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Side chain liquid crystal copolymers containing electron rich and electron deficient mesogenic groups. The synthesis and characterization of the poly[ω-(4-cyanobiphenyl-4′-oxy)alkyl methacrylate]s-*co*-poly[6-(4-butylazobenzene-4′-oxy)hexyl methacrylate]s

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The synthesis and characterization of a new series of side chain liquid crystal copolymers, the poly[ω-(4-cyanobiphenyl-4′-oxy)alkyl methacrylate]s-*co*-poly[6-(4-butylazobenzene-4′-oxy)hexyl methacrylate]s, is described. These copolymers contain electron rich 4-butylazobenzene-based mesogenic groups and electron deficient 4-cyanobiphenyl units. The spacer attached to the electron rich units is held at 6 methylene units while that attached to the 4-cyanobiphenyl groups is varied in length from 3 to 12 methylene units. All the copolymers exhibit a smectic A phase and, in addition, the homologues containing a pentyl spacer or spacer lengths ≥7 methylene units exhibit either a crystal B or smectic B phase. The clearing temperatures of the copolymers are significantly greater than the average values for the corresponding homopolymers. This behaviour is interpreted in terms of a favourable specific interaction between the unlike groups in the copolymer. By comparison, the clearing entropies exhibited by the copolymers are lower than the average values of the corresponding homopolymers and it is suggested that this reflects a disruption of the efficient packing of the 4-butylazobenzene groups by the 4-cyanobiphenyl units. The sole exception to this is the copolymer containing a pentyl spacer for which the clearing entropy is greater than the average value for the homopolymers; this copolymer also exhibits the largest deviation in the clearing temperature. This strongly suggests that the specific interaction is maximized for this particular combination of spacer lengths. © 1997 Elsevier Science Ltd.

(Keywords: side chain liquid crystal polymers; noncovalent interactions; enhanced liquid crystallinity)

INTRODUCTION

Side chain liquid crystal polymers contain three structural components: a semi-rigid anisometric or mesogenic group, a polymer backbone, and connecting these, a flexible spacer, normally an alkyl chain[1,2]. In essence, the anisotropic interactions between the mesogenic groups give rise to the observation of liquid crystalline behaviour while the flexible spacer decouples these self-assembling tendencies from those of the polymer chains to adopt random coil conformations. In consequence, these materials exhibit a unique duality of properties combining the electro-optic characteristics of low molar mesogens with polymeric properties such as glassy behaviour. This combination of properties underpins a wide range of proposed applications in advanced electro-optic technologies[3,4].

The thermal behaviour of a side chain liquid crystal polymer may, to some extent, be controlled in a predictable manner by varying the chemical nature of the mesogenic group, spacer and backbone. More recently, increasing interest has focused on the role of non-covalent interactions in determining liquid crystal behaviour in polymeric systems[5]. One such specific interaction is that between electron rich and electron deficient groups. The precise nature of this interaction is unclear[6] although it is generally assumed to involve charge transfer. It is well-known, however, that it plays an important role in determining the transitional properties of mixtures of low molar mass materials containing such groups and, specifically, enhanced clearing temperatures and a strong tendency to exhibit induced smectic behaviour are observed[7–14]. This interaction has been used also to manipulate the phase behaviour of non-symmetric dimeric liquid crystals[15–17] and to induce liquid crystallinity into mixtures of mesogenic

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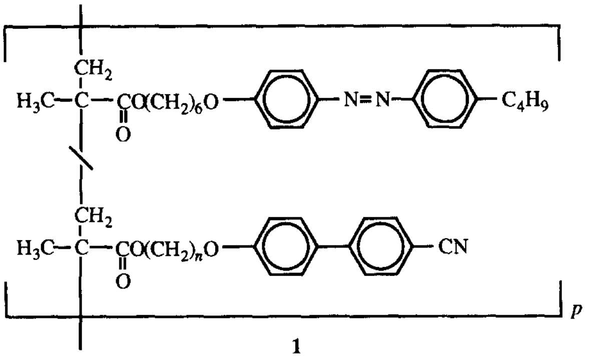
and non-mesogenic components[18–22]. There are relatively few studies, however, in which electron rich and deficient groups are incorporated into a side chain liquid crystal copolymer[23–31]. To investigate further the role of specific interactions in determining liquid crystalline behaviour and to develop new materials for electro-optic applications, we have prepared the poly[ω-(4-cyanobiphenyl-4′-oxy)alkyl methacrylate]s-*co*-poly[6-(4-butylazobenzene-4′-oxy)hexyl methacrylate]s, **1**, in which the length of the alkyl spacer in the cyanobiphenyl-based side chains is varied from 3 to 12 methylene units.



