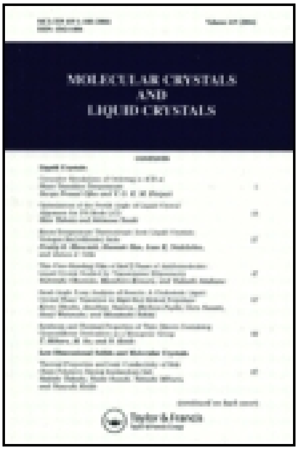

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Liquid-Crystal Polymers with Tolan Units

A. H. Al-dujaili [a] [b] , A. D. Jenkins [a] & D. R. M. Walton [a]

[a] School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ

[b] College of Education, University of Baghdad, Baghdad, Iraq

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Liquid-Crystal Polymers with Tolan Units

A. H. AL-DUJAILI,† A. D. JENKINS and D. R. M. WALTON

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ

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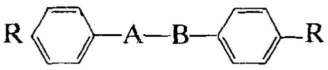
Liquid crystal polymers are reported in which the mesogen moiety has a truly linear structure, based on the diphenylacetylene (tolan) unit. The synthesis of a series of such polymers is described, and the properties of the products are discussed.

INTRODUCTION

The great majority of low molecular weight liquid-crystalline materials contain aromatic units and have the general structure



where A—B is —CH=CH—, —CH=N—, —C≡C—, —N=N, . . . etc.

The contribution of this type of structure to mesophase thermal stability appears to lie in its rigidity, linearity and polarisable π-electron density,[1] and the *p,p'*-disubstituted diphenylacetylene (tolan) [*i.e.*, (A—B) = —C≡C—] system is particularly favourable in these respects. Indeed, several studies have supported the expectation that tolan would form mesophases if substituted in the *p,p'*-positions with alkyl, alkoxy or cyano groups.[2-4]

Recently, we have reported[5] the synthesis of polymers based on

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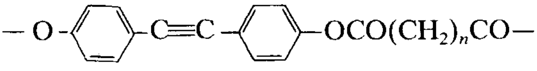
†Permanent address: College of Education, University of Baghdad, Baghdad, Iraq.

p,*p*′-dihydroxytolan and dibasic acid chlorides $ClCO(CH_2)_nCOCl$. These polymers are designated by the letter T, followed by subscript *n*, the number of methylene units in the diacid chloride. The polymers have the general structural formula:



(where $n = 4, 5, 6, 7, 8, 10, 12$)

Here we present the results of extensive investigations of these polymers, which have been characterized by the following methods: *a*) differential scanning calorimetry (DSC); *b*) optical polarising microscopy; *c*) X-ray diffraction analysis; *d*) the mutual miscibility method.

EXPERIMENTAL

All polymers were prepared from *p*,*p*′-dihydroxytolan and the appropriate diacid chloride by the interfacial polymerization procedure previously described.[5] Inherent viscosities were determined with a viscomatic MS type 5300 (Fica) viscometer at 30°C using polymer solutions (0.1–0.5 g) in a 60/40 mixture of phenol and tetrachloroethane (100 ml).

Thermal analysis was performed using a Perkin-Elmer DSC-2. A constant flow of nitrogen was maintained through the sample compartment and the usual rate of heating and cooling was 20 K min^{-1}. For the measurement of the enthalpy of transition, sample weights of 5–10 mg were chosen. Indium (ΔH 6.8 cal. g^{-1}; mp 156.6°C), zinc (ΔH 25.9 cal. g^{-1}; mp 419.0°C), and lead (ΔH 5.5 cal. g^{-1}; mp 327.5°C) of very high purity (99.99% standards) were used for temperature and ΔH calibration.

The optical observations were made using a Leitz polarising microscope Mettler FP2 equipped with heating stage and photographic camera. Some of these observations were performed by kind permission of Dr. M. R. Mackley at Cambridge University using a specially designed apparatus which allowed one to subject thin film samples of the polymers to controlled shear at elevated temperature while observing with an optical microscope.

X-ray diffraction spectra were obtained by the photographic method utilising a Debye-Scherrer method with a Phillips D1009 diffractometer using nickel-filtered CuK_α radiation. After the diffraction spectra were recorded for the unheated sample at room temperature, the sample tube was heated in a silicone oil bath a few degrees over the first phase transition temperature, and then cooled quickly to room temperature by immersing in an ice-water bath.

Differential Scanning Calorimetry

Table I provides characterization data for the tolan-based polymers. The inherent viscosities (column 2) show that all polymers formed have modest molecular weights. In order to avoid problems related to possible dependence of the phase transition temperature upon the molecular weight of the polymers, the samples were selected so as to have η_{inh} as near 0.3 dl. g^{-1} as possible.

The temperature given refers to the peak temperature of the endotherm observed upon a second heating of the polymer sample. The phase transition temperature accompanying the transformation of the polymer to the liquid crystal state is designated T_{K-N} or T_{K-S} and that to the isotropic phase T_{N-I} or T_{S-I}, and these are quoted in columns 3 and 5, respectively, in Table I. These are normally confirmed by the appearance of liquid-crystal and isotropic states in hot-stage microscopy. The temperatures given in columns 4 and 6 refer to the corresponding exotherms observed when the sample is cooled from the melt at 10 K min^{-1}; the T_{K1-K2} and T_{K2-K3} temperatures (columns 7 and 8) are also taken from the DSC thermogram and represent the solid-state transition temperatures. The temperature T_{N-I} or T_{S-I} (column 9) corresponds to the onset of the biphasic region as determined using the polarizing microscope.

