# Induction of Liquid Crystallinity in Blends of Amorphous Side-Chain Polymers and Their Analogous Copolymers

**Corrie T. Imrie* and Brian J. A. Paterson**

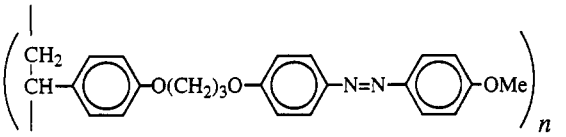
*Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland*

*Received October 13, 1993*
*Revised Manuscript Received August 4, 1994*

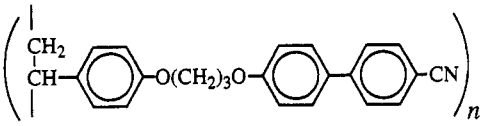
## Introduction

Conventionally, the liquid crystal properties of a side-chain polymer are controlled by the variation of its molecular structure.[1,2] In recent years, however, a different design approach has emerged which employs the principles of supramolecular chemistry[3] to modify or even to induce liquid crystallinity via specific noncovalent interactions.[4] An example of this is the control of liquid crystal properties via specific interactions between unlike mesogenic groups. This approach has been exploited for many years in binary mixtures of low molar mass mesogens in which one mesogenic unit is electron rich and the other electron poor.[5] The clearing temperature exhibited by such a mixture is normally higher than those of either single component, and often, smectic behavior is either strongly enhanced or induced. It is widely believed that the nature of the interaction in the majority of these systems is charge transfer, although this assumption has been questioned and it seems probable that for some mixtures the interaction is simply a dipolar one.[6] The effects on the clearing temperature of such an interaction can be understood within the framework of a molecular field theory developed to predict phase diagrams of binary mixtures.[7,8] This theory requires three interaction strength parameters to be defined, namely, $\epsilon_{AA}$ and $\epsilon_{BB}$, representing interactions between like mesogenic units, and $\epsilon_{AB}$, the mixed interaction between the unlike groups. The nematic–isotropic transition temperatures for such a system are predicted to exhibit a linear dependence on composition if $\epsilon_{AB}$ is the geometric mean of $\epsilon_{AA}$ and $\epsilon_{BB}$.[7] Deviations of just ±1.85% in $\epsilon_{AB}$ from the geometric mean of the like interaction parameters cause discernible changes in the predicted phase diagrams.[7,8] These deviations in $\epsilon_{AB}$ are a direct reflection of the presence of a specific interaction between the unlike mesogenic species. More recently, similar effects have been observed for side-chain liquid crystal copolymers containing electron rich and electron poor mesogenic groups.[9–14] The clearing temperatures observed for such copolymers are higher than those of either homopolymer, and by analogy to low molar mass systems, this increase has been attributed to the effect of a specific interaction on the mixed interaction strength parameter.[12,13]

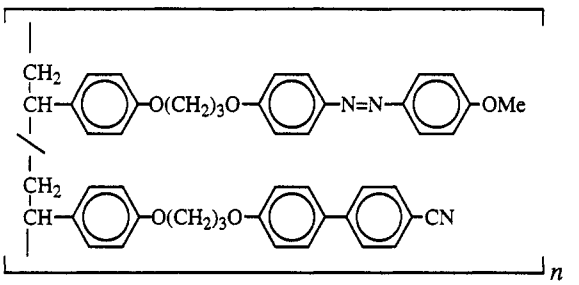
Low molar mass binary mixtures of a mesogen and non-mesogen or even two non-mesogens are also known to exhibit induced mesophases.[15] This is normally interpreted as the enhancement of the virtual transition temperatures of the individual components via specific interactions and/or the reduction of melting points, i.e. eutectic behavior, revealing liquid crystallinity. In this Note, we report the first example of such behavior for side-chain polymers. We have studied the thermal behavior of poly[4-[[1-[[1-[(4-methoxyphenyl)azo]phenyl-4]oxy]-3-propyl]oxy]styrene] (1) and poly[4-[[1-[(4-cyanobiphenyl)-4′)oxy]-3-propyl]oxy]styrene] (2), copolymers containing the same mesogenic groups (3) and their analogous blends.



1



2



3

These particular polymers were chosen because the properties of the remaining members of the homopolymer series have been described in detail elsewhere[16–18] and these data suggest that the virtual clearing temperatures for 1 and 2 approach their respective $T_g$'s. Thus relatively modest interactions between the two unlike mesogenic species should increase the clearing temperatures above $T_g$, so revealing liquid crystalline behavior.

