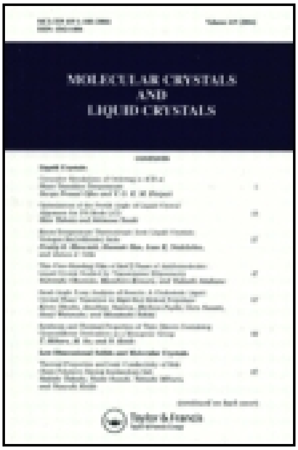

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Liquid-Crystal Polymers with p, p'-bis(hydroxyphenoxy)benzene and p, p'-bis(hydroxyphenoxy)biphenyl Units

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Liquid-Crystal Polymers with *p,p'*-bis(hydroxyphenoxy)benzene† and *p,p'*-bis(hydroxyphenoxy)biphenyl Units

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Liquid-crystal polymers are reported in which the mesogen is a *tris*(oxy-1,4-phenylene)[1] or a *bis*(hydroxyphenoxy)biphenyl unit. The synthesis of a series of such polymers is described, and the properties of the products are discussed.

INTRODUCTION

Liquid crystal polyesters with mesogenic groups and flexible spacers in the main-chain have been investigated recently.[2] The transition temperatures of such polymers from the solid to the liquid crystal state are usually very high. Many attempts have been made to obtain polymers with lower transition temperatures. For comb-like polymers, success has been achieved by introducing a flexible spacer between the main-chain backbone and the pendant mesogenic group.[3] It should also be possible to lower the transition temperatures of the main-chain type of polymers by introducing a flexible group adjacent to the rigid mesogenic molecules.

In our previous paper[1] we reported the synthesis of a new series of liquid crystal polymers which include *tris*(oxy-1,4-phenylene) units

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†In our previous paper[1] the name *tris*(oxy-1,4-phenylene) was used to denote this unit.

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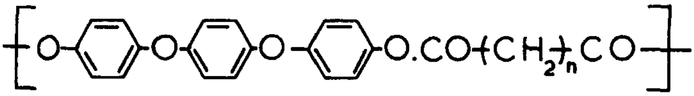
as the mesogenic unit; comparison was made with polymers containing triphenylene units as the mesogen, as prepared by Meurisse *et al.*,[4] to demonstrate the enhanced flexibility conferred on the structure by the inclusion of oxygen atoms between the aromatic rings.

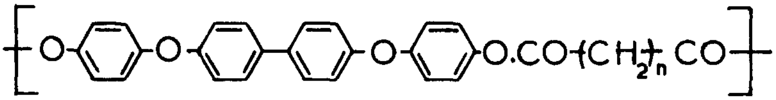
In this paper the investigation of these polymers by differential scanning calorimetry (DSC), polarising microscopy, X-ray diffraction and other methods is described. Further, a new system of liquid crystal polymers with *p,p'*-*bis*(hydroxyphenoxy)biphenyl units is reported and their properties are compared with those mentioned above.

Series I polymers contain *p,p'*-*bis*(hydroxyphenoxy)benzene units connected by a flexible polymethylene spacer, containing from two to eight methylene units. This polymer is designated TP*n*, where *n* is the number of methylene units, and has the following structural formula:



SERIES I

Polymers of Series II contain *p,p'*-*bis*(hydroxyphenoxy)biphenyl units, and either pentamethylene or octamethylene spacers; these polymers are designated TPB5 and TPB8, respectively and have the following structural formula:



SERIES II

The liquid crystal behavior of both series in relation to their structures was investigated to show the effect on physical properties of modifying the backbone mesogen units by: *a*) introduction of oxygen in the series TP*n*, which increases the degree of molecular rotational freedom, and *b*) the replacement of a phenylene by a biphenylene group in the series TPB*n*, which tends to decrease the degree of molecular rotational freedom, *i.e.*, to counteract the effect of the oxygen atoms.

CHARACTERIZATION OF TP*n* AND TPB*n*

All polymers in the two series are soluble in 1,1,2,2-tetrachloroethane (TCE), trifluoroacetic acid (TFA), and also in a mixture of 60/40 (w/w) TCE/phenol. The polymer compositions were confirmed by ^{1}H NMR spectroscopy, using TFA as solvent, and also by IR spectroscopy using KBr discs.

The characteristic features of these series are shown in the NMR spectrum of TP8 (Figure 1). The peaks at 8.51–8.53 ppm are assigned to the protons of the aromatic rings: two broad peaks at 2.91 ppm and 3.31 ppm and that at 4.16 ppm are ascribed to the protons of the methylene unit of the dibasic acid residue. The observed area ratio of the peaks provides values for polymer composition which tally with those expected from the parent monomer mixture.

The IR spectra of all the polymers showed no trace of hydroxy groups, thus indicating essentially complete reaction of the monomer.

The elemental analyses of the polymers verified the molecular structures and gave the percentages for C and H correct to within ±0.4%.

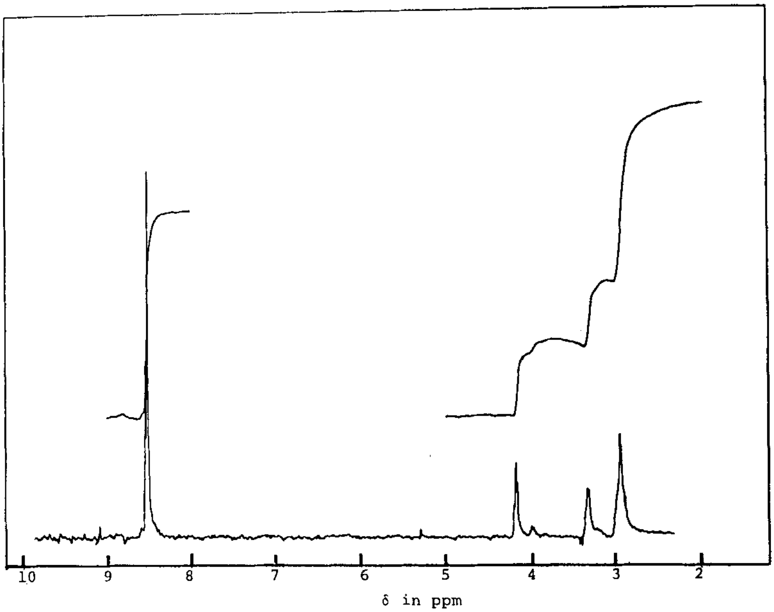


FIGURE 1 NMR spectrum of polymer TP8 (solvent: trifluoroacetic acid).

