Side-chain liquid-crystalline copolymers containing charge transfer groups

C. T. Imire[a]; F. E. Karasz[a]; G. S. Attard[b]

[a] Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts, U. S. A. [b] Department of Chemistry, The University, Southampton, England

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by C. T. IMRIE and F. E. KARASZ

Polymer Science and Engineering, University of Massachusetts, Amherst,
Massachusetts 01003, U.S.A.

and G. S. ATTARD

Department of Chemistry, The University, Southampton SO9 5NH, England

A series of side-chain liquid crystal copolymers have been prepared based on a polystyrene backbone and having 4-nitro-4'-oxyazobenzenealkyloxy and 4-methoxy-4'-oxyazobenzenealkyloxy pendant groups. All the polymers exhibit solely smectic behaviour. The thermal stability of the smectic phase is significantly enhanced in the copolymers when compared to the homopolymers. This is compared to the behaviour of the analogous monomeric compounds. The enhancement of the thermal stability is attributed to a specific interaction, possibly charge transfer.

1. Introduction

It is well known that the transitional behaviour of a binary mixture of liquid-crystalline monomers containing an electron acceptor, for example a 4-nitro-4'-substituted azobenzene, and an electron donor, for example a 4,4'-dialkyloxy-substituted Schiff's base, is strongly non-ideal (see, for example [1]). In general, a smectic A phase is induced in such systems or if such a phase is exhibited by either component then its thermal stability is greatly enhanced in the mixture. The origin of this non-ideal behaviour is thought to be a charge transfer interaction between the two molecules. This effect has been shown recently also to affect dramatically the properties of asymmetric dimeric liquid crystals in which the electron acceptor and donor are now linked through a flexible spacer [2]. In this paper we investigate the extent to which charge transfer interactions can modify the properties of side-chain liquid-crystalline polymers. This approach which is of importance in the development of mixtures of low molar mass liquid crystals for both fundamental and technological reasons has been used surprisingly rarely in the design of liquid-crystalline polymers (see, for example [3]). Meredith *et al.* [4] described several methacrylate copolymers containing groups which may form charge transfer complexes,
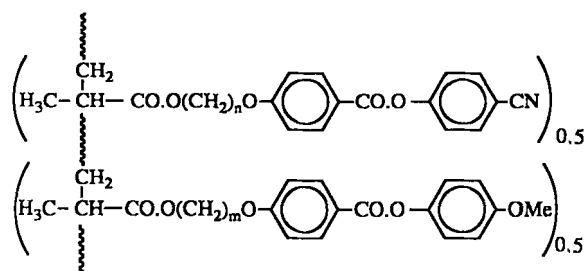
$$m, n = 3, 6.$$

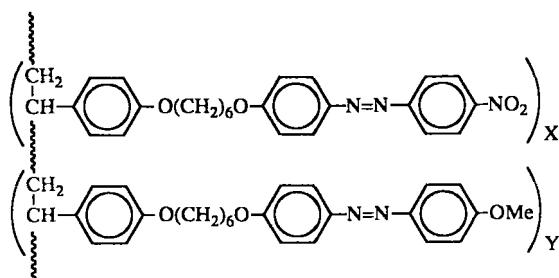It was clear from this work that the copolymer has an increased clearing point over that of the parent homopolymers but this aspect lay outside the authors' area of interest. Their primary reason for synthesizing these copolymers was to obtain a host material which they doped with 4-dimethylamino-4'-nitrostilbene in order to investigate second-order non-linear properties of thin films. Portugall *et al.* [5] reported the properties of a number of acrylate copolymers containing potential charge transfer groups,

$$\left(\begin{array}{l} CH_2 \\ CH-CO.O(CH_2)_6O-\bigcirc-CO.O-\bigcirc-CN \end{array}\right)_Y$$