All the DSC curves of previously untreated polymer samples showed multiple endotherms (Figure 1). The highest temperature in all cases (if no decomposition occurs) corresponds to the transition from a liquid-crystal phase to the isotropic phase. In cases of multiple transitions, it is presumed that the solid to liquid–crystal transition corresponds to the temperature at which evidence of fluidity is found by hot-stage microscopy. Multiple melting endotherms are fairly common for liquid-crystalline polyesters.[6] We have found that these multiple peaks are very sensitive to the annealing process and the heating rate of the polymer samples during the DSC scan.[7]

All the polymers described above exhibit enantiotropic liquid-crystal properties: the phase transition from the solid to the liquid-crystal phase and from the liquid-crystal phase to the isotropic phase occur reversibly, provided that the decomposition temperature of the sample is not reached. A typical continuous decrease in the phase-transition temperatures is found as the number of methylene units (*n*)

TABLE I

General characteristics of tolan homopolyesters

Polymer designation	η_{inh}[a] dL/g	T_{K-N} or T_{K-S} °C		T_{N-I} or T_{S-I} °C		T_{K1-K2} °C	T_{K2-K3} °C	microscopy T_{N-I} or T_{S-I} °C
		heating	cooling	heating	cooling			
T4	0.26	263	257	—[b]	—	64	100	250
T5	0.31	239	234	—	—	68	128	200
T6	0.32	305	301	362	—	257	277	230
T7	0.27	235	229	317	—	126	177	165
T8	0.20	247	233	350	341	111	244	220
T10	0.37	150	131	190	173	108	137	130
T12	0.13	147	135	179	141	111	136	125

[a] η_{inh} Measured on a 0.1–0.5 g/100 ml solution of samples in phenol/1,1,2,2-tetrachloroethane solvent mixture (vol. ratio 60/40) at 30°C.

[b] Signifies that the transition temperature is obscured by decomposition.

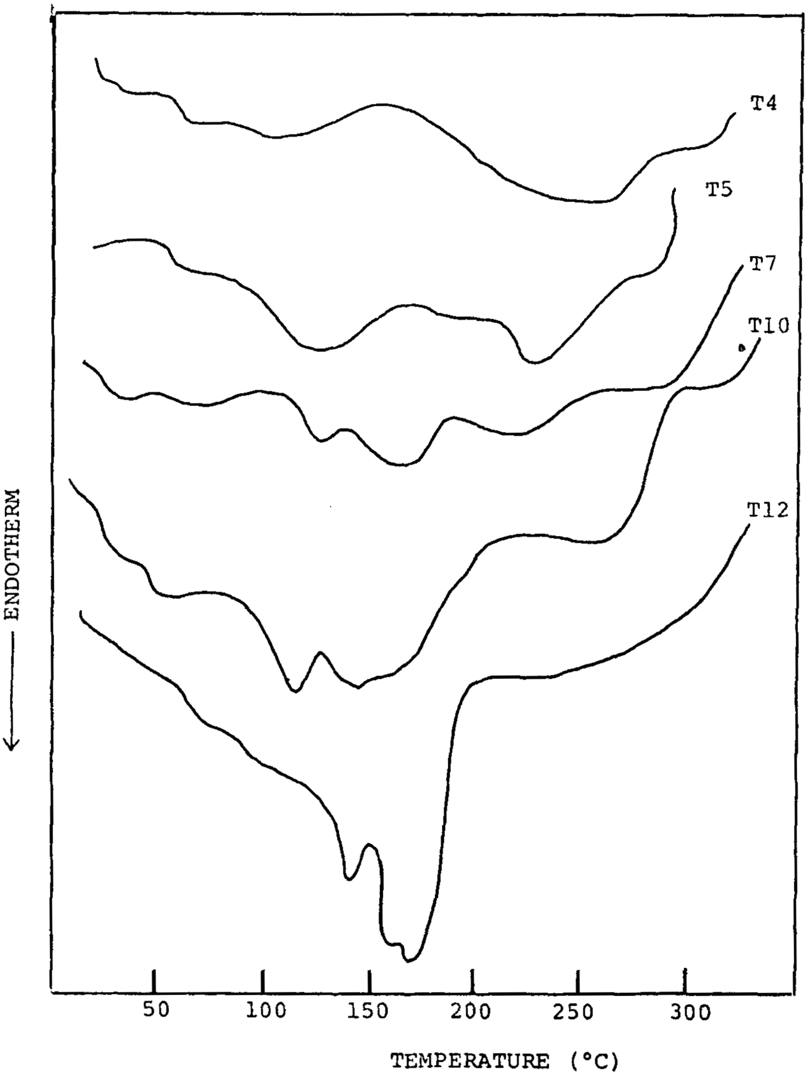


FIGURE 1 DSC thermograms of untreated samples of tolan polymers.