EXPERIMENTAL

Both series, TP*n* and TPB*n*, were prepared by the interfacial polymerization procedure previously described[1] using *p,p'-bis*(hydroxyphenoxy)benzene or *p,p'-bis*(hydroxyphenoxy)biphenyl as the sources of the mesogens.

Inherent viscosities were determined with a viscomatic MS type 5300 (Fica) Viscometer at 30°C using polymer solution (0.5 g) in 100 ml of 1,1,2,2-tetrachloroethane.

Thermal analysis was performed using a Perkin-Elmer DSC-2 differential scanning calorimeter. A constant flow of nitrogen was maintained through the sample compartment and the usual rate of heating and cooling was 20°K/min. For the measurement of the thermodynamic parameters, *i.e.*, (ΔH, ΔS), sample weights of 5–10 mg were chosen. Indium (ΔH 6.8 cal/g^{-1}; mp 156.6°C) of purity 99.99% was used for temperature and ΔH calibration. The traces shown correspond to reproducible heat-cycling behavior.

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

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

THERMAL ANALYSIS

Results of the DSC measurements on the polymers are presented in Table I, together with the inherent viscosities. The transition temperatures from the solid to the liquid crystal (smectic) state are labelled T_{K-S}, while T_{S-I} refers to the temperature of the transition to the isotropic state; the same subscript notation is used to designate the enthalpy and entropy changes which are given in columns 5, 6, 7 and 8.

TABLE I

Transition temperature and thermodynamic properties of the polymers TP*n* and TPB*n*

Polymer designation		T_{K-S} °C	T_{S-I} °C	ΔH_{K-S} (kcal/mol^{-1})	ΔS_{K-S} (cal/mol^{-1} K^{-1})	ΔH_{S-I} (kcal/mol^{-1} K^{-1})	ΔS_{S-I} (cal/mol^{-1} K^{-1})	$\Delta T = T_{S-I} - T_{K-S}$ (°C)
TP2	0.25	205	239	1.01	2.11	2.29	4.47	34
TP3	0.20	186	205	0.45	0.98	1.22	2.55	19
TP4	0.07	195	217	0.85	1.82	2.48	5.06	22
TP5	0.17	146	169	0.19	0.45	1.60	3.56	23
TP6	0.26	151	181	0.33	0.78	2.86	6.30	30
TP7	0.25	141	159	0.47	1.14	1.76	4.07	18
TP8	0.35	144	171	0.51	1.22	3.13	7.04	27
TPB5	0.18	228	267	1.10	2.20	1.72	3.19	39
TPB8	0.21	211	243	0.75	1.55	5.42	10.50	32

The transition temperatures for the TP*n* series are plotted as a function of the number of methylene units, as in a previous paper.[1] The narrowing of the mesophase interval, *i.e.*, ($\Delta T = T_{S-I} - T_{K-S}$), by comparison with the polymers of Meurisse *et al.*, which is indicative of the limited temperature range of the liquid crystal state, is clearly seen (column 9 in Table I). Thus, the introduction of oxygen atoms between the phenylene groups results in polymer melt properties which can be investigated without risk of thermal decomposition or oxidative degradation. The incorporation of oxygen atoms between the mesogenic units also solubilises the polymers. Unfortunately, the insertion of oxygen atoms produces a dramatic narrowing of the mesophase range. As we transfer from TP*n* series to TPB*n* series, we find that the longer rigid mesogenic groups in the latter polymers must be responsible for much enhanced thermal stability of the mesophases and increased phase transition temperatures.

Another point of interest is that the width of the thermal phase range (ΔT) is also greater for TPB*n*. Figure 2 allows comparison of the thermal stabilities of TP*n* and TPB*n* and the polymers of Meurisse *et al.*[4] containing triphenylene units, illustrating the narrow range of liquid crystallinity for the TP*n* series. This narrowing presumably arises from the dilution effect by both flexible units, *i.e.*, the oxygen atoms and the polymethylene chains in the central parts of the polymer molecules. The replacement of the phenylene unit in the TP*n*

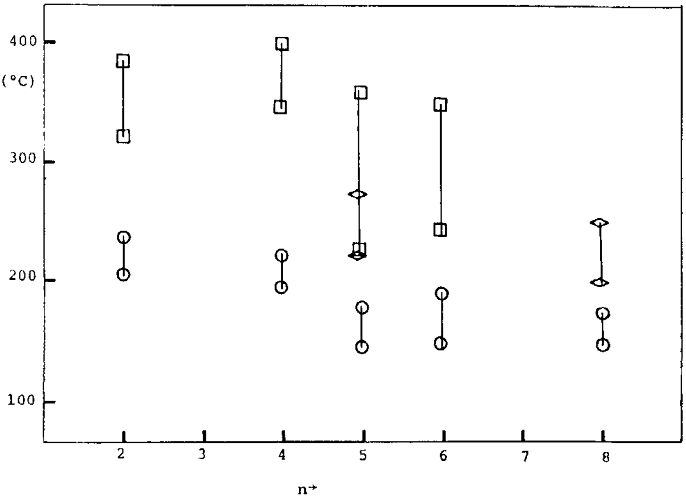


FIGURE 2 Comparison between the thermal stabilities of the Meurisse polymers[4] (□), and the polymers of the series TP*n*, (○) and TPB*n* (◇).

series by the biphenylene unit in TPB*n* series stabilises both the solid phase and the mesophase.