## Experimental Section

The homopolymers, 1 and 2, were prepared via the phase-transfer-catalyzed reaction of poly(4-hydroxystyrene) ($M_w = 10^4$, PolySciences Inc.) with 1-[(4-methoxyazobenzene-4′)oxy]-3-bromopropane or 1-[(4-cyanobiphenyl-4′)oxy]-3-bromopropane, respectively, as described in detail elsewhere.[16,18] The preparation of the copolymers, 3, employed identical conditions. The degree of substitution can be conveniently monitored using IR spectroscopy,[19] and this reaction does not result in any significant molecular weight degradation.[16] The structures of the copolymers were confirmed using $^1$H-NMR spectroscopy while their compositions were verified using elemental analysis.[20] The $^1$H-NMR spectra of the copolymers did not contain isolated peaks arising from just one of the two repeat units. Thus, in order to assess composition, the ratios of the intensities of the aromatic (5.8–8.4 ppm), the aromatic ether (3.4–4.6 ppm), and the alkane (0.6–2.8 ppm) regions of the spectra have been used, and the values obtained agree well with the feed ratios.[20] The blends were prepared by codissolving the polymers in methylene chloride, allowing the solvent to evaporate slowly, and then drying the products under vacuum for several days. The thermal characterization of the blends and copolymers was performed by differential scanning calorimetry[21] and polarized light microscopy.

## Results and Discussion

**Homopolymers, 1 and 2.** The DSC traces for the homopolymers (see Figure 1) revealed the presence of just a second-order transition corresponding to the glass transition, and the associated temperatures are given in Table 1. When viewed through the polarizing microscope,

* To whom correspondence should be addressed.

0024-9297/94/2227-6673$04.50/0 

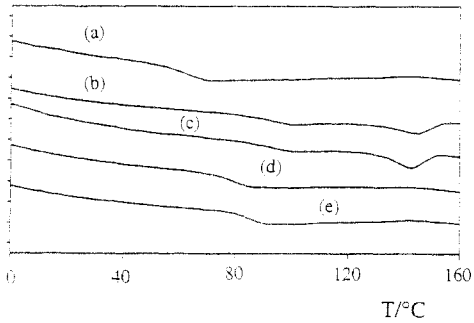



**Figure 1.** Second heating normalized DSC traces for (a) homopolymer **1**, (b) copolymer containing 75 mol % **1**, (c) copolymer containing 50 mol % **1**, (d) copolymer containing 25 mol % **1**, and (e) homopolymer **2**.

**Table 1. Thermal Properties Determined by DSC of the Homopolymers, Copolymers, and Blends**

| sample | mol fraction of cyanobiphenyl/% | $T_g$/°C | $T_{SI}$/°C | $\Delta H_{SI}$/J g$^{-1}$ |
|---|---|---|---|---|
| homopolymer | 100 | 85 | | |
| homopolymer | 0 | 62 | | |
| blend | 25 | 64 | 124–139[a] | |
| blend | 50 | 71 | 129–135[a] | |
| blend | 75 | 79 | 125–138[a] | |
| copolymer | 25 | 91 | 144 | 4.69 |
| copolymer | 50 | 92 | 143 | 5.53 |
| copolymer | 75 | 79 | | |

[a] Data obtained by optical microscopy. Each blend was cooled slowly, 0.2 °C min$^{-1}$, from 10 deg above the clearing temperature to room temperature and then reheated at 5 °C min$^{-1}$. The transition temperatures were recorded on heating.

both polymers form isotropic glasses on cooling from approximately 40 deg above their respective $T_g$'s at both 10 °C min$^{-1}$ and at 0.2 °C min$^{-1}$. However, if the sample was subjected to stress at temperatures slightly higher than $T_g$, then induced birefringence was observed. The optical textures obtained were not sufficiently well-developed to allow for phase characterization. The observation of birefringence suggests, as suspected,[16,18] that the clearing temperatures of these polymers are close to their respective $T_g$'s.

**Copolymers, 3.** Table 1 lists the thermal properties of the copolymers, and their DSC traces are also shown in Figure 1. For the copolymer containing 75 mol % **2**, DSC indicated the presence of just a glass transition and no birefringence was observed on cooling at either 10 or 0.2 °C min$^{-1}$ from the isotropic phase. As with the homopolymers, however, a poorly defined birefringent texture was obtained on stressing the sample above $T_g$.