$$\left(\begin{array}{l} CH_2 \\ CH-CO.O(CH_2)_6O-\bigcirc-CO.O-\bigcirc-\bigcirc-OMe \end{array}\right)_X$$
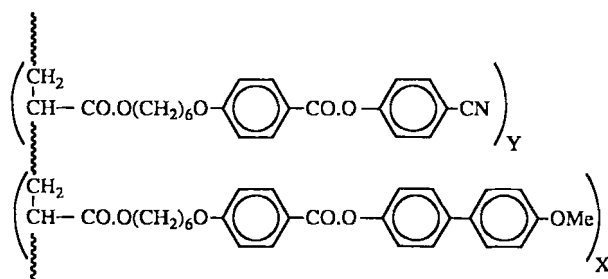
and showed that the behaviour of these materials did indeed appear to be influenced by charge transfer interactions. This was particularly evident in the appearance of an induced smectic phase. However, only half the phase diagram was explored in this study. Most recently, Griffin *et al.* [6] described a number of copolymers containing a nitroaromatic moiety and an alkyloxyphenyl group; several of these exhibit smectic A phases whose thermal stability was attributed to charge transfer interactions.

We considered it important therefore to construct a complete phase diagram for such a system and chose to synthesize copolymers containing nitroazobenzene and methoxyazobenzene groups,

$$\left(\begin{array}{l} CH_2 \\ CH-\bigcirc-O(CH_2)_6O-\bigcirc-N=N-\bigcirc-NO_2 \end{array}\right)_X$$

$$\left(\begin{array}{l} CH_2 \\ CH-\bigcirc-O(CH_2)_6O-\bigcirc-N=N-\bigcirc-OMe \end{array}\right)_Y$$

This particular structure was selected for two reasons; first, the polystyrene backbone yields materials having relatively high glass transition temperatures [7, 8] which may prove to be important for their application potential and second, the properties of the nitroazobenzene polymers are known [9].

In addition, we compare the phase diagram of the copolymers with that of their monomeric analogues, 4-hexyloxy-4'-nitroazobenzene

$$O_2N-\bigcirc-N=N-\bigcirc-OC_6H_{13}$$
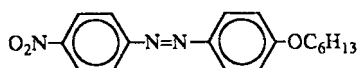
which we describe with the acronym NABO6 and 4-hexyloxy-4′-methoxyazobenzene, MeOAB06,

$$MeO-\langle \bigcirc \rangle-N{=}N-\langle \bigcirc \rangle-OC_6H_{13}$$
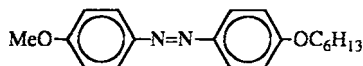
2. Experimental

2.1. *Synthesis*

The polymers were prepared using a scheme consisting of three steps:

Scheme

The coupling of phenol with a diazotised 4-substituted aniline is described in detail elsewhere [10]: the 4-hydroxy-4′-substitutedazobenzenes were recrystallized from methanol. These were reacted with a ten-fold excess of dibromohexane using potassium carbonate as base in dry acetone following the method described by Crivello *et al.* [7]. The 1-bromo-6-(4-substitutedazobenzene-4′-oxy)hexanes wer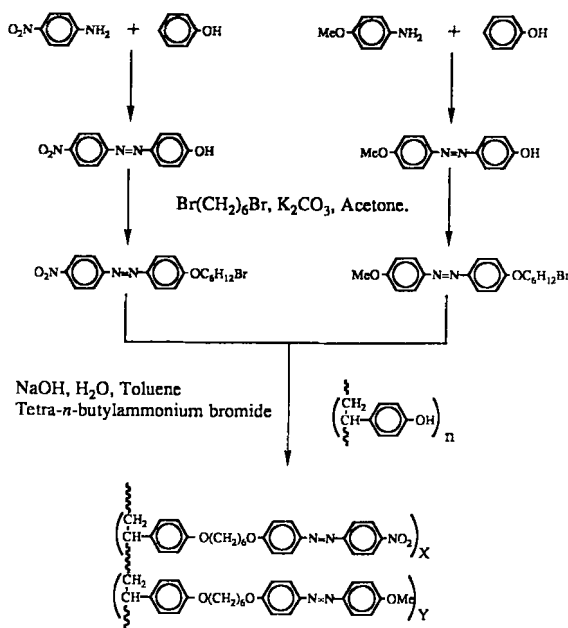e recrystallized twice from ethanol with hot filtration to ensure the removal of any dimeric 1,6-bis-(4-substitutedazobenzene-4′-oxy)hexanes. The phase catalysed reaction of the 1-bromo-6-(4-substitutedazobenzene-4′-oxy)hexanes with poly(4-hydroxystyrene) (PolySciences, Inc., M_w = 9000–11000) was performed using sodium hydroxide as base and tetra-*n*-butylammonium bromide as catalyst in a toluene–water mixture [7]. The reaction mixture was refluxed for 20 hours and then extracted using dichloromethane. The organic extracts were washed with water, dried and the solvents removed. The polymer was redissolved in a small amount of dichloromethane and then precipitated from methanol. In order to remove any unreacted monomer the polymer was extracted in Soxhlet apparatus using methanol for up to 48 hours. Elemental analysis