increases. Further, the phase transition temperatures are higher for polymers having an even number of methylene units than for those with an odd number, as shown in Figure 2, but there is no regular variation of the T_{N-I} temperatures with n. In addition, the thermal stability range of the mesophase, *i.e.*, the temperature range over which the liquid-crystal state exists, decreases as n increases. A similar

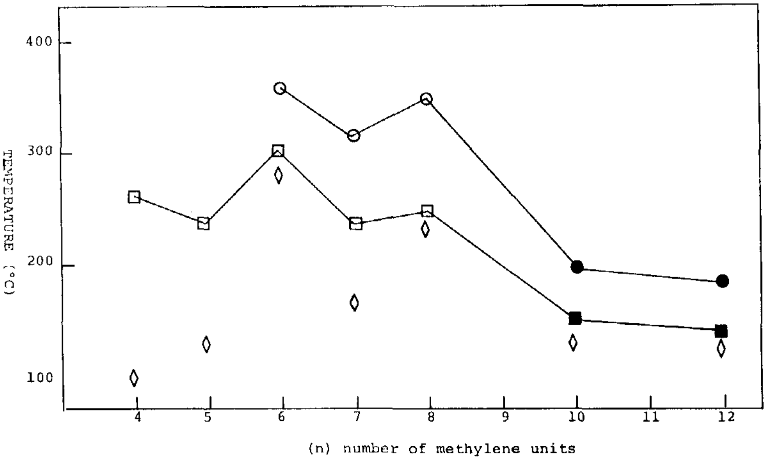


FIGURE 2 Transition temperatures T_{K-N} □ or T_{K-S} ■, T_{N-I} ○ or T_{S-I} ●, T_{K2-K3} ◇ as functions of the number of methylene units, n, in the dibasic acid for tolan homopolymers.

effect is found for small molecules.[1] The observation that the phase-transition and thermal stability temperatures decrease upon increasing the number of the flexible spacers may be attributed qualitatively to decreasing polarity and molecular rigidity with increase in the hydrocarbon character.

The thermodynamic properties of the tolan polymers are listed in Table II. The same subscript temperature notation is used to designate the corresponding enthalpy and entropy changes. For all tolan polymers, the melt-transition enthalpies were determined; for T8, T10 and T12 the isotropisation enthalpy was also measured.

Column 5 of Table II gives the values of ΔH_{total} which represents the total enthalpy change for the crystal to liquid–crystal transition. The ΔH_{total} steadily increased as the length of the flexible spacers, n, increased (discounting the slight odd-even effect). The higher ΔH_{total} values for the polymers T10 and T12 indicate that they have higher degrees of orientation in their mesophases than do those with shorter flexible spacers, *i.e.*, $n \leq 8$.

Figure 3 shows the general trend of the enthalpies when plotted as functions of the number of methylene units in the dibasic acid. ΔH_{K-N} (ΔH_{K-S}) increases smoothly while ($\Delta H_{K1-K2} + \Delta H_{K2-K3}$) decreases as n increases. By contrast, ΔH_{K1-K2} is small and is almost independent of n.

Entropy changes for first-order transitions were also calculated and the data for ΔH_{total} are given in column 9, Table II. The average

TABLE II

Thermodynamic properties of tolan polymers

Polymer designation	ΔH_{K1-K2}[a]	ΔH_{K2-K3}	ΔH_{K-N} or ΔH_{K-S}	ΔH_{total}	ΔS_{K1-K2}[b]	ΔS_{K2-K3}	ΔS_{K-N} or ΔS_{K-S}	ΔS_{total}	ΔH_{N-I} or ΔH_{S-I}	ΔS_{N-I} or ΔS_{S-I}
T4			0.21	0.21			0.37	0.37		
T5	0.25	0.30	0.31	0.86	0.73	0.74	0.61	2.08		
T6	0.18	0.28	0.44	0.90	0.34	0.51	0.76	1.61		
T7	0.24	0.10	0.65	0.99	0.60	0.22	1.28	2.10		
T8	0.24	0.11	0.73	1.08	0.69	0.21	1.40	2.30	0.60	0.96
T10	0.27	0.12	0.85	1.25	0.71	0.29	2.00	3.00	0.90	1.94
T12		0.21	1.34[c]	1.55		0.51	2.96	2.47	2.20[c]	4.87

[a] Transition enthalpies are given in kcal per mole of repeating unit. The data are reproducible from sample to sample within 10%.

[b] Transition entropies are given in units of cal $mol^{-1}K^{-1}$.