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The acronym *n*-CNBip/6-BuAzB is used to refer to series **1** in which *n* indicates the number of methylene units in the flexible spacer linking the 4-cyanobiphenyl moiety to the polymethacrylate backbone and 6-BuAzB indicates the presence of the 4-butylazobenzene mesogenic unit. This particular series was chosen because the electron rich azobenzene and electron deficient cyanobiphenyl groups are expected to exhibit a specific interaction and, also, the properties of the homopolymers are known[32].

EXPERIMENTAL

The *n*-CNBip/6-BuAzB copolymer series, **1**, was prepared using the synthetic route shown in *Scheme 1*. The synthesis of the α-bromo-ω-(4′-cyanobiphenyl-4-yloxy)alkanes, **6**, and the ω-[4-cyanobiphenyl-4′-yloxy]-alkyl methacrylates, **7**, have been described in detail elsewhere[32].

Materials

α,ω-Dibromoalkanes (Aldrich) were distilled under reduced pressure using a Kugelrohr apparatus immediately prior to use. Benzene and tetrahydrofuran (THF) were distilled over calcium hydride. Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from toluene, washed with petroleum spirits (80–100°C) and dried *in vacuo*. All other reagents were used as received.

4-n-Butyl-4′-hydroxyazobenzene (**2**)

Compound **2** was prepared according to the method described by Stewart and Imrie[33]. Thus, 4-n-butylaniline (75.7 g, 510 mmol) was dissolved in 3 M hydrochloric acid (750 ml) and the solution was cooled in an ice–salt–water bath. To this was slowly added a cooled solution of sodium nitrite (35.4 g, 510 mmol) in distilled water (200 ml) with vigorous stirring. The resulting diazonium salt solution was then slowly added to a stirred solution of phenol (47.8 g, 510 mmol) in 10% aqueous sodium hydroxide (500 ml) at 0°C. After addition, the reaction mixture was allowed to stir for 30 min and then acidified. The resulting precipitate was collected by filtration, washed with copious amounts of water and dried *in vacuo*. Compound **2** was used without further purification.

Yield: 76.1 g, 59%; melting point: 71°C. Infrared i.r. (KBr) ν cm^{-1}: 3428 (OH). ^{1}H n.m.r. ($CDCl_3$) δ: 6.9, 7.3, 7.9 (*m*, 8H, aromatic), 2.7 (*t*, 2H, $J = 7.7$ Hz, $ArCH_2$), 1.7 (*m*, 2H, $ArCH_2CH_2$), 1.4 (*m*, 2H, CH_2CH_3), 1.0 (*t*, 3H, $J = 7.3$ Hz, CH_3).

1-Bromo-6-(4-n-butylazobenzene-4′-oxy)hexane (**3**)

Compound **3** was prepared using the synthetic method described in detail elsewhere[34] and was recrystallized from ethanol.

Yield: 39.5 g, 86%; melting point: 67.1°C. ^{1}H n.m.r. ($CDCl_3$) δ: 7.0, 7.3, 7.8 (*m*, 8H, aromatic), 4.0 (*t*, 2H, $J = 6.4$ Hz, OCH_2), 3.4 (*t*, 2H, $J = 6.1$ Hz, CH_2Br), 2.7 (*t*, 2H, $J = 7.7$ Hz, CH_2Ar), 1.2–2.0 (*m*, 12H, CH_2), 0.9 (*t*, 3H, $J = 7.3$ Hz, CH_3).

6-(4-n-Butylazobenzene-4′-oxy)hexyl methacrylate (**4**)

Compound **4** was prepared using the synthetic method described in detail by Craig and Imrie[35] and was recrystallized from ethanol.

Yield: 7.7 g, 62%; melting point: 52.5°C. I.r. (KBr) ν cm^{-1}: 1714 (vs C=O), 1637 (C=C). ^{1}H n.m.r. ($CDCl_3$) δ: 7.0, 7.3, 7.8 (*m*, 8H, aromatic), 5.6, 6.1 (*s*, 2H, $CH_2{=}C$), 4.2 (*t*, 2H, $J = 6.6$ Hz, $H_2COC(O)$), 4.0 (*t*, 2H, $J = 6.4$ Hz, OCH_2), 2.7 (*t*, 2H, $J = 7.8$ Hz, CH_2Ar), 2.0 (*s*, 3H, CH_3), 1.3–1.9 (*m*, 12H, $CH_2CH_2CH_2$), 0.9 (*t*, 3H, $J = 7.2$ Hz, CH_3).