The isotropization entropies and enthalpies (ΔH_{S-I} and ΔS_{S-I}) increase in a zig-zag fashion with odd–even chain length alternation (Figure 3 and Figure 4). Those polymers with an even number of methylene groups (n) exhibit larger ΔH_{S-I} and ΔS_{S-I} values than those with an odd number. In contrast, the enthalpy of the crystal-to-smectic liquid crystal transition (ΔH_{K-S}) does not display a regular odd-even effect (Figure 5). This can be ascribed to polymorphism in the crystalline state, where crystals which have been subjected to different thermal treatments can exhibit different heats of transition when passing into the mesomorphic state.

The total molar isotropization entropy (ΔS_i) (the entropy changes accompanying the transition from the liquid crystal state) shows a marked increase with increasing length of flexible spacers for liquid crystal polymers exhibiting the smectic mesophase,[5] while only a very small progressive variation is observed, apart from the fluctuation due to the even-odd effect, when the only liquid crystal phase is nematic.[5] The higher order normally associated with smectic phases is probably responsible for the significantly higher ΔH_i and ΔS_i values, while molecular order in the nematic phase causes no marked variance in these parameters.

The average ΔS_{S-I} for the TP*n* series is approximately 4.72 cal/mol^{-1} K^{-1}, a value which is considerably larger than the average, 0.96 cal/mol^{-1} K^{-1}, reported[6] for the nematic phase of the tolan

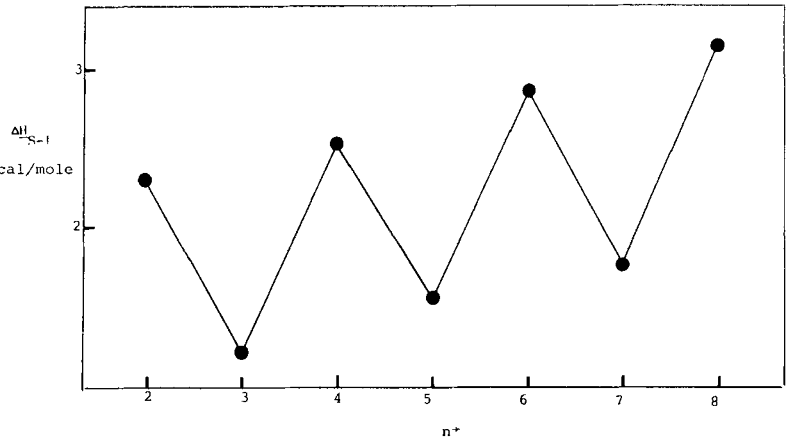


FIGURE 3 Effect of methylene chain length *n* on the liquid crystal–isotropic transition enthalpy (ΔH_{S-I}) for the TP*n* polymer series.

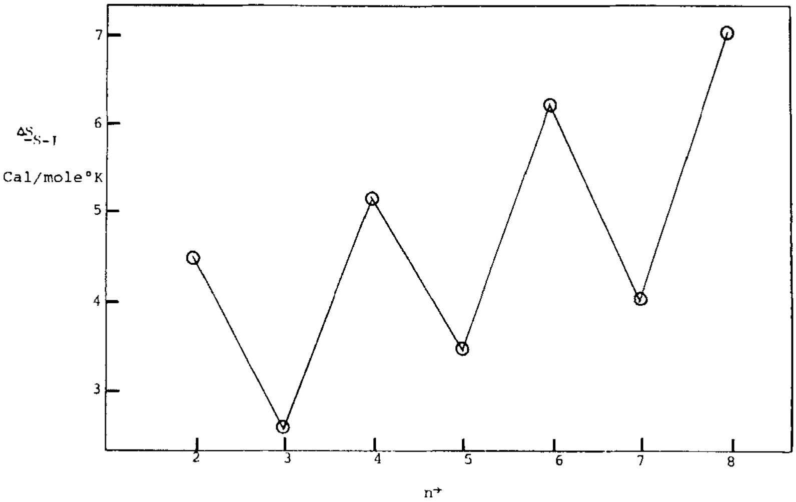


FIGURE 4 Effect of methylene chain length *n* on the liquid crystal–isotropic transition entropy (ΔS_{S-I}) for the TP*n* polymer series.

polymers. It is also higher than the average value for the smectic phase of the tolan polymers (T10 and T12),[6] *i.e.*, 2.95 cal/mol^{-1} K^{-1}. These comparisons indicate that the mesophase of the TP*n* polymer series is more highly ordered than the smectic C phase of T10 and T12.

Blumstein *et al.*[7] have reported thermodynamic data for *p,p'*-dihydroxy-2,2'-dimethylazoxybenzene-alkandioic acid polymers. These

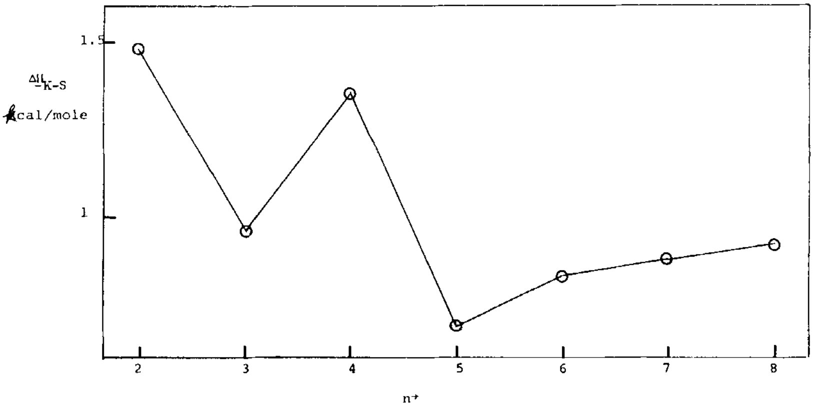


FIGURE 5 Effect of methylene chain length *n* on the crystal–liquid crystal transition enthalpy (ΔH_{K-S}) for the TP*n* polymer series.

polymers showed clear and regular odd-even effects in ΔH_i and ΔS_i values for the nematic–isotropic transitons. The calculated average increments $\Delta(\Delta H)$ and $\Delta(\Delta S)$ per methylene unit were 0.11 kcal/mol^{-1} and 0.36 cal/mol^{-1} K^{-1}, respectively. Higher values of $\Delta(\Delta H) = 0.43$ kcal/mol^{-1} and $\Delta(\Delta S) = 0.94$ cal/mol^{-1} K^{-1} were observed with TP*n* (calc. from Figure 3 and Figure 4), which also suggests a higher degree of order than the nematic mesophase of Blumstein's polymers.