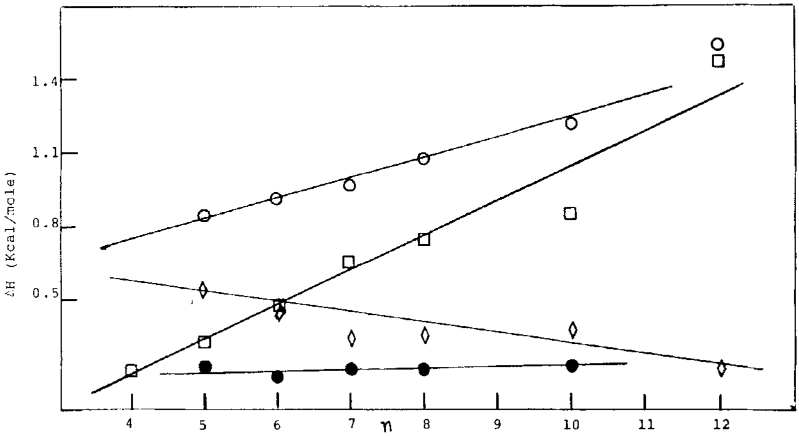


FIGURE 3 Enthalpy changes (● ΔH_{K1-K2}), (◇ $\Delta H_{K1-K2} + \Delta H_{K2-K3}$), (○ ΔH_{total}) and (□ ΔH_{K-N} or ΔH_{K-S}) for the tolan polymers plotted as functions of the number of methylene units (n) in the diacid chlorides.

ΔS_{total} value for polymers T4 to T8 equals 1.4 cal/mol^{-1} K^{-1} and, for the last two polymers, 2.8 cal/mol^{-1} K^{-1}. For T10 and T12, the value is 3.4 cal/mol^{-1} K^{-1} for the isotropisation entropy compared with 0.96 cal/mol^{-1} K^{-1} for T8, indicating that T10 and T12 have more ordered mesophases than the others. This result probably reflects increasing conformational entropy for the molecules in the isotropic phase as the length of the flexible units is increased.

Generally, the enthalpy change associated with polymer melting is very dependent on the thermal history of the sample. For virgin samples, or when the molten polymer has been cooled at different rates, the melting endotherm is very variable, and no thermal effect could accurately be measured. The isotropisation of the liquid–crystal state was, on the contrary, readily detectable, and the isotropisation temperature and molar enthalpy changes appear to be independent of any thermal manipulation of the sample.

Krigbaum and Watanabe[8] reported that the average ΔH_{N-I} or ΔH_{S-I} values for some mesomorphic polymers with flexible spacers in the main-chain typically correspond to nematic properties, whilst others reflect a smectic mesophase. The average value given for a nematic mesophase is 0.66 kcal/mol^{-1} and for a low-order smectic (*e.g.*, S_A) 1.4 kcal/mol^{-1}; that for a high-order smectic (S_H) is 4.8 kcal/mol^{-1}. If we consider our polymer T8 to be a representative example of the T4–T8 series, the average value, 0.60 kcal/mol^{-1} is close to that reported for nematics, while the average value for T10 and T12 is 1.55 kcal/mol^{-1}, in good agreement with that for low-order smectic mesophases.

Texture Observations

The textures observed using the polarizing microscope show that every polymer is unique; nevertheless, on the basis of the texture observations, the tolan polymers can be divided into two groups; T4–T8, and T10 and T12. These two groups will be discussed with special reference to their own characteristic textures, then in terms of general group character.

The first interesting feature of the texture observations is that, at room temperature, the polymers show the dense, *schlieren*-like texture (Figure 4). As the temperature increases, evidence of fluidity is seen and the polymer spontaneously gives rise to an anisotropic fluid with a birefringent background. However, the number of *schlieren* decreases with increase in the temperature; indeed there is a strong tendency for them to shrink and, to a greater extent, disappear. As the polymer reaches the T_{N-I} temperature, it adopts a homeotropic state. Thus, under crossed polars, this texture appears dark, resembling a pseudo-isotropic phase; however, slight shearing of the sample disrupts the homeotropic texture and produces bright flow lines with an extreme birefringent region. Upon release of the shearing, the

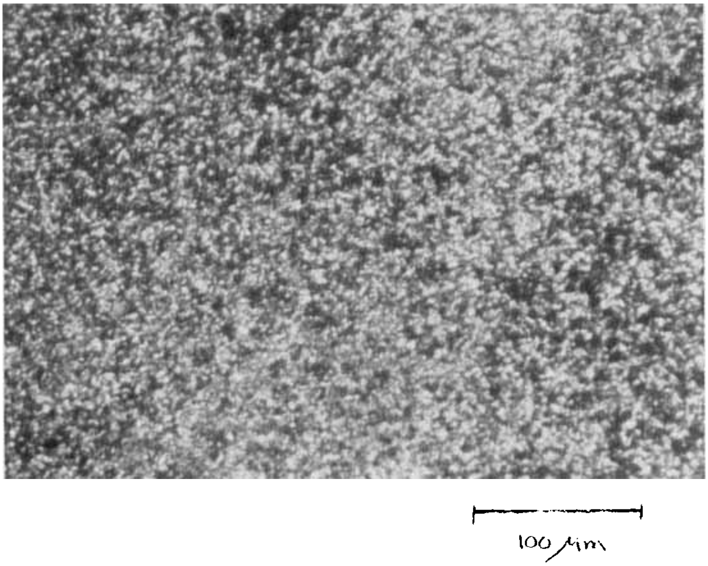


FIGURE 4 *Schlieren* texture of T4 at room temperature. See Color Plate I.

dark homeotropic texture reforms; sometimes it shows no *schlieren* and exhibits a homogeneous color over large areas when viewed between crossed polars. When the sample is cooled to room temperature, the uniform dense *schlieren*-like texture reforms.