The DSC traces for the copolymers containing 50 and 75 mol % **1** contained, in addition to the glass transition, a first-order transition (see Figure 1) corresponding to the liquid crystal–isotropic transition. On cooling the samples from approximately 10 deg above the clearing temperature at 0.2 °C min$^{-1}$, bâtonnets developed which coalesced, giving a clear, characteristic focal conic fan texture in coexistence with regions of homeotropic alignment. Thus, the phase was assigned as a smectic A phase. The values of the enthalpy change associated with the clearing transitions for these copolymers (see Table 1) support this phase assignment.

Figure 2 shows the dependence of the transition temperatures on the copolymer composition. The glass transition temperatures exhibited by the mesogenic copolymers are considerably higher than expected, allowing for a linear dependence of $T_g$ on composition. The smectic phase possesses less free volume than the isotropic phase, and hence higher $T_g$'s would be anticipated for the

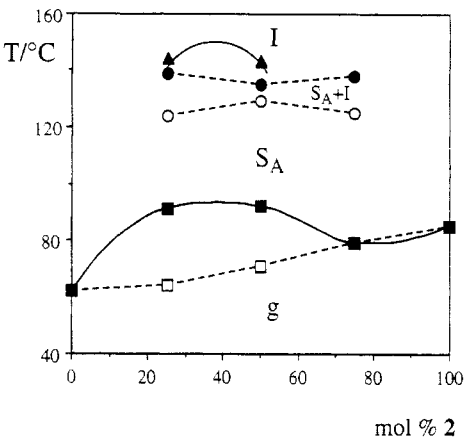



**Figure 2.** Dependence of transition temperatures on the mole percent of cyanobiphenyl-substituted side chains in the copolymers. ■ represents the glass transition temperature, and ▲ denotes the smectic A–isotropic transition temperature; in the blends, □ represents the glass transition temperature, and ○ the lower boundary and ● the upper boundary of the smectic A and isotropic biphasic region.

mesogenic copolymers.[16] A dramatic stabilization of liquid crystallinity is evident in the phase diagram. The driving force for this induced mesogenicity is presumably the specific interaction between the unlike mesogenic groups. It is interesting to note that the region of smectic behavior in the phase diagram (see Figure 2) is shifted away from the equimolar composition and toward the methoxyazobenzene-based homopolymer, **1**. The methoxyazobenzene-based polymers exhibit higher clearing temperatures than the analogous cyanobiphenyl-substituted material,[16,18] and thus it can be assumed that **1** exhibits a higher virtual clearing temperature than **2**. The clearing temperature of the induced liquid crystal phase is higher, therefore, when the copolymer is richer in the side chain possessing the higher virtual transition temperature. This observation is in complete accord with the behavior of many low molar mass binary mixtures for which it was found that the maximum in the induced smectic behavior was shifted toward the component possessing the greater smectic tendencies.[22]

**Blends.** The DSC traces obtained on reheating the blends (see Figure 3) were identical to those of the homopolymers, containing just a glass transition, and the associated temperatures are also listed in Table 1. In contrast to the behavior of the homopolymers, however, liquid crystallinity was observed optically. Thus, on cooling the isotropic phase of each blend from 10 deg above the clearing temperature at 0.2 °C min$^{-1}$, clear, characteristic focal conic fan textures were obtained, indicative of a smectic A phase. The isotropic phases exhibited by the blends were, however, phase-separated, and this was particularly evident because of the strong difference in color between **1** and **2**. The phase separation was not complete, but rather there were regions rich or poor in either component, and the separation was least pronounced for the equimolar blend. The failure of DSC to detect phase separation was a reflection of the close proximity of the $T_g$'s. For the 75 mol % **2** blend, the bâtonnets developed initially in the more yellow regions of the preparation, i.e. those rich in **1**. On reheating, the smectic A–isotropic transition is particularly broad, 125–138 °C, with the paler regions clearing first. On cooling at a faster rate, 5 °C min$^{-1}$, again fans develop in the yellow regions but the paler regions remain isotropic. Thus a biphasic smectic A and isotropic texture is obtained at room temperature. The increase in sample viscosity as the glass