confirmed the removal of monomeric material. The final polymer yields ranged up to 73 per cent.

The model monomeric compounds were prepared by reacting the 4-hydroxy-4'-substitutedazobenzene with bromohexane using potassium carbonate as base in dimethylformamide. The reaction mixture was refluxed for 3 hours, allowed to cool and then poured into cold water. The resulting solid was filtered off and recrystallized several times from ethanol.

2.2. *Characterization*

The structural characterization of all the compounds was performed by IR spectroscopy using an IBM System 9000 FT-IR Spectrometer and ^{1}H-NMR spectroscopy using a Varian XL200 NMR Spectrometer as well as elemental analysis; typical data for the monomers are given in table 1 and for the polymers in table 2. The IR spectra in all cases were consistent with the proposed structures. The composition of the copolymers is quoted in terms of the feed ratios but as can be seen in table 2 this value is in very good agreement with those obtained using ^{1}H-NMR spectroscopy and elemental analysis. The high purity of all the materials was verified using thin layer chromatography. The substitution on to the polyhydroxystyrene backbone was determined to be 100 per cent within our detection limits; this is particularly evident in the IR spectra of the starting polymer and the final products. The very strong OH stretching band in the polyhydroxystyrene spectrum is not present in the final polymers. The molecular weight of the polymers was determined using polystyrene standards by gas permeation chromatography using a Waters 590 GPC chromatograph equipped with a Waters 410 Differential Refractometer. All the polymers exhibited a broad peak with a high molecular weight fraction. This was most pronounced for the nitro-substituted polymer. Crivello *et al.* observed a similar molecular weight distribution for the cyano-substituted polymers [7] and we believe that the high molecular weight fraction may be the result of a small amount of cross-linking possibly due to phenolic oxidation; this is currently under investigation.

Table 1. The structural characterization of the monomeric compounds.

Compound	Elemental analysis/%†	^{1}H-NMR/ppm
NABO6	C 66·16(66·04) H 6·49(6·47) N 12·74(12·84)	0·9(m, 3 H), 1·4(m, 6 H), 1·8(m, 2 H), 4·0(t, 2 H), 7·0(d, 2 H), 7·9(m, 4 H), 8·3(d, 2 H).
MeOABO6	C 73·01(73·04) H 7·79(7·74) N 8·90(8·97)	0·9(m, 3 H), 1·4(m, 6 H), 1·8(m, 2 H), 3·9(s, 3 H), 4·0(t, 2 H), 7·0(m, 4 H), 7·9(m, 4 H).
NABO6Br	C 52·81(53·21) H 5·02(4·96) N 10·11(10·34) Br 20·00(19·67)	1·6(m, 4 H), 1·9(m, 4 H), 3·5(t, 2 H), 4·1(t, 2 H), 7·0(m, 2 H), 8·0(m, 4 H), 8·3(m, 2 H).
MeOABO6Br	C 58·49(58·32) H 6·00(5·92) N 7·17(7·16) Br 20·30(20·42)	1·5(m, 4 H), 1·9(m, 4 H), 3·4(t, 2 H), 3·8(s, 3 H), 4·0(t, 2 H), 7·0(m, 4 H), 7·9(m, 4 H).

† The theoretical figures are bracketed.

