Problems of the kinetics and mechanisms of the polymerisation and the physical properties and applications of diacetylenes and polyacetylenes were examined above mainly in relation to their single crystals, because the ability to form single crystals is their characteristic feature and determines many of their experimentally observed parameters and properties. In practice, with the exception of several illustrative examples, diacetylenes capable of forming monolayers and multilayers have not been considered. This class of acetylenes has recently attracted special attention in view of the prospects for their practical applications (see Section IX of this review).

The class of diacetylenes capable of forming monolayers and multilayers includes asymmetrically substituted DA, one of the substituents of which is markedly hydrophobic while the other is hydrophilic, and which usually have the structure $H(CH_2)_m-C{=}C-C{\equiv}C-(CH_2)_nCOOX$, where $m,n \geq 0$ and X = H or alkali metal cation. These diynoic acids, transferred from a solvent onto the surface of water, are oriented on the latter in a strictly defined manner. If a support whose surface has been specially treated to increase the extent of its interaction with the hydrophobic end of the DA molecule begins to be immersed in the liquid phase, then the monomolecular DA layer can be "removed" from the surface of water and transferred onto the support with retention of the orientation of the substituents; the diacetylenic bonds are themselves oriented in a specific manner under these conditions. Thus the monolayer on the support has been specially prepared for subsequent topochemical polymerisation. This procedure, involving the transfer of the monolayer from the surface of water onto the support, can be repeated many times; the number of deposited layers is determined by the number of immersions of the support in water. This method for the preparation of monolayers and multilayers has been called the Langmuir–Blodgett method§.

§ The First International Conference on Langmuir–Blodgett films whose Proceedings have been published in Thin Solid Films, 1983, **99**, Nos.1–3, has been held recently (Proceedings of the First International Conference on Langmuir–Blodgett Films, Durham, 1982). The history of the problem is described in the same volume; it contains methods for the preparation of films of this kind, particularly those based on DA, the methods for their investigation, the results of the latter, as well as a series of practical applications.

Without considering in detail all the problems associated with DA monolayers and multilayers in view of the limited size of this review, we shall nevertheless mention a number of the most important studies. The synthesis and polymerisation of diynoic acids[257–266], the structure and morphology of the monolayers and multilayers formed[267–275], and their properties[276–280] have been described and their practical applications have been considered[190,252,253,281,282]. Naturally related problems have also been dealt with in some investigations.

Monolayers and multilayers which serve as models of biological membranes and are distinguished from other similar objects by improved properties have been created on the basis of diacetylenes. The syntheses and properties of compounds of this kind have been described[283–289].

The field of polymer and physical chemistry associated with the study of DA and polymers based on them is at present in a period of growth: the classes of newly synthesised DA are being expanded, the spectrum of their physical properties is increasing, new and interesting qualities of these materials have been discovered, and their practical applications have been extended. The studies which have been carried out are of interest also because the results obtained and the conclusions reached have a general bearing on all polymers with a conjugation system. The fact that many diacetylenes are obtained in the form of single crystals provides a unique possibility for their investigation by the latest experimental methods, many of which can be used also in the study of other polymers with conjugated bonds.

The investigations carried out have explained many hitherto obscure problems, for example, the influence of the system of conjugated bonds on the physical properties, the characteristics of the optical absorption and the role of excitons, the character and mechanism of the dark conductivity and photoconductivity, the problems of the initiation, mechanism and kinetics of polymerisation, and many others. Naturally there are also many unsolved problems in these fields. The study of the phase transitions in polydiacetylenes, which are accompanied by an alteration of many physical properties, is also of great interest. In this connection one must determine the order parameters and the critical parameters and compare the observed transitions with some kind of known model based on the theory of critical phenomena. Possibly one should also create an intrinsic theory.

The purely scientific interest and especially the prospects for the practical application of polydiacetylenes constitute an effective stimulus for their investigation and for general progress in this field.

REFERENCES

1. G.Wegner, Z.Naturforsch., 1969, **B24**, 824.
2. G.Wegner, in "Molecular Metals" (Edited by W.E.Hatfield), Plenum Press, New York, 1979, p.209.
3. R.H.Baughman and K.C.Yee, Macromol.Rev., 1978, **13**, 219.
4. D.Bloor, Lecture Notes in Physics, 1980, No.113, 14.
5. D.Bloor, Amer.Chem.Soc., Symposia, 1981, No.162, 81.
6. D.Bloor, F.H.Preston, D.J.Ando, and D.N.Batchelder, in "Structural Studies on Macromolecules by Spectroscopic Methods" (Translation from English edited by A.L.Buchachenko), Izd.Khimiya, Moscow, 1980, p.85.
7. V.Enkelmann, Lecture Notes in Physics, 1980, No.113, 1.