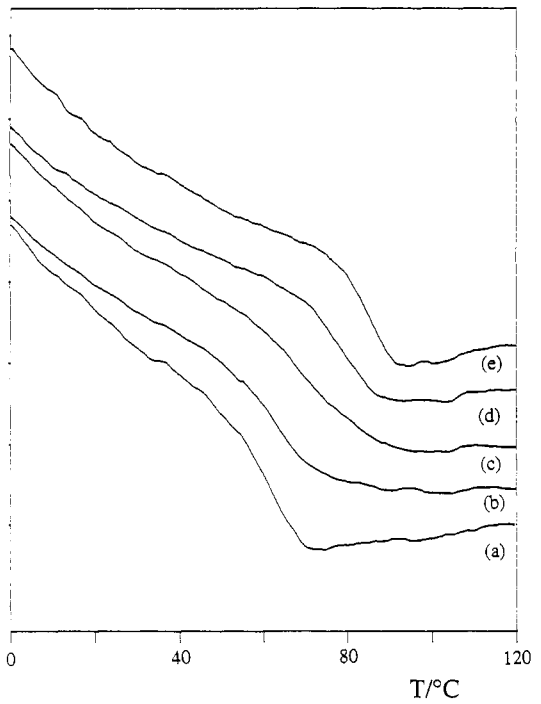



**Figure 3.** Second heating normalized DSC traces for (a) homopolymer 1, (b) blend containing 75 mol % 1, (c) blend containing 50 mol % 1, (d) blend containing 25 mol % 1, (e) homopolymer 2.

transition is approached prevents the formation of the smectic A phase in the regions poor in 1.

When a slowly cooled preparation of the equimolar blend was reheated, a sharper clearing temperature was observed (see Table 1). On cooling at 5 °C $min^{-1}$, a poorly defined texture is observed which develops initially in the paler regions of the preparation, although a uniform texture is obtained at room temperature. On cooling from the isotropic phase at 10 °C $min^{-1}$, a biphasic texture is observed at room temperature.

The 25 mol % 2 blend behaved in a fashion similar to that of the 75 mol % 2 blend except that, on cooling, the bâtonnets developed initially in the paler regions, i.e., those rich in 2. On reheating at 5 °C $min^{-1}$, the more yellow areas cleared first, 124–132 °C, giving rise to a biphasic regime. The paler regions subsequently cleared over the temperature range 131–139 °C. On cooling from the isotropic phase at 5 °C $min^{-1}$, fans develop in the paler regions, and this biphasic texture persists to room temperature. The breadth of the biphasic region coupled to the phase-separated morphology prevented the detection of the clearing transition in the blends by DSC.

Figure 2 shows the dependence of the transition temperatures on the composition of the blends. The glass transition temperatures of the blends, extracted from the DSC data, vary in essentially a linear manner with composition. This may initially be seen as a surprising result given the dependence of $T_g$ on copolymer composition described earlier, in which a positive deviation from linearity was observed. This was rationalized in terms of the difference in the specific free volume between the isotropic and smectic phases. It must be remembered, however, that at the cooling rate used for the DSC experiments, the blends remain largely isotropic and so a linear dependence on $T_g$ would be expected.

The smectic A–isotropic transition temperatures are essentially independent of composition, although the biphasic region exhibited by the equimolar blend is somewhat narrower than that shown by the other two blends. This suggests that the specific interaction between the unlike mesogenic units assists the miscibility of the polymers. The manner in which the liquid crystal phase develops in the blends also supports the view that a specific interaction between the unlike mesogenic groups is driving the phase formation. In the phase-separated isotropic phase exhibited by the blend containing 25 mol % 1, focal conic fans first appear in the regions rich in 1, whereas for the 75 mol % 1 composition, the fans develop initially from the domains rich in 2. Given the limited miscibility between these polymers, the regions composed largely of the minor component will contain the larger relative fraction of the second component and, thus, the interactions between the unlike groups will be maximized. The nature of this interaction, possibly charge transfer or dipolar, is unclear but currently under investigation.

**Acknowledgment.** C.T.I. gratefully acknowledges the University of Aberdeen Research Committee for a grant to purchase the PL-DSC differential scanning calorimeter.