An explanation of the odd-even alternation of the thermal properties of isotropization for low molecular weight liquid crystal mesophases has been given by Gray.[8] He attributed this effect to the regularly recurring properties of the *trans*-conformation derived from the thermodynamically stable zig-zag structure of the alkyl chain. However, it must not be forgotten that, in polymers, the aliphatic chains are connected at both ends to the mesogenic groups, and it has been suggested by Blumstein *et al.*[9] that this stability will propagate along the chain in both directions. For an even number of bonds (n = odd) this would lead to destructive interference and hence to lowering of the average ratio for *trans/gauche* conformers. For an odd number of bonds (n = even), constructive interference would prevail, strongly favoring the *trans*-conformers. Thus, one would expect a higher degree of extension and a far better alignment of the flexible aliphatic chains when n is even.

As expected, the ΔH_{S-I} and ΔS_{S-I} for the TPB*n* series are higher than those for the TP*n* series. The biphenylene unit increases the rigidity of the mesogen, leading to the formation of a less flexible structure.

TEXTURE OBSERVATIONS

The microscopic textures of the TP*n* and TPB*n* series were studied by polarizing microscopy. Generally, at room temperature, the annealed films made from the melt of a TP*n* polymer show liquid crystal like texture with a poor birefringence (Figure 6a). During heating, one observes that the polymer exists in a relatively viscous liquid crystal phase: there is little evidence of fluidity. Just below the isotropic point, the polymer starts to flow, forming groups of birefringent regions, in addition to regions of isotropic phase (Figure 6b); on further heating, the sample changes completely to the isotropic state. When the biphasic system is cooled to room temperature, one can distinguish two regions, the first resulting from the pre-isotropization isotropic islands having a poorly defined texture, and the second,

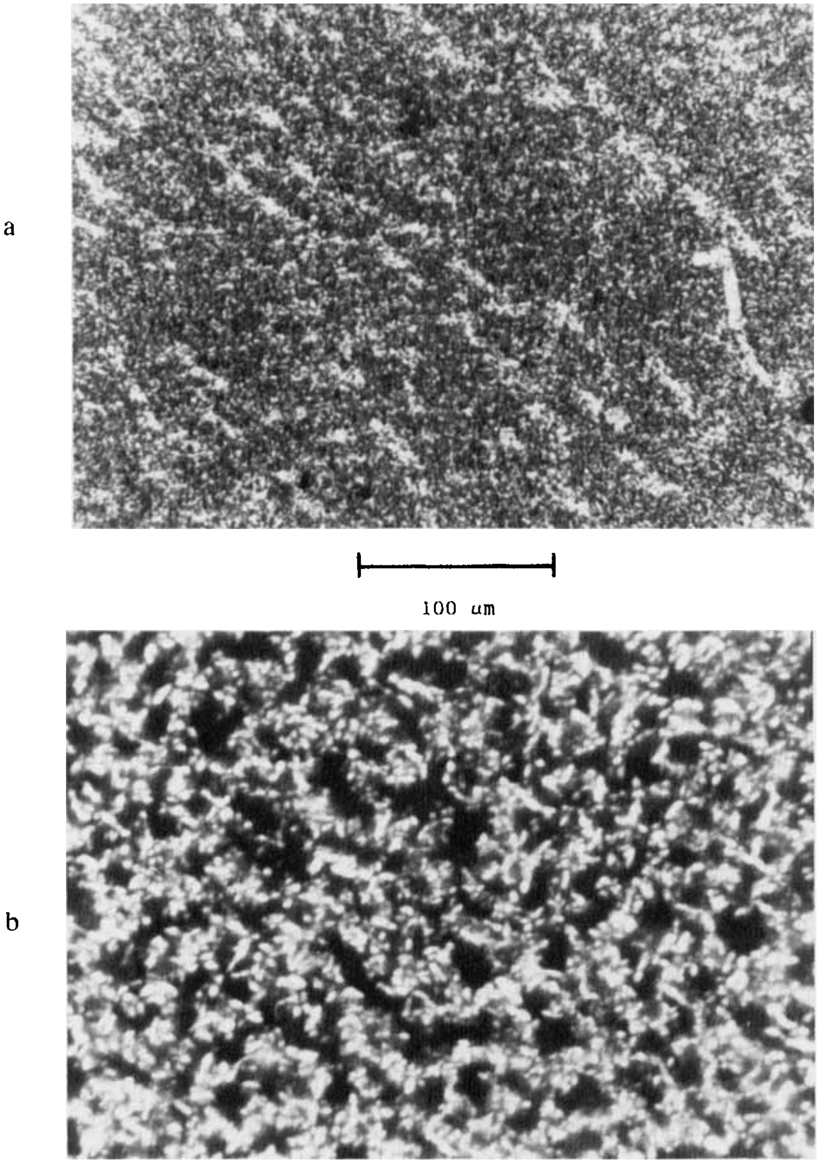


FIGURE 6 The optical texture of TP3 viewed between crossed polarisers *a*) at room temperature, *b*) at 195°C. **See Color Plate V. See Color Plate VB.**

arising from the birefringent areas, appearing as a region with enhanced birefringence.*

A very interesting feature shown by this series is that all the polymers, when cooled from the isotropic to the liquid crystal state, show a speckled texture. Figure 7a displays the speckled texture of TP4 at 150°C when cooled form the isotropic state at 220°C. If, during the cooling, a shearing force is applied by pressing down on the cover slip, a much more ordered texture results (striated texture, Figure 7b). Such a texture is generally seen with small liquid crystal molecules at temperatures immediately below the isotropic–smectic transition.[10] This is also called the myelinic or chevron texture. Meurisse *et al.*[4] have reported this texture for liquid crystal polymers forming smectic mesophases. The striations run parallel to the shear direction, and can probably be attributed to the high degree of order normally associated with the smectic phase.