Mackley *et al.*[9] have reported optical microscopic observations for a thermotropic copolyester, and recently Graziano and Mackley[10] also have reported such observations for a copolyester prepared from chlorophenylene terephthalate and bisphenoxyethane carboxylate (50/50 mole %). As these authors have pointed out, the core and behavior of these *schlieren* depend mainly on the induced shear and temperature. As the shear rate is increased, the thread-like structures break into short, dark, curled entities, which flow along the streamlines whilst continuously changing their shapes. (They call the texture dominated by these entities the "worm texture.") The density of these worms increases as the shear rate increases. By increasing the shear rate, a transformation to a more ordered texture occurs, especially at lower temperatures. Our observations agree well with the above description.

In studies of the optical texture of low molecular weight liquid crystal materials, threads are associated with the existence of point singularities known as disclinations. The optical characteristics of the *schlieren* texture consist of dark brushes which start from point singularities. These point singularities are characterized by the parameter S = number of brushes/4. There are points with four or two dark brushes. The sign of the point is positive when brushes orient in the same direction as the rotated polarisers, and negative when they turn in the opposite direction.[11,12]

The texture illustrated in Figure 5 for T7 was taken at high magnification. The *schlieren* show a striking similarity to textures observed in nematic phases of low molecular mass materials. It seems that the point singularities of T7 are consistent with a disclination of strength ∓ 1. However, it is difficult to ascertain which of these possibilities was actually present. It is interesting to note that in polymer nematic mesophases, disclinations of singularities $S = \mp 1$ are generally preferred to others.

It is worth emphasizing again that the homeotropic state of our polymer is uniquely associated with the nematic structure near T_{N-I}. In fact, above this temperature, the number of chain ends probably increases, which may favor homeotropic orientation. As suggested by Meyer,[13] one can describe a perfect ideal polymer nematic as composed of infinite chains, in which each chain end can be considered as a defect. If macromolecular chains are infinite, *i.e.*,

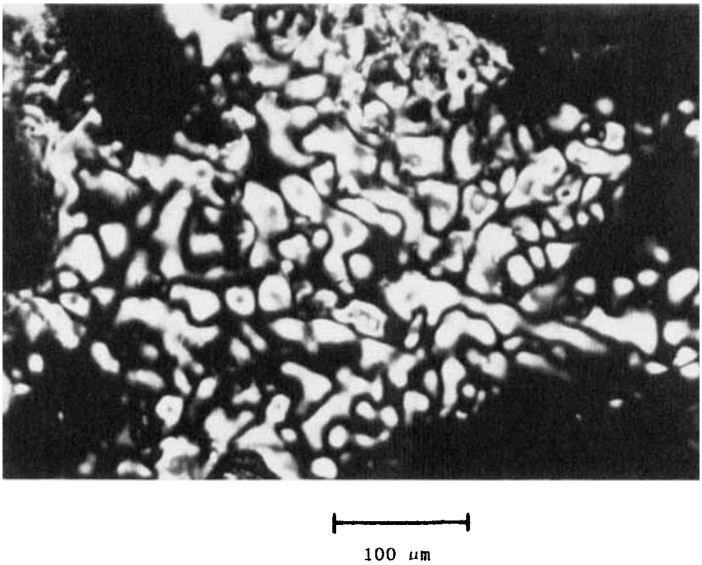


FIGURE 5 Nematic *schlieren* texture of the quenched melt of T7 (between crossed polars). **See Color Plate II.**

without ends, they must lie parallel to the adjacent glass surfaces for energetic reasons. For finite, but long macromolecules, entropy tends to keep chain ends "dissolved" in the bulk rather than "condensed" on the surfaces. On the other hand, short chains, *i.e.*, abundant chain ends, may favor a homeotropic texture. Indeed, while entropy tends to distribute chain ends randomly, energy tends to place them so as to relieve strains.

The final feature is the observation of polyphase transitions in biphasic regions. Figure 6 illustrates the changes which occur for polymer T6 with increasing temperature in the biphasic region.

Figure 6a illustrates the quiescent texture which is characteristic of the *schlieren* regime; Figure 6b shows the black regions of the homeotropic phase which appear at the onset of the biphasic region, and which increase in area until complete conversion to the homeotropic phase (Figure 6c shows only a portion of the *schlieren* texture remaining at 180°C). Figure 6d illustrates the cooling of the T6 sample to 100°C, and the thread-like texture reforming as bands of threads.