Table 2. The structural characterization of the polymers.

| Polymer	M_w/g mol^{-1}	Elemental analysis/%†	^{1}H-NMR/ppm
100%MeO	29200	C 73·95(75·22) H 6·84(7·02) N 6·35(6·51)	1·5, 1·8(m, 11 H), 3·9(m, 7 H), 6·6, 6·9, 7·8(m, 12 H)
100%NO$_2$	21900	C 70·47(70·17) H 6·24(6·11) N 9·25(9·43)	1·6, 1·8(m, 11 H), 3·9(m, 4 H), 6·6, 6·9(m, 6H), 7·9, 8·3(m, 6 H)
60%MeO	26400	C 72·18(73·19) H 6·68(6·65) N 7·78(7·70)	1·5, 1·8(m, 2·0 H), 3·9(m, 1·2 H), 6·6, 6·9(m, 1·5 H), 7·8, 8·3(m, 1 H)‡

† The theoretical figures are bracketed.
‡ This data implies 57% MeO in the copolymer.

The thermal properties of the products were investigated using a Zeiss polarizing microscope equipped with a Linkam hot-stage. In addition the polymers were characterized by differential scanning calorimetry using a Perkin–Elmer DSC-7 differential scanning calorimeter. The transition temperatures quoted for the polymers are extracted from the calorimetry data. The UV-visible spectra of the materials were recorded using a Perkin–Elmer Lamda 9 UV/VIS/NIR Spectrophotometer interfaced to a Perkin–Elmer 7500 Laboratory Computer.

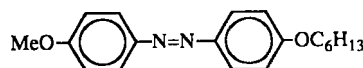## 3. Results and discussion

3.1. *Model monomeric compounds*

The transition temperatures of the two model compounds are:
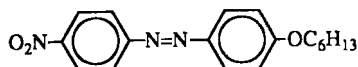
C 98°C S$_A$ (89°C) N 99°C I,

and

C 97°C N 105°C I.

On cooling the isotropic phase of both compounds a schlieren texture develops containing both types of point singularity. In addition the phase flashes when subjected to mechanical stress. In consequence this phase is assigned as a nematic. On cooling the nematic phase of NABO6 the schlieren texture changes to give regions of focal conic fan texture and homeotropically aligned areas. The lower temperature phase is assigned therefore as a smectic A. The T_{NI} of MeOABO6 is higher than that of NABO6 and this is in accord with the order of terminal group efficiency in enhancing T_{NI} [11].

The phase diagram for MeOABO6 and NABO6 is shown in figure 1; this was constructed by determining the transitional behaviour of mixtures of known composition. The assignments of the nematic and smectic A phases were performed using the arguments described for the pure components. It is evident in figure 1 that T_{NI} varies in a non-ideal fashion although this is a relatively weak deviation. In contrast to this, however, the stability of the monotropic smectic A phase exhibited by NABO6 is greatly enhanced by the addition of MeOABO6. The maximum in the S$_A$–N
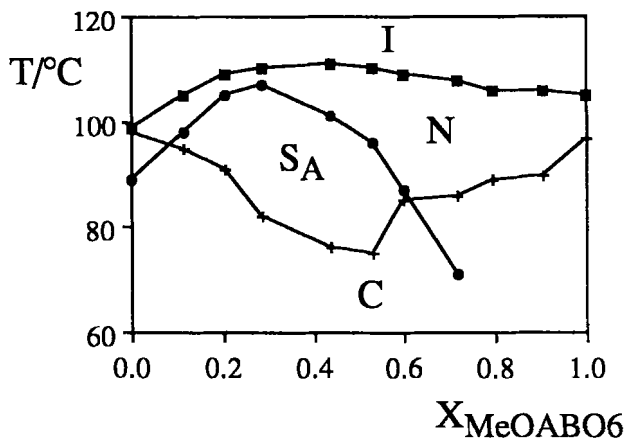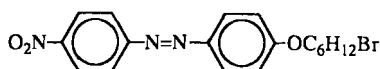
Figure 1.   The phase diagram for MeOABO6 and NABO6 as a function of the mole fraction of MeOABO6.