Poly[6-(4-n-butylazobenzene-4′-oxy)hexyl methacrylate] (**5**)

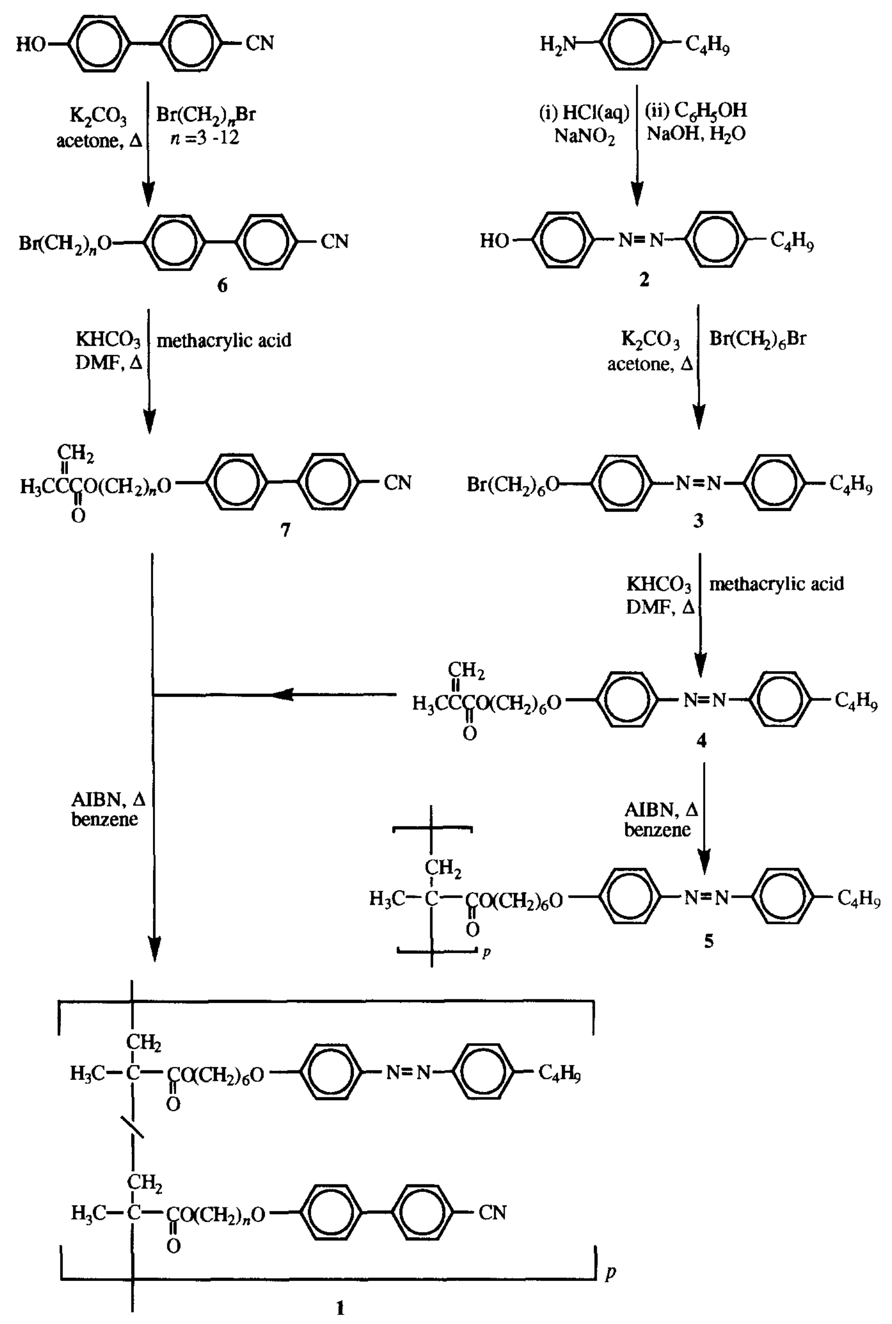
The polymerization of 6-(4-*n*-butylazobenzene-4′-oxy)-hexyl methacrylate, **4**, was performed using a reaction procedure described elsewhere[35], except that 3 mol% AIBN was added as the initiator. The polymer was purified by several precipitations from THF into methanol.