On moving from the TP*n* to the TPB*n* series, one expects to see a well-defined texture, due to the increase in thermal stability, as indicated by the phase transition temperatures. In TPB8, the liquid crystal texture (Figure 8) appears to be better defined than that for the TP*n* series, and consists of a mixture of extinction bands and birefringent regions. On further heating, some isotropic regions appear, and at 243° the polymer is in its isotropic state. When the polymer is cooled from the isotropic state to 100°C, a continuous, homogeneous texture results, which is very similar to the so-called mosaic texture (which is normally seen in the higher ordered smectic mesophases of low molar mass mesogens), but with very much smaller domains Figure 9.

Figure 10 illustrates the texture of the TPB5 polymer after cooling from the isotropic state to room temperature. This resembles the spherulite texture which is frequently seen in conventional polymers, but with highly colored wedges; *i.e.*, it forms pseudospherulities.

Demus *et al.*[10] observed, for highly ordered smectic mesophases formed by the small liquid crystal molecules mentioned above, that this kind of texture may be regarded as formed by a special kind of spherulite. These spherulites are composed of assemblies of wedge-shaped material, each wedge having a different orientation and being defined by sharp boundaries. Close inspection of Figure 10 reveals a similarity between the above description and the spherulites appearing in our polymers.

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*Prof. H. R. Kricheldorf has pointed out to us that there is an alternative explanation of some of the textural observations. He believes that some of these systems may contain truly crystalline material together with an isotropic phase.

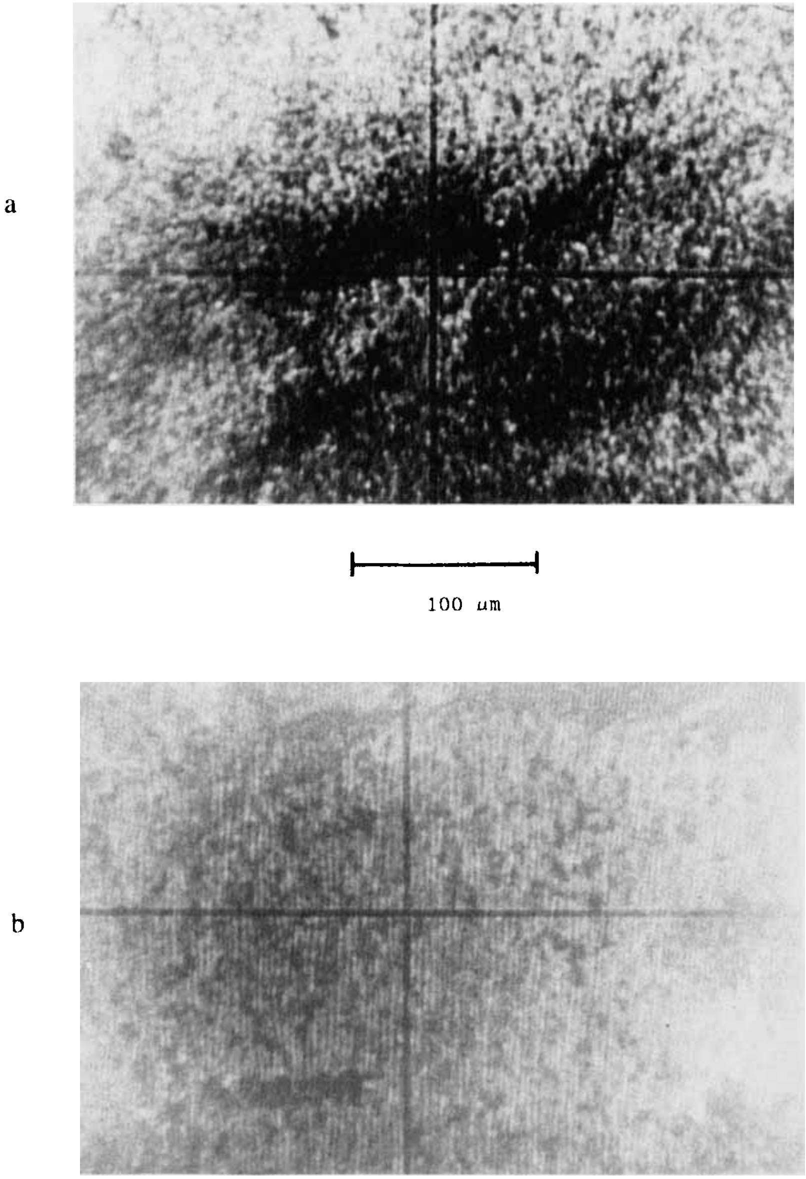


FIGURE 7 Photomicrographs of TP4 texture viewed between crossed polarisers on cooling from the isotropic state to a temperature of 190°C *a*) cooling without shearing, forming speckled texture; *b*) cooling with shearing, forming striated texture.

See Color Plate VI. See Color Plate VIB.