8. G.N.Patel and G.G.Miller, J.Macromol.Sci.-Phys., 1981, **B20**(1), 111.
9. G.Wegner, Faraday Discuss., 1979, No.68, 494.
10. R.H.Baughman and R.R.Chance, Annals N.Y.Acad. Sci., 1978, **313**, p.705.
11. G.Wegner, in "Chemistry and Physics of One-Dimensional Metals" (Edited by H.J.Keller), Plenum Press, New York, 1977, p.297.
12. J.O.Williams, "Advances in Physical Organic Chemistry", Acad.Press, London, 1978, **16**, p.159.
13. R.H.Baughman, J.Polymer Sci., Polymer Phys.Ed., 1974, **12**, 1511.
14. R.H.Baughman, in "Contemporary Topics in Polymer Science" (Edited by E.M.Pearce and J.R.Schaefgen), Plenum Press, New York, 1977, **12**, p.205.
15. J.Kaiser, G.Wegner and E.W.Fisher, Isr.J.Chem., 1972, **10**(2), 157.
16. D.Bloor and G.C.Stevens, J.Polymer Sci.Polymer Phys.Ed., 1977, **15**, 703.
17. G.Wegner, Makromol.Chem., 1972, **154**, 35.
18. G.N.Patel, E.N.Duesler, D.Y.Curtin and I.C.Paul, J.Amer.Chem.Soc., 1980, **102**, 461.
19. D.Bloor, D.J.Ando, D.A.Fisher, and C.L.Hubble, in "Molecular Metals" (Edited by W.E.Hatfield), Plenum Press, New York, 1979, p.249.
20. V.Enkelmann, J.Mater.Sci., 1980, **15**, 951.
21. R.B.Wilson, E.N.Duesler, D.Y.Curtin, I.C.Paul, R.H.Baughman, and A.F.Preziosi, J.Amer.Chem. Soc., 1982, **104**, 509.
22. K.Takeda and G.Wegner, Makromol.Chem., 1972, **160**, 349.
23. M.Ch.Rao and D.Balasubramanian, J.Phys.Chem., 1982, **86**, 939.
24. R.R.Chance, G.N.Patel, E.A.Turi, and Y.P.Khanna, J.Amer.Chem.Soc., 1978, **100**, 1307.
25. G.N.Patel, R.R.Chance, E.A.Turi, and Y.P.Khanna, J.Amer.Chem.Soc., 1978, **100**, 6644.
26. A.R.McGhie, P.S.Kalyanaraman, and A.F.Garito, J.Polymer Sci.Polymer Letters Ed., 1978, **16**, 335.
27. P.A.Albouy, P.Keller, and J.P.Pouget, J.Amer. Chem.Soc., 1982, **104**, 6556.
28. R.R.Chance, K.C.Yee, G.N.Patel, and A.Lyons, Amer.Chem.Soc., Polymer Prepr., 1978, **19**(2), 148.
29. A.F.Garito, A.R.McGhie, and P.S.Kalyanaraman, in "Molecular Metals" (Edited by W.E.Hatfield), Plenum Press, New York, 1979, p.255.
30. K.C.Yee, Amer.Chem.Soc. Polymer Prepr., 1978, **19**(2), 165.
31. G.G.Miller and G.N.Patel, Polymer J.(Tokyo), 1981, **13**, 1075.
32. D.Day and J.B.Lando, J.Polymer Sci., Polymer Phys.Ed., 1978, **16**, 1009.
33. G.N.Patel, Amer.Chem.Soc., Polymer Prepr., 1978, **19**(2), 154.
34. B.Tieke and D.Bloor, Makromol.Chem., 1981, **182**, 133.
35. R.H.Baughman, J.Chem.Phys., 1978, **68**, 3110.
36. R.R.Chance and J.M.Sowa, J.Amer.Chem.Soc., 1977, **99**, 6703.
37. G.N.Patel, J.Polymer Sci., Polymer Phys.Ed., 1979, **17**, 1591.
38. V.Enkelmann, R.J.Leyrer, and G.Wegner, Makromol. Chem., 1979, **180**, 1787.
39. R.H.Baughman and R.R.Chance, J.Chem.Phys., 1980, **73**, 4113.
40. K.Lochner, H.Bässler, and Th.Hinrichsen, Ber. Bunsenges.Phys.Chem., 1979, **83**, 899.