Yield: 30%. I.r. (KBr) ν cm^{-1}: 1728 (vs C=O). ^{1}H n.m.r. ($CDCl_3$) δ: 7.0, 7.3, 7.8 (*m*, 8H, aromatic), 3.9 (*m*, 4H, OCH_2, $H_2COC(O)$), 2.6 (*m*, 2H, CH_2Ar), 1.2–2.0 (*m*, 14H, $CH_2CH_2CH_2$), 0.9 (*m*, 6H, CH_3).

n-CNBip/6-BuAzB (**1**)

Equimolar amounts of **4** (0.47 g, 1.1 mmol) and **7** (0.45 g, 1.1 mmol) were dissolved in benzene (10 ml) and 1 mol% AIBN added as initiator. The reaction mixture was flushed with argon for 20 min and then heated in a water bath at 60°C to initiate the polymerization. After 48 h the reaction was terminated by the addition of THF (15 ml) and the copolymer was precipitated in a large volume of methanol. The product was redissolved in chloroform and then reprecipitated in methanol. The removal of monomer from the copolymer was monitored using i.r. and ^{1}H n.m.r. spectroscopy.

Yield of 8-CNBip/6-BuAzB: 41%. I.r. (KBr) ν cm^{-1}: 2223 (s NC), 1728 (vs C=O). ^{1}H n.m.r. ($CDCl_3$) δ: 6.9, 7.2, 7.4, 7.5, 7.8 (*m*, 18.4H, aromatic), 3.9 (*m*, 8.2H, OCH_2, $H_2COC(O)$), 2.6 (*m*, 2H, CH_2Ar), 1.2–2.1 (*m*, 30.6H, CH_2), 0.8–1.1 (*m*, 9.5H, CH_3).



Scheme 1

Characterization

The proposed structures of all the compounds were verified using ^1H n.m.r. and i.r. spectroscopy. The ^1H n.m.r. spectra were measured in $CDCl_3$ on a Bruker AC-F 250 MHz spectrometer. The i.r. spectra were recorded using a Nicolet 205 Fourier transform i.r. spectrometer. The molecular weights of the polymers were measured by gel permeation chromatography using a Knauer Instruments chromatograph equipped with two PL gel 10 μm mixed columns and controlled by Polymer Laboratories GPC SEC V5.1 Software. THF was used as the eluent. A calibration curve was obtained using polystyrene standards.

The thermal properties of the polymers were determined by differential scanning calorimetry (d.s.c.) using a Polymer Laboratories PL-DSC equipped with an autocool accessory and calibrated using an indium standard. Two samples were used for each copolymer and the results averaged. The time–temperature profile for each copolymer was identical. Thus, each sample was heated from 35 to 230°C, maintained at 230°C for 3 min, cooled to −50°C, maintained at −50°C for 3 min, and finally reheated to 230°C. The heating and cooling rate in all cases was 10°C min^{-1}. Phase identification was performed by polarized light microscopy using an Olympus BH-2 optical microscope equipped with a Linkam THMS 600 heating stage and TMS 91 control unit. Clear, characteristic optical textures from which phase assignments were possible were obtained by cooling at either 0.2 or 0.1°C min^{-1} from *ca* 10°C above the clearing temperature to below the glass transition temperature or, in the absence of glassy behaviour, to room temperature.

RESULTS AND DISCUSSION

The molecular weights, polydispersities and number average degrees of polymerization for the *n*-CNBip/6-BuAzB series, **1**, and poly[6-(4-*n*-butylazobenzene-4′-oxy)hexyl methacrylate], (6-BuAzB), **5**, are listed in *Table 1*. The number average molecular weights are in the range 17 500–60 200 g mol^{-1}, with associated degrees of polymerization between 39 and 70. These high molecular weights ensure that the thermal properties of the copolymers lie outside the molecular weight dependent regime[36]. The actual copolymer composition could not be accurately determined using ^{1}H n.m.r. spectroscopy due to the absence of isolated peaks in the spectrum arising from only one of the repeat units. We have shown recently, however, that the addition of a mesogenic side chain to methyl methacrylate does not affect its reactivity ratio in copolymerization with methyl methacrylate and that the copolymerization is random and azeotropic in nature[37]. By analogy, therefore, the copolymerization of **4** with members of series **7** is expected to yield random copolymers.

The thermal data for the *n*-CNBip/6-BuAzB copolymers are listed in *Table 2*. These data were extracted from the second heating cycle of the d.s.c. time–temperature profile; the traces are shown in *Figure 1*. The d.s.c. trace of the homopolymer, 6-BuAzB, contains two endothermic peaks (see *Figure 1*). On cooling from the isotropic phase, a poorly defined focal conic fan texture developed and thus the phase was assigned as a smectic A phase. The magnitude of the associated entropy change is consistent with this assignment (see *Table 2*). No change in the optical texture was observed on cooling to temperatures below that associated with the second endotherm and, hence, this is presumably a crystal B or smectic B–smectic A phase transition.