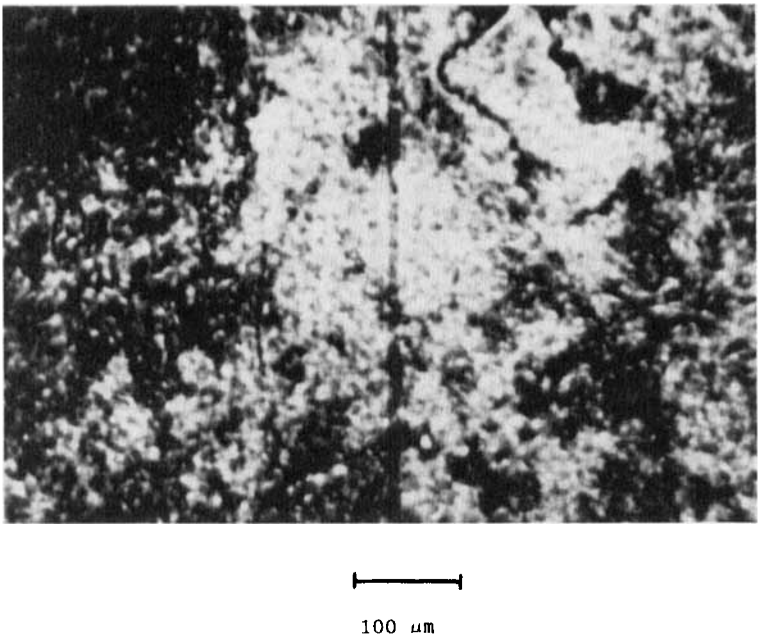


FIGURE 8 The texture of TPB8 (between crossed polarisers). **See Color Plate VII.**

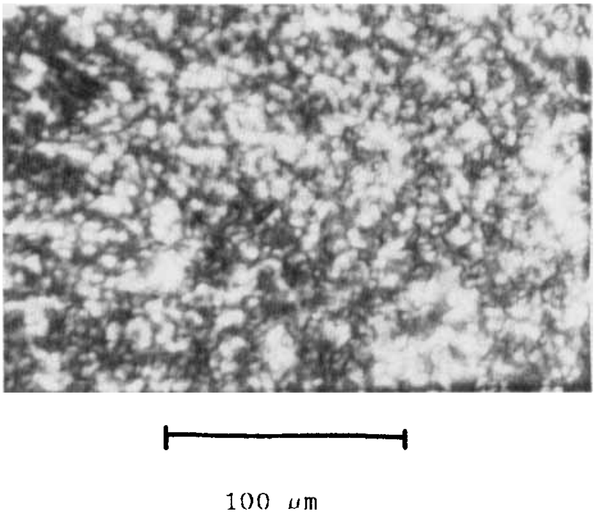


FIGURE 9 Uniform texture of TPB8 formed on cooling from the isotropic state (243°C) to about 100°C (between crossed polars). **See Color Plate VIII.**

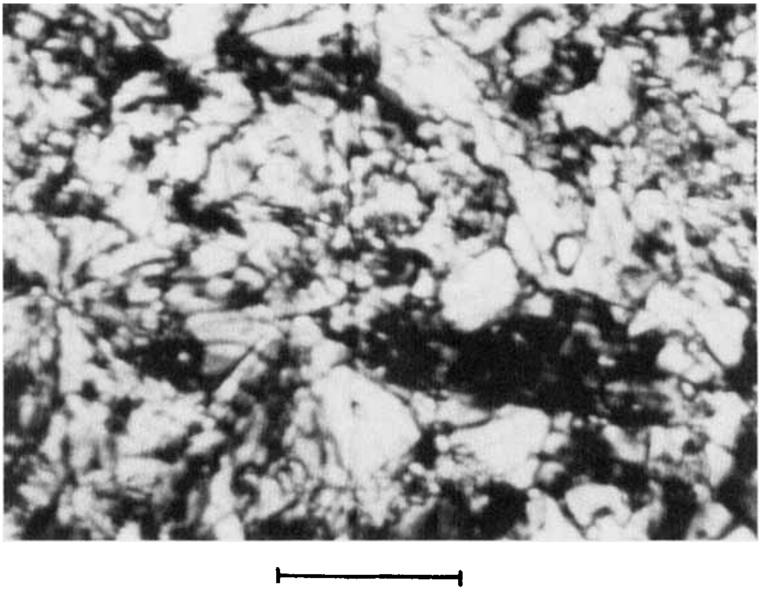


FIGURE 10 The pseudospherulitic texture of the TPB5 polymer formed after cooling from the isotropic state to room temperature. **See Color Plate IX.**

X-RAY DIFFRACTION

X-ray diffraction is a valuable and precise method for investigating mesophases. It provides information concerning the arrangement and mode of packing of the molecules and also the type of order present in the mesophase.

Table II gives the lattice distances and diffraction intensities for the TP*n* polymer powders at room temperature and for samples quenched from the liquid crystal state. The diffraction patterns of the polymers obtained after melting and subsequent cooling are identical, as far as the positions of reflections are concerned, but show intensity variations. Generally, when the polymer is heated above its isotropic point, the diffraction pattern shown in Figure 11 is recorded. As expected, a diffuse halo is obtained, since the polymer is in its amorphous liquid state. Figure 12 shows the diffraction patterns of the liquid crystal states of TP2 and TP5, which are normally the same for all the polymers.

TABLE II

X-ray diffraction spacings (*d*) of TP*n* polymer series with different thermal histories

Polymer designation	Thermally untreated samples at room temperature, *d*Å	Samples quenched from the liquid-crystalline state, *d*Å	Samples treated as indicated below, *d*Å	
TP2	4.48(s) 4.83(s) 5.15(vs) 14.52(w)	4.48(s) 4.82(s) 5.14(vs) 13.50(s)		
TP3	4.43(vs) 4.79(s) 5.10(vs) 15.00(s)	4.47(s) 5.16(vs) 14.63(s)	4.47(s) 5.16(vs) 15.10(w)[a]	
TP4	4.42(vs) 4.82(s) 5.04(vs) 15.70(w)	4.42(s) 4.80(s) 5.07(vs) 15.13(s)	4.70(halo)[b] 15.07(s) 14.60(vw)	4.44(s) 4.77(w)[c] 5.00(vs) 8.13(w)
TP5	4.46(s) 4.78(s) 5.10(vs) 16.48(s)	4.51(s) 5.26(vs) 15.80(s)	4.51(s) 4.18(vs) 16.01(s)	
TP6	4.44(vs) 4.80(s) 5.10(vs) 17.20(s)	4.48(s) 5.12(vs) 16.43(s)		
TP7	4.52(vs) 4.81(s) 5.13(vs) 17.80(s)	4.53(s) 5.15(vs) 17.20(s)		
TP8	4.47(s) 4.76(vs) 5.14(vs) 18.08(s)	4.50(s) 5.05(vs) 17.74(s)		
TPB5	4.43(s) 5.00(s) 5.16(vs) 17.63(w)	4.49(s) 5.08(vs) 14.47w		
TPB8	4.39(s) 4.90(s) 5.16(vs) 17.71(w)	4.46(s) 5.03(vs) 15.25(s)		