41. K.Lochner and H.Bässler, Ber.Bunsenges.Phys. Chem., 1980, **84**, 880.
42. H.Grimm, Phys.Rev., 1982, **B25**, 1709.
43. G.N.Patel, Macromolecules, 1981, **14**, 1170.
44. Y.Hori and L.D.Kispert, J.Amer.Chem.Soc., 1979, **101**, 3173.
45. C.Bubek, H.Sixl, and W.Newmann, Chem.Phys., 1980, **48**, 269.
46. P.Eichele, M.Schwoerer, R.Huber and D.Bloor, Chem.Phys.Letters, 1976, **42**, 342.
47. G.C.Stevens and D.Bloor, Chem.Phys.Letters, 1976, **40**, 37.
48. G.C.Stevens and D.Bloor, J.Polymer Sci., Polymer Phys.Ed., 1975, **13**, 2411.
49. R.R.Chance and G.N.Patel, J.Polymer Sci., Polymer Phys.Ed., 1978, **16**, 859.
50. J.K.Burdett, J.Amer.Chem.Soc., 1980, **102**, 5458.
51. K.Lochner, Th.Hinrichsen, W.Hofberger, and H.Bässler, Phys.Stat.Solidi, 1978, **A50**(1), 95.
52. C.Kröhnke, V.Enkelmann, and G.Wegner, Chem. Phys.Letters, 1980, **71**, 38.
53. R.J.Leyrer and G.Wegner, Ber.Bunsenges.Phys. Chem., 1979, **83**, 470.
54. W.Schermann, G.Wegner, J.O.Williams, and J.M.Thomas, J.Polymer Sci., Polymer Phys.Ed., 1975, **13**(4), 753.
55. C.Flytzanis, Amer.Chem.Soc., Polymer Prepr., 1982, **23**(2), 153.
56. M.Bertault, J.L.Fave, and M.Schott, Chem.Phys. Letters, 1979, **62**, 161.
57. B.Tieke and G.Wegner, Makromol.Chem., 1978, **179**, 2573.
58. F.Braunschweig and H.Bässler, Ber.Bunsenges. Phys.Chem., 1980, **84**, 177.
59. J.P.Fouassier, B.Tieke, and G.Wegner, Isr.J. Chem., 1979, **18**(3–4), 227.
60. C.Bubek, B.Tieke, and G.Wegner, Ber.Bunsenges. Phys.Chem., 1982, **86**, 499.
61. D.J.Ando, D.Bloor, C.L.Hubble, and R.L.Williams, Makromol.Chem., 1980, **181**, 453.
62. R.L.Williams, D.J.Ando, D.Bloor, and M.B.Hursthouse, Polymer, 1980, **21**, 1269.
63. D.Bloor, D.J.Ando, C.L.Hubble, and R.L.Williams, J.Polymer Sci., Polymer Phys.Ed., 1980, **18**, 779.
64. D.J.Ando, D.Bloor, and B.Tieke, Makromol.Chem. Rapid Comm., 1980, **1**, 385.
65. V.Enkelmann, Makromol.Chem., 1978, **179**, 2811.
66. A.R.McGhie, P.S.Kalyanaraman, and A.F.Garito, Mol.Cryst.Liq.Cryst., 1979, **50**(1–4), 287.
67. W.Newmann and H.Sixl, Chem.Phys., 1980, **50**, 273.
68. V.Enkelmann, G.Schleier, G.Wegner, H.Eichele, and M.Schwoerer, Chem.Phys.Letters, 1977, **52**, 314.
69. K.C.Yee and R.R.Chance, J.Polymer Sci., Polymer Phys.Ed., 1978, **16**, 431.
70. V.Enkelmann, R.J.Leyrer, G.Schleier, and G.Wegner, J.Mater.Sci., 1980, **15**(1), 168.
71. Y.Hori and L.D.Kispert, J.Chem.Phys., 1978, **69**, 3826.
72. C.Bubek, W.Hersel, W.Newmann, H.Sixl, and J.Waldmann, Chem.Phys., 1980, **51**, 1.
73. R.Huber, M.Schwoerer, C.Bubek, and H.Sixl, Chem.Phys.Letters, 1978, **53**, 35.
74. W.Hartl and M.Schwoerer, Chem.Phys., 1982, **69**, 443.
75. W.Hersel, H.Sixl, and G.Wegner, Chem.Phys. Letters, 1980, **73**, 288.
76. C.Bubek, H.Sixl, and H.C.Wolf, Chem.Phys., 1978, **32**, 231.