Table 1 Molecular weights, polydispersities (PD) and number average degrees of polymerization (DP) for the *n*-CNBip/6-BuAzB series, **1**, and for the homopolymer, 6-BuAzB, **5**

n	$\overline{M}_{\rm n}$ (g mol^{-1})	$\overline{M}_{\rm w}$ (g mol^{-1})	PD	DP
6-BuAzB	17 500	36 000	2.10	41
3	50 000	110 000	2.20	67
4	39 100	90 000	2.29	52
5	50 700	104 000	2.05	66
6	31 000	65 000	2.09	39
7	47 300	100 000	2.12	59
8	42 100	86 000	2.03	52
9	54 200	116 000	2.15	65
10	54 200	124 000	2.29	64
11	60 200	136 000	2.27	70
12	49 000	101 000	2.05	56

The d.s.c. traces for 3-CNBip/6-BuAzB, 4-CNBip/6-BuAzB and 6-CNBip/6-BuAzB, all exhibit an endothermic peak and a weak second order transition (see *Figure 1*). The latter transition is assigned as a glass transition. On cooling from the isotropic phase, 3-CNBip/6-BuAzB and 6-CNBip/6-BuAzB develop well defined focal conic fan textures which are characteristic of smectic A phases. 4-CNBip/6-BuAzB develops a poorly defined focal conic texture and this is also assigned as a smectic A phase. The magnitudes of the associated entropy changes are in agreement with these assignments (see *Table 2*).

The d.s.c. traces for 5-CNBip/6-BuAzB, 7-CNBip/6-BuAzB and 9-CNBip/6-BuAzB contain two endothermic peaks (see *Figure 1*). The higher temperature endotherm is associated with the clearing transition; on cooling from the isotropic phase these homologues develop well defined focal conic fan textures indicative of a smectic A phase. On cooling further to temperatures below those associated with the second endotherm, no further change in the optical texture is observed and hence this lower temperature phase is assigned as either a crystal B or smectic B phase.

The d.s.c. traces for 8-CNBip/6-BuAzB, 10-CNBip/6-BuAzB, 11-CNBip/6-BuAzB and 12-CNBip/6-BuAzB show an endothermic peak associated with the clearing transition and a considerably weaker, lower temperature endothermic peak. On cooling from the isotropic phase, well defined focal conic fan textures develop and these are assigned as smectic A phases. Cooling to temperatures below those associated with the lower temperature endotherm produced no further change in the optical texture; hence, the lower temperature phase is assigned as either a crystal B or smectic B phase. The magnitude of the entropy change associated with the smectic–smectic phase transition, however, is indicative of a smectic B–smectic A transition (see *Table 2*).

Figure 2 shows the dependence of the transition temperatures of the *n*-CNBip/6-BuAzB copolymers, **1**, on the number of methylene units in the alkyl spacer attached to the cyanobiphenyl-based side chain. The glass transition temperatures appear to show an initial decrease on increasing the length of the spacer, although just three glass transitions were detected using d.s.c. The clearing temperatures of the *n*-CNBip/6-BuAzB series

Table 2 Thermal properties of the *n*-CNBip/6-BuAzB series, **1**, and for the homopolymer, 6-BuAzB, **5**

n	$T_{\rm g}$ (°C)	$T_{\rm SS}$ (°C)	$T_{\rm SI}$ (°C)	$\Delta H_{\rm SS}$ (kJ mol^{-1})	$\Delta H_{\rm SI}$ (kJ mol^{-1})	$\Delta S_{\rm SS}/R$	$\Delta S_{\rm SI}/R$
6-BuAzB	—	82	96	0.43	4.56	0.15	1.49
3	70	—	146	—	3.74	—	1.07
4	52	—	126	—	2.64	—	0.79
5	—	92	158	2.64	4.31	0.87	1.20
6	54	—	136	—	2.79	—	0.82
7	—	83	152	2.79	3.89	0.94	1.10
8	—	67	139	1.17	3.01	0.42	0.88
9	—	74	136	2.01	3.54	0.69	1.04
10	—	57	120	0.95	2.98	0.35	0.91
11	—	60	125	1.04	3.41	0.37	1.03
12	—	54	119	0.61	3.20	0.23	0.98