temperature curve is shifted towards pure NABO6 and such a shift towards the component exhibiting the highest $T_{S_A N}$ is observed for other binary mixtures [12]. This behaviour is indicative of a complexation, possibly a charge transfer interaction between the two components. In order to investigate this possibility we measured the UV-visible spectra of dilute solutions of the single components and the mixtures. There is no evidence of a charge transfer band in the spectra of the mixture but, of course, this does not exclude the possibility of such an interaction occurring in a condensed phase.
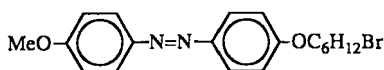
3.2. *Precursor monomers*

The transition temperatures of the two precursor monomers are:

$$O_2N\text{—}\bigcirc\text{—}N{=}N\text{—}\bigcirc\text{—}OC_6H_{12}Br$$

C 89°C N (72°C) I

and

$$MeO\text{—}\bigcirc\text{—}N{=}N\text{—}\bigcirc\text{—}OC_6H_{12}Br$$

C 107°C N (102°C) I.

The nematic phases were assigned on the basis of the schlieren optical textures observed when viewed through the polarizing microscope. The replacement of a terminal proton by a bromine atom has reduced T_{NI} of the nitroazobenzene derivative by 27°C whereas T_{NI} of the methoxy substituted compound is depressed by just 3°C. The cyano-substituted analogue of these compounds has a T_{NI} of 103·4°C [7]. This is difficult to compare with CNABO6 because the T_{NI} of this has been reported as 116·3°C [13] and 139°C [14]. This implies a reduction in T_{NI} of either 12·9°C or 35·9°C which are both significantly larger than that observed for MeOABO6. It is well known that terminal polar groups such as nitro and cyano are particularly efficient in enhancing T_{NI} as a result of their ability to form anti-parallel dimers which serve to minimize dipole interactions. The introduction of the C–Br dipole into the molecule

reduces the molecular inhomogeneity and hence the ability to form the specific dimers. Thus, the nematic–isotropic transition temperatures of NABO6 and CNABO6 are predicted to be effected more by the introduction of a terminal bromine atom than MeOABO6 and this is indeed observed. The anomalous behaviour of similar mesogens has been discussed elsewhere [15].

3.3. *Polymers*

The transitional properties of the homo- and copolymers are listed in table 3. On cooling the isotropic phase of the polymers a fluid birefringent texture developed from which no assignment was possible; an example of this is shown in plate 1. Annealing this close to the clearing point for up to 48 hours resulted in no significant textural change. We found, however, that if the polymer is cooled very slowly, typically $0.1°C \, min^{-1}$, from within the isotropic phase then bâtonnets develop at the transition temperature. On further cooling these coalesce to yield a focal conic fan texture an example of which is shown as plate 2. The fans are particularly evident towards the edges of the preparation. In consequence, we assign the mesophases exhibited by the polymers as a smectic A phase. We suggest that this technique of cooling a polymer very slowly in order to develop a texture for phase identification should be used routinely in annealing experiments. The glass phases of the polymers were allowed to anneal for several days at room temperature and the measurements repeated. Only the nitro-substituted polymer appeared to crystallize partially. The inversion in the clearing points of the homopolymers if compared to the model compounds is possibly a consequence of the smectic nature of the polymers. The nitro-substituted polymer presumably forms an interdigitated phase stabilized by the electrostatic interaction between the polar nitro group and the polarizable azobenzene moiety. In contrast, the methoxy polymer is anticipated to exhibit the classic monolayer S_{A_1} phase with no additional stabilization. Further speculation, however, must await the results of detailed structural studies using X-ray diffraction.

Table 3. The transition temperatures and enthalpies and entropies of transition for the homo- and copolymers.