77. R.Huber and M.Schwoerer, Chem.Phys.Letters, 1980, **72**, 10.
78. W.Newmann and H.Sixl, Chem.Phys., 1981, **58**, 303.
79. H.Niederwald, K.H.Richter, W.Güttler, and M.Schwoerer, Mol.Cryst.Liq.Cryst., 1983, **93**, 247.
80. H.B.Bhattacharjee and G.N.Patel, J.Photochem., 1981, **16**(2), 85.
81. M.L.Shand and R.R.Chance, J.Chem.Phys., 1982, **76**, 5834.
82. R.R.Chance and M.L.Shand, J.Chem.Phys., 1980, **72**, 948.
83. A.Prock, M.L.Shand, and R.R.Chance, Macromolecules, 1982, **15**, 238.
84. R.Mondong and H.Bässler, Chem.Phys.Letters, 1981, **78**, 371.
85. F.Braunschweig and H.Bässler, Chem.Phys.Letters, 1982, **90**, 41.
86. C.Bubek, B.Tieke and G.Wegner, Ber.Bunsenges. Phys.Chem., 1982, **86**, 495.
87. G.N.Patel, Rad.Phys.Chem., 1981, **18**, 913.
88. H.Gross, H.Sixl, C.Kröhnke, and V.Enkelmann, Chem.Phys.1980, **45**, 15.
89. R.R.Chance, G.N.Patel, and J.D.Witt, J.Chem. Phys., 1979, **71**, 206.
90. G.N.Patel and E.K.Walsh, J.Polymer Sci.Polymer Letters.Ed., 1979, **17**, 203.
91. K.Se, H.Ohmura, and T.Kotaka, Polymer J.(Tokyo), 1982, **14**, 895.
92. C.Plachetta and R.C.Schulz, Makromol.Chem.Rapid. Comm., 1982, **3**, 815.
93. D.Bloor, D.N.Batchelder, D.J.Ando, R.T.Read, and R.J.Young, J.Polymer Sci., Polymer Phys.Ed., 1981, **19**, 321.
94. A.A.Ovchinnikov, I.I.Ukrainskii, and G.F.Kventsel', Uspekhi.Fiz.Nauk, 1972, **108**, 81.
95. I.I.Ukrainskii, Phys.Stat.Solidi, 1981, **B106**, 55.
96. R.H.Baughman and R.R.Chance, J.Polymer Sci., Polymer Phys.Ed., 1976, **14**, 2037.
97. E.G.Wilson, J.Phys.C: Solid State Phys., 1975, **8**, 727.
98. D.E.Parry, Chem.Phys.Letters, 1976, **43**, 597.
99. M.-H.Whangbo, R.Hoffmann, and R.B.Woodward, Proc.Roy.Soc., 1979, **A366**, 23.
100. D.S.Boudreaux and R.R.Chance, Chem.Phys. Letters, 1977, **51**, 273.
101. D.S.Boudreaux, Chem.Phys.Letters, 1976, **38**, 341.
102. K.Balasubramanian and D.R.Yarkony, Chem.Phys. Letters, 1980, **70**, 374.
103. D.E.Parry, Chem.Phys.Letters, 1977, **46**, 605.
104. D.R.Yarkony, Chem.Phys., 1978, **33**, 171.
105. M.R.Philpott, Chem.Phys.Letters, 1977, **50**, 18.
106. U.Dinur and M.Karplus, Chem.Phys.Letters, 1982, **88**, 171.
107. M.Kertész, J.Koller, and A.Azman, Chem.Phys., 1978, **27**, 273.
108. M.Kertész, Chem.Phys.Letters, 1978, **56**, 18.
109. F.Jagodic, J.Koller, M.Kertész, and A.Azman, Prepr. Short Comm.IUPAC, 1979, Macro Mainz, **3**, 1483.
110. A.J.Karpfen, Phys.C: Solid State Phys., 1980, **13**, 5673.
111. J.L.Brédas, R.R.Chance, R.Silbey, G.Nicolas, and P.Durand, J.Chem.Phys., 1981, **75**, 255.
112. J.L.Brédas, R.R.Chance, R.H.Baughman, and R.Silbey, J.Chem.Phys., 1982, **76**, 3673.
113. A.A.Berlin, G.A.Vinogradov, and A.A.Ovchinnikov, J.Macromol.Sci.-Chem., 1977, **A1**, 1701.