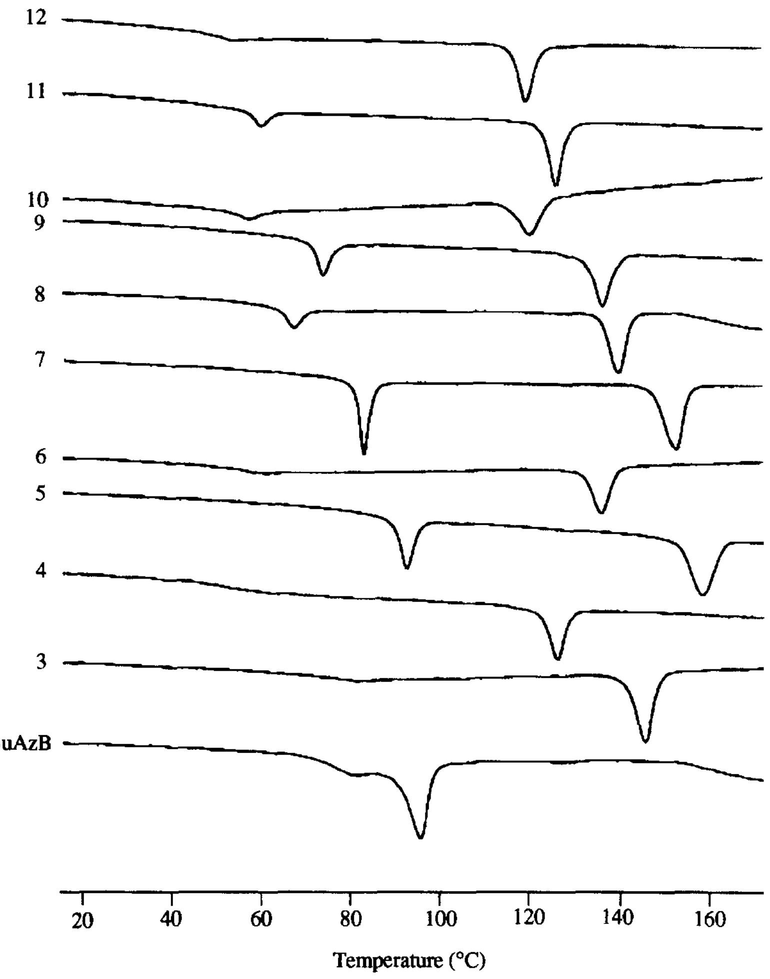


Figure 1 Normalized d.s.c. traces obtained on the second heating of the *n*-CNBip/6-BuAzB series, **1**, and for the homopolymer, 6-BuAzB, **5**

display an odd–even effect in which the odd members exhibit the higher values although the clearing temperature of 10-CNBip/6-BuAzB appears to be *ca* 10°C lower than expected. This effect is attenuated on increasing the length of the spacer. The alternation in the clearing temperatures may be attributed to the role played by the spacer in determining the relative orientations of the mesogenic groups[32,35,38]. In essence, for an odd membered spacer there exists conformations in which the mesogenic units are orthogonal with respect to the polymer backbone. This allows for the efficient packing of the groups and the anisotropic interactions between them are, therefore, maximized, resulting in enhanced clearing temperatures. For an even membered spacer the mesogenic groups are constrained to lie at some angle with respect to the backbone and this reduces the degree of interaction between the groups, resulting in lower clearing temperatures. The attenuation in the alternation exhibited by the clearing temperatures reflects the increasing number of conformations available to the spacer on increasing its length; these dilute the change in the average shape of the side chain on varying the spacer parity.

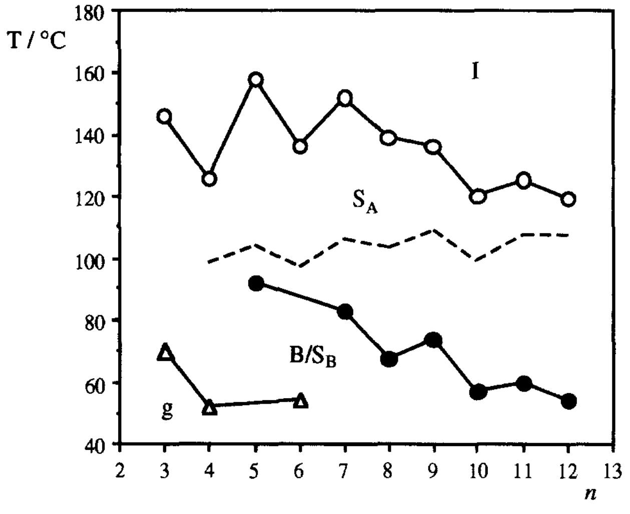


Figure 2 Dependence of the transition temperatures on varying the length of the alkyl spacer, *n*, for the *n*-CNBip/6-BuAzB series, **1**. Dotted line indicates the expected clearing temperature for ideal equimolar copolymers. Glass transition temperatures (△), smectic B/B–smectic A(●), smectic A–isotropic (○). I, isotropic; S_A, smectic A; B, crystal B; S_B, smectic B