MeO/%	NO$_2$/%	T_g/°C	$T_{S_A I}$/°C	$\Delta H_{S_A I}$/J g^{-1}	$\Delta S_{S_A I}$/R
100	0	81	144	14·2	1·76
80	20	77	172	9·95	1·17
60	40	73	182	7·98	0·92
40	60	71	193	8·28	0·94
20	80	65	191	7·07	0·81
0	100	55	165	4·84	0·59

Table 3 lists the enthalpies associated with the smectic A–isotropic transition, these are also quoted as $\Delta S/R$ for which the molecular weight of the repeat unit was used in the conversion. The enthalpy of transition for the nitro-substituted polymer is $4.84 \, J \, g^{-1}$ whereas Crivello *et al.* found for the analogous cyano-substituted polymer a $\Delta H_{S_A I}$ of $5.2 \, J \, g^{-1}$ and considered this indicative of a nematic phase [7]. In addition, the authors note that this polymer forms a texture consisting of very small domains from which no classification could be made and this remained unchanged on annealing. This is clearly very similar to the behaviour of our polymers and it appears probable that the cyano-substituted polymers also exhibit smectic rather than nematic
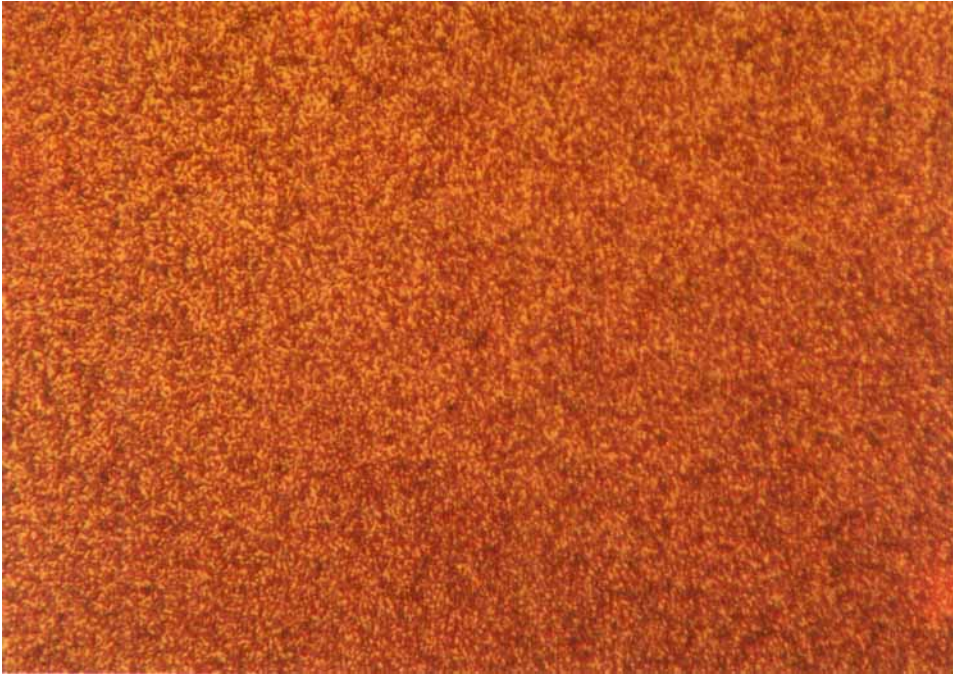
C. T. Imrie *et al.*