114. D.Bloor, D.J.Ando, F.H.Preston, and G.C.Stevens, Chem.Phys.Letters, 1974, **24**, 407.
115. R.J.Hood, H.Müller, C.J.Eckhardt, R.R.Chance, and K.C.Yee, Chem.Phys.Letters, 1978, **54**, 295.
116. D.Bloor and F.H.Preston, Phys.Stat.Solidi, 1976, **A37**, 427.
117. H.Müller, C.J.Eckhardt, R.R.Chance, and R.H.Baughman, Chem.Phys.Letters, 1977, **50**, 22.
118. H.Eckhardt, C.J.Eckhardt, and K.C.Yee, J.Chem. Phys., 1979, **70**, 5498.
119. D.Bloor, L.Koski, G.C.Stevens, F.H.Preston, and D.J.Ando, J.Mater.Sci., 1975, **10**, 1678.
120. G.N.Patel, R.R.Chance, and J.D.Witt, J.Polymer Sci., Polymer Letters Ed., 1978, **16**, 607.
121. G.N.Patel, R.R.Chance, and J.D.Witt, J.Chem.Phys., 1979, **70**, 4387.
122. C.J.Eckhardt, H.Müller, and R.R.Chance, Mol. Cryst.Liq.Cryst., 1980, **52**(1–4), 269.
123. B.Reimer, H.Bässler, J.Hesse, and G.Weiser, Phys.Stat.Solidi, 1976, **B73**, 709.
124. D.Bloor, Chem.Phys.Letters, 1976, **42**, 174.
125. D.Bloor, W.Hersel, and D.N.Batchelder, Chem. Phys.Letters, 1976, **45**, 411.
126. D.Bloor, F.H.Preston, and D.J.Ando, Chem.Phys. Letters, 1976, **38**, 33.
127. R.R.Chance and R.H.Baughman, J.Chem.Phys., 1976, **64**, 3889.
128. B.Reimer and H.Bässler, Phys.Stat.Solidi, 1975, **A32**, 435.
129. M.R.Philpott and J.D.Swallen, J.Chem.Phys., 1978, **69**, 2912.
130. M.R.Philpott, A.Brillante, I.R.Pockrand, and J.D.Swallen, Mol.Cryst.Liq.Cryst., 1979, **50**(1–4), 139.
131. K.Higaya, Kagaku To Kogyo (Tokyo), 1980, **33**(5), 349; Ref.Zhur.Khim., 1980, 24S91.
132. L.Sebastian and G.Weiser, Chem.Phys.Letters, 1979, **64**, 396.
133. L.Sebastian and G.Weiser, Phys.Rev.Letters, 1981, **46**, 1156.
134. L.Sebastian and G.Weiser, Chem.Phys., 1981, **62**, 447.
135. D.Bloor and F.H.Preston, Phys.Stat.Solidi, 1977, **A39**, 607.
136. C.J.Eckhardt, H.Müller, J.Tylicki, and R.R.Chance, J.Chem.Phys., 1976, **65**, 4311.
137. H.Müller and C.J.Eckhardt, J.Chem.Phys., 1977, **67**, 5386.
138. D.N.Batchelder and D.Bloor, Chem.Phys.Letters, 1976, **38**, 37.
139. R.R.Chance, K.C.Yee, R.H.Baughman, H.Eckhardt, and C.J.Eckhardt, J.Polymer Sci., Polymer Phys. Ed., 1980, **18**, 1651.
140. V.Enkelmann and G.Wegner, Makromol.Chem., 1977, **178**, 635.
141. V.Enkelmann, Acta Cryst., 1977, **B33**, 2842.
142. D.Bloor, D.N.Fisher, D.N.Batchelder, R.Kennedy, A.C.Cottle, and W.F.Lewis, Mol.Cryst.Liq.Cryst., 1979, **52**(1–4), 83.
143. D.Bloor and R.Kennedy, J.Chem.Phys., 1980, **47**, 1.
144. I.Engeln and M.Meissner, J.Polymer Sci. Polymer Phys.Ed., 1980, **18**, 2227.
145. B.Reimer, H.Bässler, and T.Debaerdemaeker, Chem.Phys.Letters, 1976, **43**, 85.
146. K.C.Yee, J.Org.Chem., 1979, **44**, 2571.
147. C.Cojan, G.P.Agrawal, and C.Flytzanis, Phys.Rev., 1977, **B15**, 909.