This behavior might be related to two factors. Firstly, the molecular weight distribution in the polymer, *i.e.* the polydispersity. The polymer was prepared using the interfacial method, which normally gives rise to high average molecular weight,[14] but the polymer inevitably comprises a wide range of molecular chain lengths. Then, according

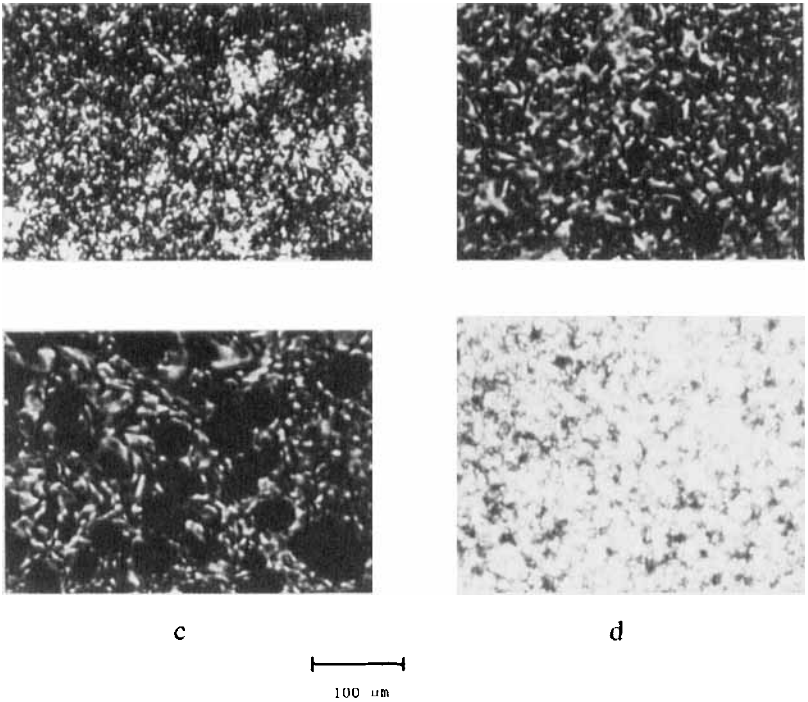


FIGURE 6 Texture variation for T6 in the biphasic region. *Schlieren* texture at *a*) 150°C *b*) 160°C *c*) homotropic islands with some homogeneous regions at 180°C, and *d*) *schlieren* texture formed on cooling from the homeotropic state at 100°C.
See Color Plate III.

to our optical observations, the long chains would prefer the planar texture, while the others would tend to favor the homeotropic texture (see Meyer's suggestion *vide supra*). A well-fractionated sample might allow a more quantitative determination of the relationship to be made between molecular weight and the texture observations.

Secondly, the occurrence of polyphase behavior for low molar mass materials often provides evidence for one or more transitions, *i.e.* of the smectic mesophase. As shown by X-ray and miscibility techniques, in these polymers only one phase exists. We conclude that the transition seen in T7 and T6 involves a second crystalline morphology.

Although the optical observations for these polymers display large differences compared to low molar mass nematics (probably due to the difference in molecular structures), the texture of the polymers resembles the familiar nematic type, and can be used to characterize the mesophase, especially as all the polymers show a large number of *schlieren* and have a marked tendency to be homeotropic. It is our belief that main-chain liquid-crystal materials, with molecular weights large enough to be considered as polymers, will not readily exhibit textures characteristic of low molar mass liquid crystals.

The textures observed for T_{10} and T_{12} indicated mesophases different from those of the other polymers (T4–T8). The texture is a mixture of birefringent areas and extinct bands, or sometimes bands of *schlieren* spread over a region several microns wide. On heating the samples, the polymer melts formed were very viscous, so that the flow temperature was difficult to detect with any degree of accuracy. Nevertheless, in the liquid-crystal state, the polymers display a birefringent texture with broad, diffuse extinction bands (see Figure 7), which are preserved unchanged up to the isotropisation point. Note that there is no indication of the occurrence of the homeotropic state. The general observation of a relatively viscous liquid-crystal phase suggests, to a certain extent, that this phase in these polymers can be considered to be smectic, despite its lack of clear textural identity. However, additional characterisation studies may provide more definitive information which is necessary if these polymers are fully to be characterized.

X-ray Diffraction

X-ray diffraction patterns have mainly been analysed according to methods devised by de Vries[15] based on low molecular weight liquid crystalline materials, and some liquid crystal polymers do not fit the de Vries classification.[16]

The positions of reflections are converted into an interplanar spacing by means of the de Vries modification of the Bragg equation:

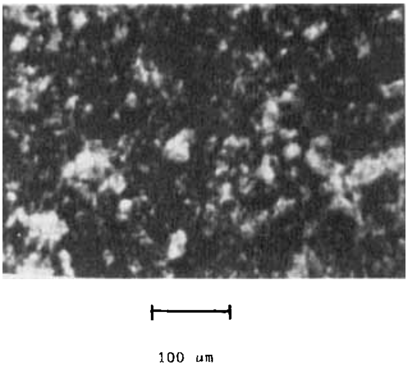


FIGURE 7 The texture of T10 viewed at room temperature. See Color Plate IV.

$2d\sin\theta = 1.117\,\lambda$. This equation has been used successfully[17] for cases of nematic and smectic mesophases with no preferred orientation of the molecules.

The lattice distances obtained for the original polymer powder and for quenched samples, along with a visual indication of their intensities, are listed in Table III. The original T4–T8 samples each showed only a few diffraction rings (Figure 8), typical of semicrystalline polymers. These correspond to a low degree of crystallinity compared to the diffraction patterns found with T10 and T12 (Figure 9). This is in accord with our previous texture observations which indicate that the latter polymers appear more viscous than the T4–T8 polymers, probably because they have a higher degree of order.