## References and Notes

(1) Percec, V.; Pugh, C. In *Side Chain Liquid Crystal Polymers*; McArdle, C. B., Ed.; Blackie and Sons: Glasgow, 1989; Chapter 3.
(2) Percec, V.; Tomazos, D. In *Comprehensive Polymer Science, First Supplement*; Aggarwal, S. L., Russo, S., Eds.; Pergamon Press: Oxford, U.K., 1992; Chapter 14.
(3) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89.
(4) Imrie, C. T. *Trends Polym. Sci.*, submitted for publication.
(5) See, for example: Pelzl, G.; Demus, D.; Sackmann, H. *Z. Phys. Chem.* **1968**, *238*, 22. Sharma, N. K.; Pelzl, G.; Demus, D.; Weissflog, W. *Z. Phys. Chem.* **1980**, *261*, 579. Schneider, F.; Sharma, N. K. *Z. Naturforsch.* **1981**, *36A*, 1086. Demus, D.; Pelzl, G.; Sharma, N. K.; Weissflog, W. *Mol. Cryst. Liq. Cryst.* **1981**, *76*, 241. Sadowska, K. W.; Zywocinski, A.; Stecki, J.; Dabrowski, R. *J. Phys. (Paris)* **1982**, *43*, 1673. Boy, A.; Adomenas, P. *Mol. Cryst. Liq. Cryst.* **1983**, *95*, 59. Srikanta, B. S.; Madhusudana, N. V. *Mol. Cryst. Liq. Cryst.* **1983**, *99*, 203. Weissflog, W.; Pelzl, G.; Demus, D. *Cryst. Res. Technol.* **1986**, *21*, 117. Pelzl, G.; Novak, M.; Weissflog, W.; Demus, D. *Cryst. Res. Technol.* **1987**, *22*, 125.
(6) Takenaka, S.; Hirohata, T.; Shimohara, I.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1121.
(7) Humphries, R. L.; James, P. G.; Luckhurst, G. R. *Symp. Faraday. Soc.* **1971**, *5*, 107.
(8) Humphries, R. L.; Luckhurst, G. R. *Chem. Phys. Lett.* **1973**, *23*, 567.
(9) Portugall, M.; Ringsdorf, H.; Zentel, R. *Makromol. Chem.* **1982**, *183*, 2311.
(10) Meredith, G. R.; Vandusen, J. G.; Williams, D. J. In *Nonlinear Optical Properties of Organic and Polymeric Materials*; Williams, D. J., Ed.; ACS Symposium Series No. 233; American Chemical Society: Washington, DC, 1983; Chapter 5.
(11) Griffin, A. C.; Bhatti, A. M.; Hung, R. S. L. In *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum Publishing Corp.: New York, 1988; p 375.
(12) Imrie, C. T.; Karasz, F. E.; Attard, G. S. *Liq. Cryst.* **1991**, *9*, 47.
(13) Schleeh, T.; Imrie, C. T.; Rice, D. M.; Karasz, F. E.; Attard, G. S. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 1859.
(14) Kosaka, Y.; Kato, T.; Uryu, T. *Macromolecules* **1994**, *27*, 2658.
(15) See, for example: Schroeder, J. P.; Schroeder, D. C. *J. Org. Chem.* **1968**, 591. Araya, K.; Matsunaga, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3079. Araya, K.; Matsunaga, Y. *Mol. Cryst. Liq. Cryst.* **1981**, *67*, 153. Araya, K.; Matsunaga, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2430. Homura, N.; Matsunaga, Y.; Suzuki, M. *Mol. Cryst. Liq. Cryst.* **1985**, *131*, 273.
(16) Imrie, C. T.; Karasz, F. E.; Attard, G. S. *Macromolecules* **1992**, *25*, 1278.
(17) Imrie, C. T.; Karasz, F. E.; Attard, G. S. *Macromolecules* **1993**, *26*, 3803.
(18) Imrie, C. T.; Karasz, F. E.; Attard, G. S. *J. Macromol. Sci.—Chem.* **1994**, *A31*, 1221.
(19) Attard, G. S.; Dave, J. S.; Wallington, A.; Imrie, C. T.; Karasz, F. E. *Makromol. Chem.* **1991**, *192*, 1495.

(20) Anal. Calcd for $C_{24}H_{23.25}N_{1.75}O_{2.75}$: C, 75.82; H, 6.16; N, 6.45. Found: C, 75.33; H, 6.01; N, 6.20. $^1$H-NMR: aromatic/ether calcd 1.92, found 1.89; alkane/ether calcd 0.80, found 0.74. Calcd for $C_{24}H_{22.5}N_{1.5}O_{2.5}$: C, 77.50; H, 6.10; N, 5.65. Found: C, 78.03; H, 6.05; N, 5.52. $^1$H-NMR: aromatic/ether calcd 2.18, found 2.11; alkane/ether calcd 0.91, found 0.91. Calcd for $C_{24}H_{21.75}N_{1.25}O_{2.25}$: C, 79.26; H, 6.03; N, 4.81. Found: C, 77.14; H, 6.06; N, 4.48. $^1$H-NMR: aromatic/ether calcd 2.53, found 2.54; alkane/ether calcd 1.05, found 1.00.

(21) A Polymer Laboratories PL–DSC equipped with an autocool accessory was used for these studies. Each sample was treated in an identical manner, namely, heated from −30 to +200 °C, isothermed for 3 min, cooled from +200 to −30 °C, isothermed for 3 min, and heated from −30 to +200 °C. In all instances the heating/cooling rate was 10 °C min$^{-1}$.

(22) DeJeu, W. H.; Longa, L.; Demus, D. *J. Chem. Phys.* **1986**, *84*, 6410.