Plate 1. The optical texture formed by cooling the methoxy-homopolymer at $10°C\,min^{-1}$ and annealing at $138°C$ for 48 hours.
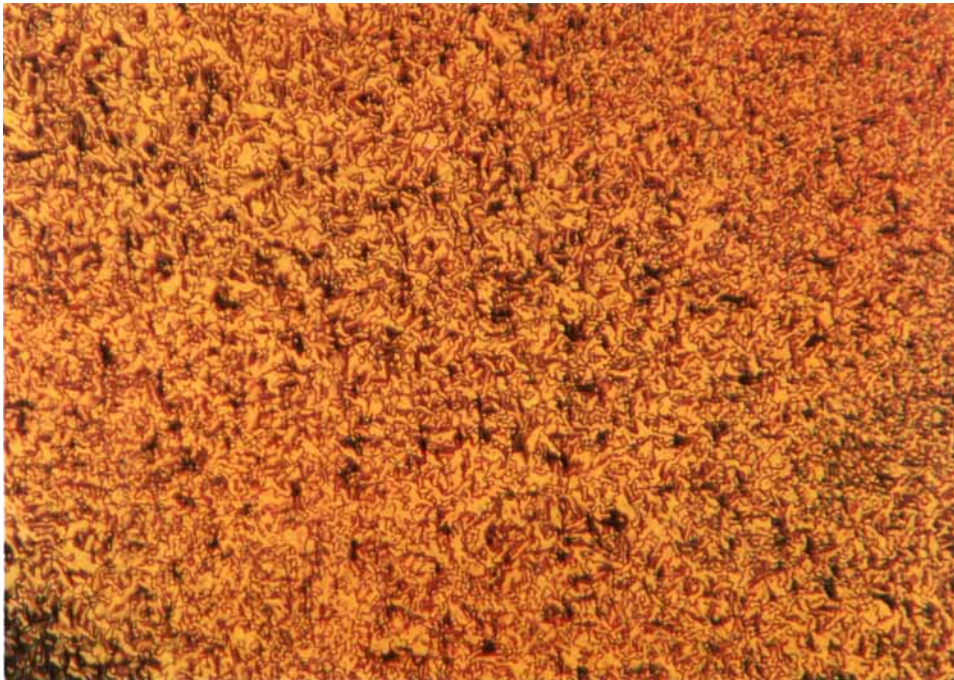

Plate 2. The focal–conic fan texture developed by cooling the methoxy-homopolymer at $0.1°C\,min^{-1}$ from $155°C$ to $138°C$.

phases. In addition, we have prepared a homologous series of polystyrene polymers with 4-fluoroazobenzene-4′-oxyalkanes attached and these are also solely smectic in nature [8]. It appears, therefore that the polystyrene backbone strongly favours the formation of smectic phases. This is presumably a consequence of the relatively stiff backbone. The decrease in $\Delta S_{S_A1}/R$ on increasing the mole fraction of the nitro-substituted group is difficult to interpret unambiguously although may reflect changes in the orientational order within the smectic phase resulting from an increase in the concentration of the cis-isomer at elevated temperatures. A similar explanation was offered recently to rationalize the low $\Delta S_{N1}/R$ observed for a series of dimeric nitroazobenzenes [2]. In order to characterize the molecular organization within the mesophase we have prepared deuteriated analogues of these polymers and plan to investigate them using deuterium N.M.R. spectroscopy.

Figure 2 shows the dependence of the transition temperatures upon the mole fraction of the methoxy-substituted group in the polymers. The thermal stability of the smectic A phase is enhanced significantly in the copolymers. The shape of the clearing curve is similar to that of the monomer phase diagram shown in figure 1. Notably, the maximum in the curve is shifted towards the component exhibiting the higher transition temperature. The glass transition temperature appears to have a linear dependence on the side-chain composition. Figure 3 shows the dependence of the transition temperatures on the mole fraction of the electron donating group for the acrylate polymers reported by Portugall *et al.* [5] and described in the Introduction. In contrast to the behaviour seen in figure 2 the clearing temperature appears to vary linearly across the phase diagram although the smectic thermal stability is enhanced. If we make the rather simplistic assumption that the clearing temperature reflects the strength of the interaction between the mesogenic units then it is apparent that the mixed core interaction in our copolymers is stronger than either like core interaction. In both cases the nonlinear behaviour of the transitional properties is presumably a consequence of complexation between the differing mesogenic groups. In our polymers however this appears to be a stronger interaction and possibly involves charge transfer. Figure 4 shows the UV-visible spectra of dilute solutions of
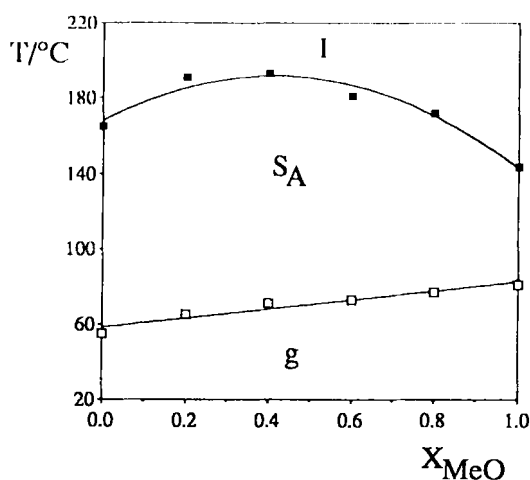