148. G.P.Agrawal, C.Cojan, and C.Flytzanis, Phys. Rev.Letters, 1977, **38**, 711.
149. C.Flytzanis, C.Cojan, and G.P.Agrawal, Nuovo Cim., 1977, **B39**, 488.
150. I.Hatta, T.Nakayama, and T.Matsuda, Phys.Stat. Solidi, 1980, **A62**, 243.
151. P.Robin, J.P.Pouget, R.Comes, and A.Moradpour, J.Phys., 1980, **41**, 415.
152. P.Robin, J.P.Pouget, R.Comes, and A.Moradpour, Chem.Phys.Letters, 1980, **71**, 217.
153. M.Bertault, M.Krauzman, M.Le Poctollec, R.M.Pick, and M.Schott, J.Phys., 1982, **43**, 755.
154. J.N.Patillon, P.Robin, P.A.Albouy, J.P.Pouget, and R.Comes, Mol.Cryst.Liq.Cryst., 1981, **76**(3–4), 297.
155. D.Q.Xiao, D.J.Ando, and D.Bloor, Chem.Phys. Letters, 1982, **90**, 247.
156. Z.Iqbal, R.R.Chance, and R.H.Baughman, J.Chem. Phys., 1977, **66**, 5520.
157. H.Müller and C.J.Eckhardt, Mol.Cryst.Liq.Cryst., 1978, **45**(3–4), 313.
158. R.R.Chance, R.H.Baughman, H.Müller, and C.J.Eckhardt, J.Chem.Phys., 1977, **67**, 3616.
159. G.J.Exarhos, W.M.Risen, and R.H.Baughman, J.Amer.Chem.Soc., 1976, **98**, 481.
160. R.J.Kennedy, I.F.Chalmers, and D.Bloor, Makromol. Chem., Rapid Comm., 1980, **1**, 357.
161. G.N.Patel, J.D.Witt, and Y.P.Khanna, J.Polymer Sci., Polymer Phys.Ed., 1980, **18**, 1383.
162. G.N.Patel and Y.P.Khanna, J.Polymer Sci., Polymer Phys.Ed., 1980, **18**, 2209.
163. G.N.Patel and Y.P.Khanna, J.Polymer Sci., Polymer Phys.Ed., 1982, **20**, 1029.
164. Y.P.Khanna and G.N.Patel, Amer.Chem.Soc., Polymer Prepr., 1979, **20**(2), 457.
165. G.N.Patel, Amer.Chem.Soc., Polymer Prepr., 1979, **20**(2), 452.
166. J.H.Krieger, Chem.Eng.News, 1980, **58**(31), 24.
167. G.N.Patel, R.R.Chance, and J.D.Witt, Amer.Chem. Soc., Polymer Prepr., 1978, **19**, 160.
168. R.R.Chance, *Macromolecules*, 1980, **13**, 396.
169. H.B.Bhattacharjee, A.F.Preziosi, and G.N.Patel, J.Chem.Phys., 1980, **73**, 1478.
170. H.B.Bhattacharjee, A.F.Preziosi, and G.N.Patel, Amer.Chem.Soc., Polymer Prepr., 1980, **21**(2), 168.
171. R.R.Chance, M.L.Shand, M.Le Poctollec, and M.Schott, J.Polymer Sci., Polymer Letters, Ed., 1981, **19**, 529.
172. M.L.Shand, R.R.Chance, M.Le Poctollec, and M.Schott, Phys.Rev., 1982, **B25**, 4431.
173. D.Bloor and C.L.Hubble, Chem.Phys.Letters, 1978, **56**, 89.
174. D.Bloor, D.N.Batchelder, and F.H.Preston, Phys. Stat.Solidi, 1977, **A40**, 279.
175. R.Jankowiak, J.Kalinowski, B.Reimer, and H.Bässler, Chem.Phys.Letters, 1978, **54**, 483.
176. V.Enkelmann, Amer.Chem.Soc., Polymer Prepr., 1978, **19**(2), 142.
177. W.F.Lewis and D.N.Batchelder, Chem.Phys.Letters, 1979, **60**, 232.
178. J.Duqueng, in "Non-Linear Spectroscopy" (Translated into Russian from English), Izd.Mir, Moscow, 1979, p.369.
179. G.P.Agrawal, C.Cojan, and C.Flytzanis, Phys.Rev., 1978, **B17**, 776.
180. C.Sauteret, J.Hermann, R.Frey, F.Pradere, J.Ducuing, R.H.Baughman, R.R.Chance, Phys. Rev.Letters, 1976, **36**, 956.
181. M.L.Shand, R.R.Chance, R.Silbey, Chem.Phys. Letters, 1979, **64**, 448.
182. M.L.Shand and R.R.Chance, J.Chem.Phys., 1978, **69**, 4482.
183. R.R.Chance, M.L.Shand, C.Hogg, and R.Silbey, Phys.Rev., 1980, **B22**, 3540.
184. R.R.Chance, M.L.Shand, and R.H.Baughman, Amer.Chem.Soc., Polymer Prepr. No.2, 1982, **23**, 141.
185. M.Lequime and J.P.Hermann, Chem.Phys., 1977, **26**, 431.
186. C.J.Horner and A.F.Garito, Makromol.Chem., 1981, **181**, 19.
187. C.J.Horner, A.F.Garito, and K.N.Desai, Makromol. Chem., 1981, **182**, 1363.
188. A.F.Garito, K.D.Singer, K.Hayes, G.F.Lipscomb, S.J.Lalama, and K.N.Desai, J.Opt.Soc.Amer., 1980, **70**, 1399.
189. J.E.Sohn and A.F.Garito, Makromol.Chem., 1980, **180**, 2975.
190. C.W.Pitt and L.M.Walpita, Thin Solid Films, 1980, **68**, 101.
191. C.Bubek, H.Sixl, D.Bloor, and G.Wegner, Chem. Phys.Letters, 1979, **63**, 574.
192. G.C.Stevens and D.Bloor, Phys.Stat.Solidi, 1978, **A45**, 483.
193. G.C.Stevens and D.Bloor, Phys.Stat.Solidi, 1978, **A46**, 619.
194. D.Bloor, in "Magnetic Resonance and Related Phenomena" (Edited by H.Brunner), Gr.Ampere, Geneva, 1977, p.47.
195. A.R.Bishop, Solid State Comm., 1980, **33**, 955.
196. W.Schermann and G.Wegner, Makromol.Chem., 1974, **175**, 667.
197. W.Spannring and H.Bässler, Ber.Bunsenges.Phys. Chem., 1979, **83**, 433.
198. A.S.Siddiqui and E.G.Wilson, J.Phys.C: Solid State Phys., 1979, **12**, 4237.
199. D.Bloor, C.L.Hubble, and D.J.Ando, in "Molecular Metals" (Edited by W.E.Hatfield), Plenum Press, New York, 1979, p.243.
200. D.R.Day and J.B.Lando, J.Appl.Polymer Sci., 1981, **26**, 1605.
201. H.Nakanishi, K.Hasumi, F.Mizutani, M.Kato, K.Ichimura and F.Shoei, Sen'i Kobunshi Zairyo Kenkyusho Kenkyu Happyokai Shiryo, 1981(120), 92; Chem.Abs., 1982, **96**, 86250.
202. R.R.Chance, R.H.Baughman, R.J.Reucroft, and K.Takahashi, Chem.Phys., 1976, **13**, 181.
203. K.Lochner, B.Reimer, and H.Bässler, Chem.Phys. Letters, 1976, **41**, 388.
204. B.Reimer and H.Bässler, Chem.Phys.Letters, 1976, **43**, 81.
205. B.Reimer and H.Bässler, Phys.Stat.Solidi, 1978, **B95**, 145.
206. A.S.Siddiqui, J.Phys.C: Solid State Phys., 1980, **13**, L1079.
207. K.J.Donovan and E.G.Wilson, J.Phys.C: Solid State Phys., 1979, **12**, 4857.
208. W.Spannring and H.Bässler, Chem.Phys.Letters, 1981, **84**, 54.
209. K.J.Donovan and E.G.Wilson, Phil.Mag., 1981, **B44**, 9.
210. A.S.Siddiqui, J.Phys.C: Solid State Phys., 1982, **15**, L263.
211. B.Hupfer, H.Schupp, J.D.Andrade, and H.J.Ringsdorf, Electron Spectrosc.Relat.Phenom., 1981, **23**(1), 103.