The X-ray diffraction patterns of samples T4–T8 quenched from the liquid crystal state indicate that there is no crystallinity present. There is a very strong diffuse halo with an observable maximum at about 4.8 Å and a second weak inner reflection (T8 for example) at room temperature corresponding to a spacing of 22.7 Å. This value correlates very well with the length of the T8 repeating unit in its most highly extended conformation, as calculated on the basis of expected average values for bond angles and bond length, *i.e.*, 23.2 Å.[18] The largest *d*-value calculated from the inner ring of the quenched

TABLE III

The X-ray diffraction spacings *d* of the tolan polymers

Polymer designation	Crystalline state at room temperature *d*Å	Liquid-crystal state quenched from the melt *d*Å
T4	4.72(s) 5.74(m) 18.17(w)	4.88(halo) 15.0(w)
T5	4.52(s) 6.00(m) 19.43(m)	4.91(halo) 15.2(w)
T6	5.1(s) 6.50(m) 20.69(w)	4.81(halo) 15.4(w)
T7	4.49(s) 4.9(s) 21.95(m)	4.87(halo) 15.5(w)
T8	4.46(s) 4.96(s) 22.70(m)	4.96(halo) 15.7(w)
T10	2.44(w) 3.19(vw) 3.66(vw) 4.46(vs) 4.90(vs) 24.1(s)	4.79 (sharp halo) 18.15(s)
T12	2.34(w) 3.43(vw) 45.2(vs) 4.90(vs) 8.57(w) 25.9(vw)	4.76 (sharp halo) 19.15 (s)

Symbols: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

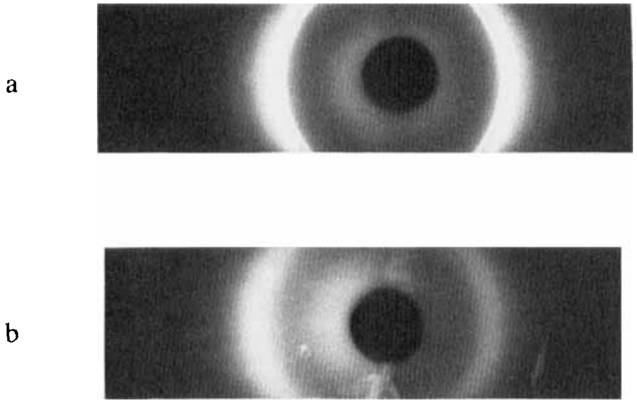


FIGURE 8 X-Ray diffraction patterns of polymer T4; *a*) diffraction pattern of the original sample, *b*) diffraction pattern of the quenched sample.

sample corresponds to 15.7 Å, less than the length of the repeating unit, indicating that the flexible methylene units were not in a fully extended conformation in the nematic state.

The X-ray diffraction pattern of T12 like that of T10, shows a considerable degree of crystallinity at room temperature. The inner ring corresponds to a molecular length spacing of 25.9 Å. This is shorter than the calculated length of the T12 repeating unit in its fully extended state (28.25 Å); 19.15 Å, the molecular length of the quenched sample, is much less than the calculated value. Hence, in the smectic

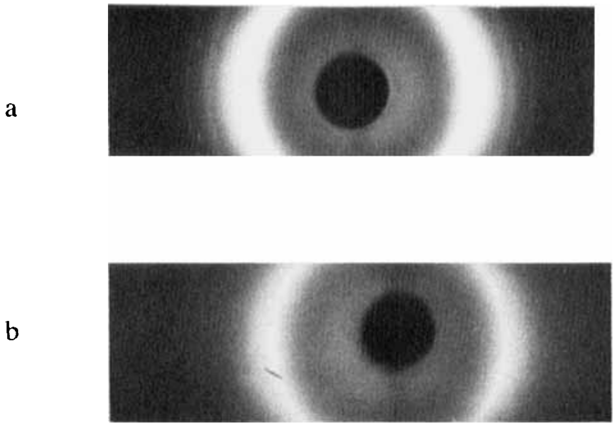


FIGURE 9 X-Ray diffraction patterns of polymer T10; *a*) diffraction pattern of T10 at room temperature, *b*) diffraction pattern of T10 from the quenched melt.

state, either the repeating units are tilted with respect to the layer normal, or the flexible spacers do not exist in their fully extended all-*trans*-conformation. Diffraction patterns of this sample are typical of the S_A or S_C polymorphic forms; the repeating units are normal to the layer in S_A and tilted in the S_C polymorphs. Our miscibility study indicates that the smectic type is S_C; it is likely, therefore, that the methylene chains of the dibasic acid make an angle with respect to the layer normal. Fayolle *et al.*[19] reported a spacing of the S_C phase of the polyester based on a terphenyl unit (polymer C) smaller than the fully extended length of the repeating unit, indicating that the S_C configuration is azimuthally disordered with the layers orientationally ordered.