Figure 2. The dependence of the transition temperatures on the fraction of the methoxy-substituted moiety for the homo- and copolymers.
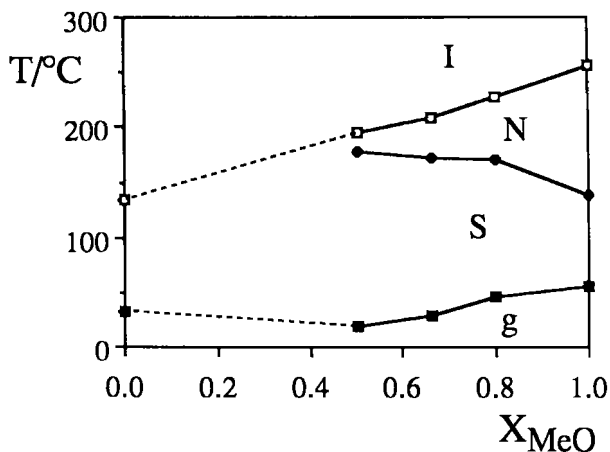
Figure 3. The dependence of the transition temperatures on the fraction of the methoxy-biphenyl moiety for a series of acrylate copolymers [5]. Crystal transitions are not shown.

the two homopolymers and a copolymer. There is no evidence of a charge transfer interaction and the spectrum of the copolymer is simply the sum of the spectra of the homopolymers. Increasing the concentrations of the solutions did not reveal a charge transfer band. It is possible, however, that such an interaction will occur in the condensed phase.
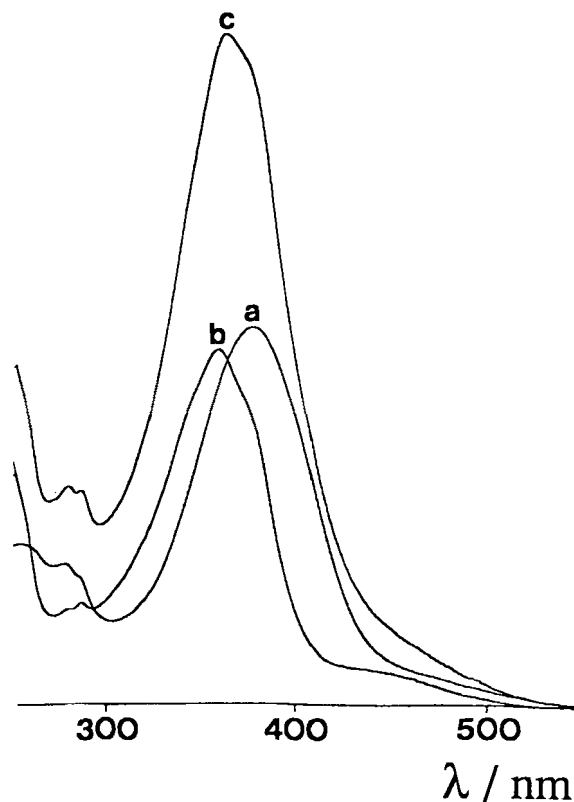
Figure 4. The UV-visible spectra of (a) the nitro and (b) the methoxy homopolymers and (c) the 60 per cent methoxy copolymer.

4. Conclusions

The liquid-crystalline properties of the copolymers appear to be determined at least in part by a specific interaction. This interaction irrespective of its form presumably reduces the dimerization of the nitroazobenzene moieties which is considered to be a serious problem in the poling of these materials and more so in the retention of this poling in the glass phase. This design approach may prove to be important, therefore, to the development of side-chain liquid-crystalline polymers for use in non-linear optic applications. We plan to investigate this complexation using dielectric relaxation spectroscopy.

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