Figure 2 also shows the expected clearing temperatures for ideal equimolar copolymers; these have been calculated using the transition temperatures of the corresponding homopolymers[32]. Ideal in this context it is used to describe a system in which the clearing temperatures vary in a linear fashion with composition, although strictly, if the molar volumes of the two differing side chains differ significantly, then the volume fraction of each component should be used instead of the mole fraction. The clearing temperatures of the *n*-CNBip/6-BuAzB copolymers are significantly higher than those calculated assuming ideal behaviour

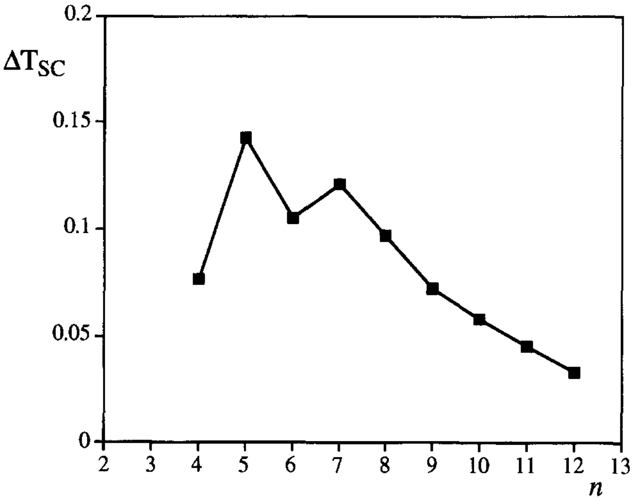


Figure 3 Dependence of ΔT_{SC} on the length of the alkyl spacer, *n*, in the cyanobiphenyl-based side chain for the *n*-CNBip/6-BuAzB series, 1

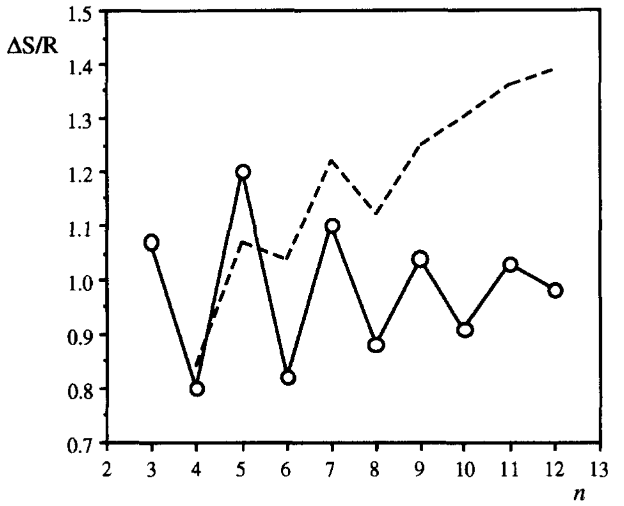


Figure 4 Dependence of the entropy change associated with the clearing transition on the length of the alkyl spacer, *n*, in the 4-cyanobiphenyl-based side chain for the *n*-CNBip/6-BuAzB series, 1. Dotted line indicates the expected values of $\Delta S/R$ for ideal equimolar copolymers

(see *Figure 2*). In order to assess the relative magnitude of these deviations from ideal behaviour a scaled deviation temperature, ΔT_{SC}, is used:

$$\Delta T_{SC} = \frac{2T_{AB} - (T_A + T_B)}{(T_A + T_B)}$$

where T_{AB} is the clearing temperature for the copolymer, and T_A and T_B are those of the homopolymers. Thus, if the copolymer has a lower clearing temperature than predicted by ideal mixing, ΔT_{SC} will be negative, while a positive value of ΔT_{SC} indicates a higher than predicted clearing temperature. *Figure 3* shows the dependence of ΔT_{SC} on *n* for the *n*-CNBip/6-BuAzB series, and ΔT_{SC} is positive for all values of *n*. These deviations in the clearing temperatures may be understood, at least at a qualitative level, within the framework of a molecular field theory developed to predict phase diagrams for binary mixtures of low molar mass nematogens[39]. This theory requires three intermolecular interaction parameters to be defined: the interaction parameters between like components, ϵ_{AA} and ϵ_{BB}, and the mixed interaction parameter between unlike components, ϵ_{AB}. The interaction parameters ϵ_{AA} and ϵ_{BB} are proportional to the nematic–isotropic transition temperatures of the pure components. If ϵ_{AB} is assumed to be the geometric mean of ϵ_{AA} and ϵ_{BB}, then the predicted transition temperatures of the mixtures are the weighted averages of those of the pure components, i.e. $\Delta T_{SC} = 0$. For many low molar mass systems it has been found experimentally that ΔT_{SC} is zero and, hence, the geometric mean approximation appears to be valid. Deviations from the geometric mean approximation give rise to a non-linear dependence of the nematic–isotropic transition temperature on composition, i.e. $\Delta T_{SC} \neq 0$. If ϵ_{AB} is greater than the geometric mean of ϵ_{AA} and ϵ_{BB}, then a curve lying above the straight line is observed, i.e. $\Delta T_{SC} > 0$, while a value of ϵ_{AB} less than the geometric mean results in a curve lying below the straight line, i.e. $\Delta T_{SC} < 0$. For binary mixtures of low molar mass mesogens in which one mesogen is electron rich and the other electron deficient, $\Delta T_{SC} > 0$, implying a favourable specific interaction between the unlike mesogens such that ϵ_{AB} is greater than the geometric mean of the like interaction parameters. It is important to note, however, that even small deviations in ϵ_{AB} give rise to curved boundaries in the calculated phase diagrams[39,40].

For side chain liquid crystal copolymers containing the same mesogenic group, but differing spacer lengths, $\Delta T_{SC} \approx 0$, suggesting that within the range of spacer lengths investigated, i.e. 3–12, the ability of the mesogenic units to interact in the homo- and co-polymers appears to be the same[29,41–46]. The positive deviations in ΔT_{SC} exhibited by the *n*-CNBip/6-BuAzB series are indicative, therefore, of a specific interaction between the unlike mesogenic groups in the copolymer. The nature of the specific interaction between the unlike groups is unclear, although for similar groups it is normally assumed to involve charge transfer. The decreasing trend in ΔT_{SC} on increasing the length of the spacer, *n*, attached to the 4-cyanobiphenyl-based side chain (*Figure 4*) presumably reflects the increase in flexibility of the side chain, which acts to dilute the specific interactions between the unlike mesogenic units. For 4-CNBip/6-BuAzB, ΔT_{SC} is significantly lower than that for 5-CNBip/6-BuAzB, suggesting that this particular combination of spacer lengths, i.e. butyl/hexyl, hinders the interaction between the unlike groups. By comparison, for 5-CNBip/6-BuAzB, the combination of spacer lengths maximizes the interaction and results in the highest value of ΔT_{SC}.

The dependence of the entropy change associated with the clearing transition, expressed as the dimensionless quantity $\Delta S/R$, on the number of methylene units, *n*, for the *n*-CNBip/6-BuAzB copolymer series is shown in *Figure 4*. A pronounced odd–even effect is apparent in which the odd members exhibit the higher values; this alternation attenuates on increasing *n*. This alternation in $\Delta S/R$ arises from the selection of elongated conformers, invoked to account for the alternation exhibited by the clearing temperatures, by the anisotropic liquid crystalline environment[32,35]. The arithmetic mean values of the clearing entropies for the corresponding homopolymers are also shown in *Figure 4*. All the copolymers, with the exception of 5-CNBip/6-BuAzB, exhibit clearing entropies which are smaller than the average values of the corresponding homopolymers. This may be accounted for by the packing of the side chains in the smectic phase. Polymers such as 6-BuAzB exhibit S_A phases in which the side chains are almost fully overlapped. This arrangement necessarily gives rise to interactions between the aromatic cores and the flexible spacers, which tend to order the flexible spacer[41]. This effect increases the conformational contribution to the overall clearing entropy and gives rise to a relatively high value of $\Delta S/R$ for a smectic A–isotropic transition (see *Table 2*). By comparison, 4-cyanobiphenyl-based homopolymers exhibit smectic A phases in which the side chains are only partially overlapped and this greatly reduces the interactions between the mesogenic groups and flexible spacers. Thus, the associated smectic A–isotropic entropy changes are smaller[31]. The calculated clearing entropies for the copolymers include the high value observed for 6-BuAzB. The actual values of $\Delta S/R$ are lower than expected due to a disruption of the packing efficiency of the butylazobenzene-based side chains in the copolymers. The clearing entropy for 5-CNBip/6-BuAzB is greater than the average value of those exhibited by the corresponding homopolymers; this combination of spacer lengths also gave rise to the highest value of ΔT_{SC} (see *Figure 3*). This strongly suggests that the specific interaction between the unlike groups is maximized in this copolymer and this increases the degree of molecular ordering and, hence, the clearing entropy.

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