Symbols: vs = very strong; s = strong; m = medium. [a]samples annealed as liquid crystal for 1 h and then quenched to room temperature. [b]samples quenched from the isotropic state and [c]sample cooled from the liquid crystalline state.

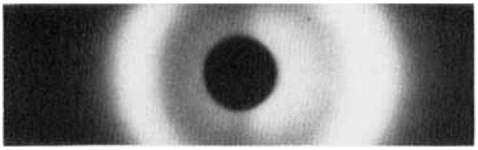


FIGURE 11 X-ray diffraction pattern of TP4 quenched from the isotropic state.

De Vries[11] has classified the smectic phases of liquid crystal materials, on the basis of the phase structure suggested by the appearance of the outer diffraction ring(s). Table III summarises the three classifications as follows.

Figure 12 shows the diffraction pattern typical of a TP5 sample heated to a temperature between T_{K-S} and T_{S-I} and then quenched to room temperature. Since the liquid crystal range is very narrow, many results were obtained by this method in order to make sure that the classification of the liquid crystal phase is correct. All the polymers show one sharp inner ring and two or three outer rings.

According to the De Vries classification, there are three kinds of smectic mesophases consistent with the appearance of two or more sharp outer reflections, *i.e.*, S_E, S_G, and S_H, which belong to class γ.

The Bragg spacing corresponding to the inner ring of the TP*n* smectic phase varies from 13.50 Å to 17.74 Å for TP2 and TP8, respectively, both significantly shorter than the fully extended length of the repeating unit (calculated to be 18.78 Å and 26.34 Å for TP2 and TP8, respectively). This indicates the presence of a tilted phase, which cannot therefore be an S_E phase.

The electron diffraction patterns of single crystals show lamellar structures which characterize the crystalline domain of these polymers. Herrmann[12] originally suggested that the molecules in mesophases rotate about their long axis, thus effectively creating cylindrical units, and that these cylinders are close-packed. Such packing would, in suitable cases, yield an hexagonal arrangement with the molecules stacked in the plane perpendicular to the long axis. Electron diffrac-

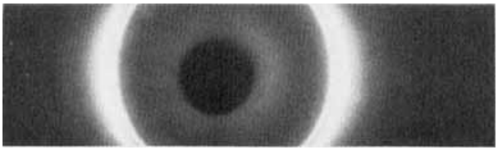


FIGURE 12 X-ray diffraction photographs of TP5 polymer quenched from the liquid crystal state.

TABLE III

Classification of smectic mesophases

Outer ring	Phase type	Class
Diffuse	A,C,E,D	α
Sharp, one	B	β
Sharp, several	E,G,H	γ

tion patterns (Figure 13) do, indeed, suggest hexagonal symmetry. Thus, we are dealing here with a smectic mesophase with hexagonal lateral packing.

From the above arguments we conclude that the smectic phase of both series is S_G rather than S_H. These phases, when investigated by X-ray scattering,[13] behave as very highly ordered systems more closely related to crystalline solids than isotropic liquids. They belong to the crystal smectic class, and this explains why our polymers have thermal properties which depend mainly upon the solid state rather than the isotropic state; it also explains the high viscosity of the mesophases.

Figure 14 shows the variation of the inner and outer ring dimensions for the smectic phase as a function of the number of methylene units (*n*) in the dibasic acid residue for the TP*n* series. As expected for this kind of mesophase, the outer reflections are independent of the value of *n*, while the inner ring spacing increases with increasing *n*.

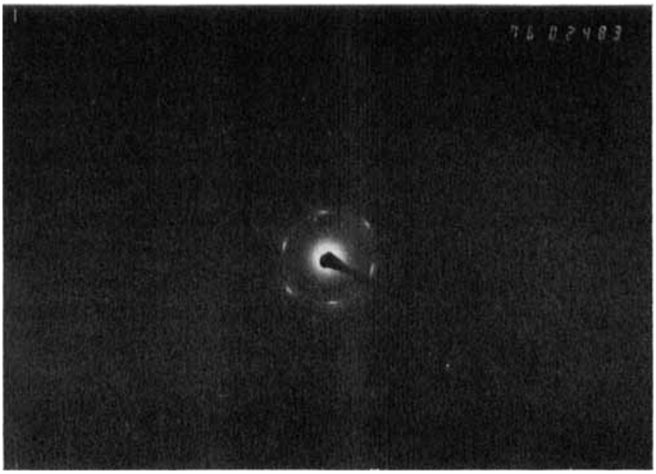


FIGURE 13 Electron diffraction photograph of the TP6 polymer. Diffraction from a few crystals with nearly identical orientation, indicating a hexagonal structure (cooled by liquid N_2).