212. R.J.Young and J.Petermann, J.Polymer Sci.Polymer Phys., Ed., 1982, **20**, 961.
213. A.S.Siddiqui, J.Phys.C: Solid State Phys., 1980, **13**, 2147.
214. E.G.Wilson, J.Phys.C: Solid State Phys., 1980, **13**, 2885.
215. E.G.Wilson, Chem.Phys.Letters, 1982, **90**, 221.
216. K.J.Donovan and E.G.Wilson, Phil.Mag., 1981, **B44**(1), 31.
217. K.Lochner, B.Reimer, and H.Bässler, Phys.Stat. Solidi, 1976, **B76**, 533.
218. S.Arnold, J.Chem.Phys., 1982, **76**, 3842.
219. K.Lochner, H.Bässler, L.Sebastian, G.Weiser, G.Wegner, and V.Enkelmann, Chem.Phys.Letters, 1981, **78**, 366.
220. D.Bloor, Physics Bulletin, 1978, **29**, 111.
221. D.Bloor, R.J.Kennedy, and D.N.Batchelder, J.Polymer Sci.Polymer Phys.Ed., 1978, **17**, 1355.
222. A.C.Cottle, W.F.Lewis, and D.N.Batchelder, J.Phys.C: Solid State Phys., 1978, **11**, 605.
223. D.N.Batchelder and D.Bloor, J.Polymer Sci., Polymer Phys.Ed., 1979, **17**, 569.
224. R.H.Baughman and K.C.Yee, J.Polymer Sci., Polymer Chem.Ed., 1974, **12**, 2467.
225. V.K.Mitra, W.M.Risen, and R.H.Baughman, J.Chem.Phys., 1977, **66**, 2731.
226. D.N.Batchelder, N.J.Poole, D.Bloor, Chem.Phys. Letters, 1981, **81**, 560.
227. H.Eichele, E.Herath, and C.Kröhnke, Chem.Phys. Letters, 1980, **71**, 211.
228. R.H.Baughman, H.Gleiter, and N.Sendfeld, J.Polymer Sci., Polymer Phys.Ed., 1975, **13**, 1871.
229. D.Bloor and A.C.Cottle, J.Mater.Sci., 1976, **11**, 1160.
230. R.J.Young and H.G.Zachmann, Makromol.Chem., 1981, **182**, 621.
231. D.N.Batchelder, J.Polymer Sci., Polymer Phys.Ed., 1976, **14**, 1235.
232. R.H.Baughman and E.A.Turi, J.Polymer Sci., Polymer Phys.Ed., 1973, **11**, 2453.
233. R.H.Baughman, J.Chem.Phys., 1973, **58**(7), 2976.
234. H.Kiess and R.Clarke, Phys.Stat.Solidi, 1978, **A49**(1), 133.
235. G.F.Lipscomb, A.F.Garito, and T.S.Wei, Ferroelectrics, 1980, **23**, 161.
236. G.E.Babbit and G.N.Patel, Macromolecules, 1981, **14**, 554.
237. D.Bloor, G.C.Stevens, P.J.Page, and P.M.Williams, Chem.Phys.Letters, 1975, **33**, 61.
238. J.Knecht, B.Reimer, and H.Bässler, Chem.Phys. Letters, 1977, **49**, 327.
239. J.Knecht and H.Bässler, Chem.Phys., 1978, **33**, 179.
240. G.C.Stevens, D.Bloor, and P.M.Williams, Chem. Phys., 1978, **28**, 399.
241. D.L.May and S.M.Gruner, J.Phys.C: Solid State Phys., 1982, **15**, L631.
242. G.N.Patel, Rad.Phys.Chem., 1979, **14**, 729.
243. G.N.Patel, A.F.Preziosi, and R.H.Baughman, US P.3999946 (1976); Chem.Abs. 1977, **87**, 44258.
244. G.N.Patel, US P.4189399 (1980); Chem.Abs., 1980, **92**, 223095.
245. K.C.Yee, A.F.Preziosi, G.N.Patel, G.G.Miller, and R.H.Baughman, European Patent EP.36899 (1982); Chem.Abs., 1982, **96**, 77587.
246. G.N.Patel and L.T.C.Lee, J.Macromol.Sci.-Phys., 1983, **B22**, 259.
247. G.N.Patel, Am.Inkmaker, 1981, **59**(6), 24; Chem.Abs., 1981, **95**, 99377.
248. G.G.Miller and G.N.Patel, J.Appl.Polymer Sci., 1979, **24**, 883.
249. K.H.Richter, W.Güttler, and M.Schwoerer, Chem. Phys.Letters, 1982, **92**, 4.
250. H.Niederwald, K.H.Richter, W.Güttler, and M.Schwoerer, Mol.Cryst.Liq.Cryst., 1983, **93**, 239.
251. A.F.Garito and K.D.Singer, Laser Focus, 1982, **18**, 59.