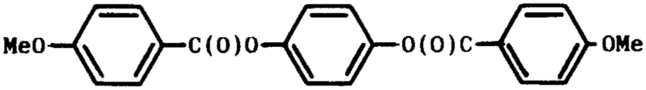
In the low-molecular weight homologous series of *p,p'*-alkoxy disubstituted tolans, the compounds having four to eight methylene units show nematic behavior, while those with ten show S_C behavior.[3] This phenomenon is echoed in the polymer state, *i.e.* T4–T8 are nematic, while T10 and T12 are S_C. Thus the liquid crystal behavior of the low molar mass compounds can directly be related to the mesomorphic properties of the polymers having equivalent structures, *i.e.*, there is a continuum of mesomorphic behavior from small molecules to polymers.

Miscibility Studies

The mixing of known mesogens with uncharacterized liquid crystal materials has been developed as a basis for the identification of liquid crystal phases in low molar mass liquid crystal systems by Sackmann and Demus.[20,21]

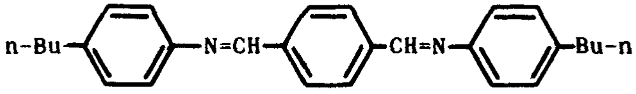
Blends of polymeric with non-polymeric liquid-crystal compounds can also, in principle, give such information.[8,22] T8 and T10 were chosen for the mutual miscibility method, since an indication from the optical observations and X-ray diffraction data suggested that T8 was nematic while T10 was smectic.

The reference compounds were chosen so as to exhibit a nematic phase in one case [*p*-phenylene-*bis*(4-methoxybenzoate)] PBMB,



K 127°C N 310°C I

and three smectic phases in addition to a nematic phase, in the other [terphthal-*bis*(4-*n*-butylaniline)] TBBA.



L 113°C S_H 144°C S_C 172°C S_A 199°C N 263°C I

The two reference compounds were prepared and gave the correct elemental analyses and phase transition temperatures.[23,24]

Samples of known composition were prepared by mixing accurate weights of the polymer and the reference compound. The mixture was homogenized by heating to the isotropic state, mixed vigorously at that temperature, and subsequently cooled to room temperature and ground into a fine powder. The phase diagram of this powder was determined by DSC. The maximum point of the melting endotherm was taken as the transition temperature.

The phase diagram shown in Figure 10 for a mixture of T8 with PBMB indicates a typical binary system with both compounds exhibiting nematic phases, in addition to crystal and isotropic phases. The crystal/nematic transition curve shows a eutectic at 12.8% T8

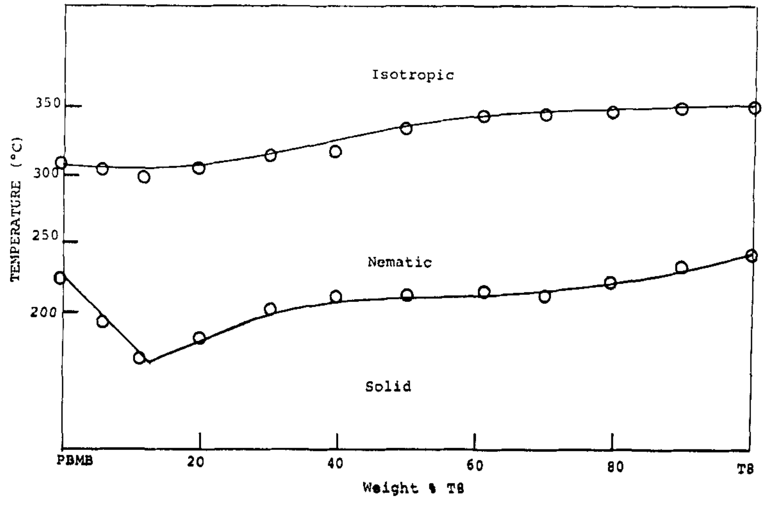


FIGURE 10 Isobaric phase diagram of the polymer T8 with the reference compound PBMB.

composition by weight, while the nematic isotropic curve is nearly linear. Mixtures of T8 and TBBA were also made in order to prove that the nematogenic polymer was miscible only with the nematic phase and not with the smectic phases of TBBA. Some miscibility studies suggest that the phase in T8 can be considered to be nematic, despite its lack of obvious textural identity.

The X-ray diffraction data indicate that T10 polymer is either an S_A or S_C mesophase, and some preliminary miscibility studies suggest that it is S_C.

The vast difference in viscosity features of the components in systems with complete miscibility appears to decrease generally from the nematic polymer to the smectic. The higher viscosity of T10 as compared to T8 seems to hamper diffusion and relaxation. When 10% of the former polymer was mixed with TBBA, three peaks completely disappeared from the DSC thermogram. The crystal–crystal and crystal–S_H phase transitions, which are beyond the temperature range of the liquid crystal state of the polymer, also disappear when the composition of the polymer reaches 70% T10, 30% TBBA. Microscopic examination of mixtures having compositions within this range indicates that T10 and TBBA do not flow beyond the crystal–smectic transition of the polymer. We think that the mobility of the polymers (especially those having modest molecular weight) still remains sufficient to enable us successfully to use the mutual miscibility method, at least to establish the nematic phase and low-order smectic phases, *i.e.*, S_A and S_C.

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