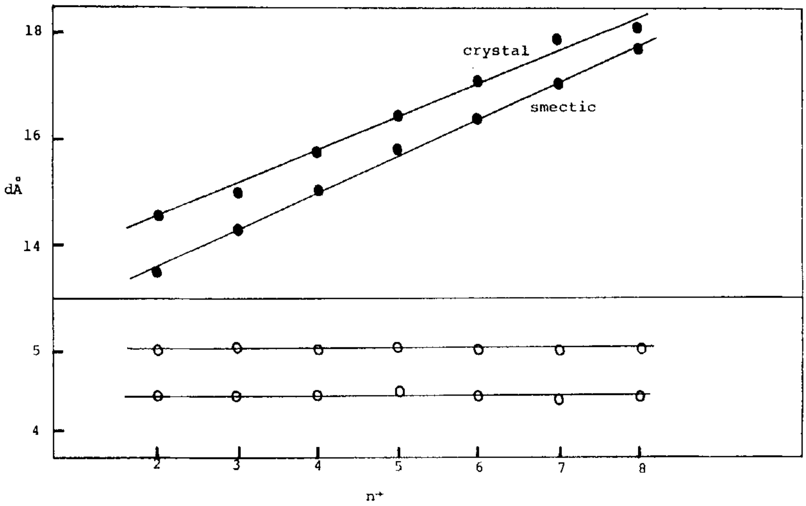


FIGURE 14 The *d* spacings (● inner-ring), (○ outer-ring) *vs* the number of methylene units *n* of TP*n* polymers.

Thus the thickness of the smectic layer increases with the length of the repeating unit while the lateral packing is almost constant, a result which is in agreement with those of many authors for smectic liquid crystal polymers.[14] From Figure 14 one can also observe that the increment in the inner ring spacing per methylene unit is 0.71 Å for this phase. This value is smaller than the projected length (1.26 Å) of a methylene unit along the chain direction, supporting our view that indeed the methylene spacer chains are not in the all-*trans*-configuration. Another point of interest is that both outer and inner ring radii are independent of the thermal history of the samples. For example, for TP4, the spacing corresponding to the outer ring (4.82, 4.70, 4.80, 4.77 Å) and that corresponding to the inner ring (15.70, 15.07, 15.13 and 14.60 Å) are always independent of temperature.

MISCIBILITY METHOD STUDY

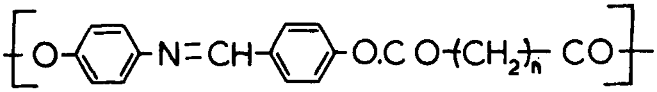
According to Arnold and Sackmann,[15] only liquid crystals having the same phase structure are miscible in all proportions. We have applied this rule successfully[16] in order to identify the nematic phase of certain tolan polymers and the smectic C phase of tolan polymers containing 10 and 12 methylene units. TBBA was used as the reference compound. In miscibility experiments,[17] this compound has been found to have the following transition temperatures during cooling from its isotropic state:

I 236°C N 199°C S_A 172°C S_C

144°C S_H 113°C S_G 68°C S_V 52°C S_C

The X-ray studies show that the type of mesophase in the TP*n* and the TPB*n* series is S_G. In an attempt to confirm these results, we applied the mutual miscibility method by preparing binary mixtures of known composition with TP4 and the standard reference TBBA, but the results were inconclusive. Krigbaum *et al.*,[14] using the mutual miscibility method, also failed to confirm the higher order S_H mesophase of liquid crystal polymers with *p,p'*-dihydroxybiphenyl mesogenic units with an even number of methylene segments (BP8). They have suggested two reasons for this; first, the large difference in appearance temperature (cooling) for the S_H (113°C) phase of the reference compound (TBBA) and that of the polymeric smectogen (280°C); second, the S_H phase in the binary phase diagram was bracketed both above and below by phases in which there is very limited miscibility of the two components. Further, we consider that the viscosity factor, especially for a smectogenic polymer, plays an important role in preventing complete miscibility between reference compound and polymer, *i.e.*, the viscosity hampers diffusion and hence the ability of defects to disappear by relaxation.

Blumstein *et al.*[18] have reported that the liquid crystal polymer of the following structure:



gives an electron–diffraction pattern quite similar to patterns found with the TP*n* series (see Figure 13). They concluded that this polymer has a highly-ordered lamellar mesophase. This result is in agreement with our conclusion from the electron–diffraction data for TP6. This material has a structure which is quite similar to that of our polymers: in both cases, the units possess, between the rigid benzene rings, a flexible molecular axis, which allows the molecules to rotate freely by passing over a much reduced potential energy barrier, permitting the mesogenic units to engage in hexagonal packing of the repeating unit.

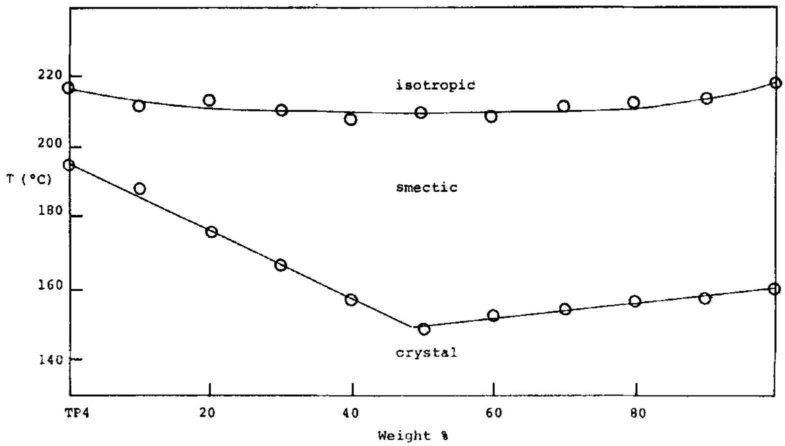


FIGURE 15 Binary phase diagram for the mixture of Blumstein's polymer and polymer TP4.

We have prepared the polymer of Blumstein *et al.*, which was reported to have the transitions C 152 S 220 I; our sample displayed the transitions: C 160 S 215 I. A typical phase diagram for a mixture of TP4 and the Blumstein polymer is shown in Figure 15. The most striking feature of this diagram is that it shows complete miscibility for all mixtures of these polymers. The resulting curves show a typical straight smectic–isotropic transition line, and a continuous solid–smectic transition curve with a eutectic at a composition of 53% TP4 by weight. We conclude that the polymer of Blumstein *et al.* could possibly have an S_G mesophase.

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