252. A.Barraud, Thin Solid Films, 1983, **99**, 317.
253. G.Fariss, J.B.Lando, and S.Richert, Thin Solid Films, p.305.
254. A.F.Garito, European Patent EP.22618 (1981); Chem.Abs., 1981, **95**, 88965.
255. E.G.Wilson, European Patent EP.77135 (1983); Chem.Abs., 1983, **99**, 14041.
256. A.F.Garito, European Patent EP.21695 (1981); Chem.Abs., 1981, **95**, 52501.
257. D.R.Day and H.Ringsdorf, J.Polymer Sci., Polymer Letters Ed., 1978, **16**, 205.
258. D.R.Day and H.Ringsdorf, Makromol.Chem., 1979, **180**, 1059.
259. D.R.Day and J.B.Lando, J.Polymer Sci., Polymer Phys.Ed., 1981, **19**, 165.
260. D.R.Day, H.Ringsdorf, and J.B.Lando, Amer. Chem.Soc., Polymer Prepr., 1978, **19**(2), 176.
261. D.R.Day and J.B.Lando, Macromolecules, 1980, **13**, 1483.
262. B.Tieke, G.Wegner, D.Naegele, and H.Ringsdorf, Angew.Chem.Int.Ed., 1976, **15**, 764.
263. B.Tieke, G.Lieser, and G.Wegner, J.Polymer Sci., Polymer Chem.Ed., 1979, **17**, 1631.
264. B.Tieke, V.Enkelmann, H.Kapp, G.Lieser, and G.Wegner, J.Macromol.Sci.-Chem., 1981, **A15**, 1045.
265. B.Tieke, V.Enkelmann, H.Kapp, G.Lieser, and G.Wegner, Org.Coat.Plast.Chem., 1980, **42**, 396.
266. R.C.Ledsham and P.Day, Chem.Comm., 1981, No.17, 921.
267. B.Tieke, G.Lieser, and K.Weiss, Thin Solid Films, 1983, **99**, 95.
268. B.Tieke and G.Lieser, J.Colloid Interface Sci., 1982, **88**, 471.
269. B.Tieke and G.Lieser, J.Colloid Interface Sci., 1981, **83**, 230.
270. G.Lieser, B.Tieke, and G.Wegner, Thin Solid Films, 1980, **68**, 77.
271. D.R.Day and J.B.Lando, Macromolecules, 1980, **13**, 1478.
272. V.Enkelmann, B.Tieke, H.Kapp, G.Lieser, and G.Wegner, Ber.Bunsenges.Phys.Chem., 1978, **82**, 876.
273. M.Sazkar and J.B.Lando, Thin Solid Films, 1983, **99**, 119.
274. S.E.Rickert, J.B.Lando, and S.Ching, Amer.Chem. Soc., Polymer Prepr., 1982, **23**(2), 139.
275. S.E.Rickert, J.B.Lando, and S.Ching, Mol.Cryst. Liq.Cryst., 1983, **93**, 307.
276. B.Tieke and D.Bloor, Makromol.Chem., 1981, **182**, 133.
277. B.Tieke and D.Bloor, Makromol.Chem., 1979, **180**, 2275.
278. B.Tieke and G.Wegner, Makromol.Chem., 1978, **179**, 1639.
279. H.Schupp, B.Hupfer, R.A.Van Wagenen, J.D.Andrade, and H.Ringsdorf, Colloid Polymer Sci., 1982, **260**, 262.
280. S.C.Steele, M.N.Wybourne, and D.Möbius, Thin Solid Films, 1983, **99**, 117.

281. F.Grunfeld and C.W.Pitt, Thin Solid Films, 1983, **99**, 249.
282. F.Kajzar and J.Messier, Thin Solid Films, p.109.
283. L.Von Gros, H.Ringsdorf, and H.Schupp, Angew. Chem., 1981, **93**, 311.
284. H.H.Hub, B.Hupfer, H.Koch, and H.Ringsdorf, J.Macromol.Sci.-Chem., 1981, **A15**, 701.
285. M.Pons, D.S.Johnstone, and D.Chapman, Biochem. Biophys.Acta, 1982, **693**, 461.
286. E.Lopez, D.F.O'Brien, and T.H.Whitesides, Biochem.Biophys.Acta, 1982, p.437.
287. M.Pons, D.S.Johnstone, and D.Chapman, J.Polymer Sci., Polymer Chem.Ed., 1982, **20**, 513.
288. E.Lopez, D.F.O'Brien, and Th.H.Whitesides, J.Amer. Chem.Soc., 1982, **104**, 305.
289. R.Büschl, B.Hupfer, and H.Ringsdorf, Makromol. Chem., Rapid Comm., 1982, **3**, 589.

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