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Role of Specific Interactions in Determining the Mesogenic Behavior of Side-Chain Liquid Crystal Polymers

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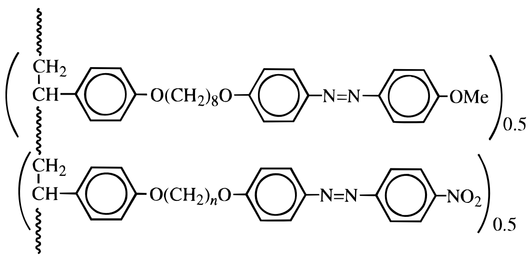
ABSTRACT: A new series of side-chain liquid crystal copolymers has been prepared, poly[4-[[[[[(4-methoxyphenyl)azo]phenyl-4]oxy]-8-octyl]oxy]styrene]-*co*-poly[4-[[α-[[[(4-nitrophenyl)azo]phenyl-4]oxy]-*ω*-alkyl]oxy]styrene]s, containing electron rich and electron deficient mesogenic groups. The length of the spacer attached to the electron rich group, 4-methoxyazobenzene, is held at 8 methylene units, while that attached to the electron deficient group, 4-nitroazobenzene, is varied in length from 3 to 12 methylene units. The thermal properties of the polymers have been characterized using polarized light microscopy and differential scanning calorimetry. All the copolymers exhibit a smectic A phase. The thermal properties of the copolymers are compared with those of the corresponding homopolymers. The glass transition temperatures of the copolymers are typically within experimental error of the weighted average of those of the respective homopolymers. By contrast, the smectic A−isotropic transition temperatures of the copolymers are significantly higher than the average of those of the corresponding homopolymers. These differences are expressed as reduced deviations and rationalized in terms of a specific interaction between the unlike mesogenic units in the copolymer.

Introduction

Side-chain liquid crystal polymers are an important class of materials not only from a technological viewpoint, where they offer considerable application potential in a range of advanced electro-optic technologies,[1,2] but also because they provide a demanding test of our understanding of self-organization in polymeric systems.[3,4] A side-chain liquid crystal polymer comprises three distinct structural components: a polymer backbone, a mesogenic group, and a flexible spacer which attaches the mesogen to the polymer. The thermal properties of such a polymer may be controlled by varying the chemical structures of these components, and empirical rules have been developed which allow for this to be performed to some extent in a rational manner.[3,4] More recently, a new class of side-chain liquid crystal polymers has emerged in which specific noncovalent interactions are used to control the thermal behavior, and these are termed supramolecular side-chain liquid crystal polymers.[5] One such specific interaction which has been exploited in the design of new materials 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. The interaction is known to be important, however, in determining the liquid crystalline properties of a wide variety of mesogenic systems including, for example, binary mixtures of conventional low molar mass liquid crystals,[7−15] nonsymmetric dimeric liquid crystals,[16−18] and mixtures of mesogenic and nonmesogenic components.[19−23] It has been shown that such interactions can affect also the properties of side chain liquid crystalline copolymers containing electron rich and electron deficient groups.[24−31] In order to investigate further the role of this specific interaction in determining thermal properties we have prepared the copolymer series poly[4-[[[[[(4-methoxyphenyl)azo]phenyl-4]oxy]-8-octyl]oxy]styrene]-*co*-poly[4-[[α-[[[(4-nitrophenyl)azo]phenyl-4]oxy]-*ω*-alkyl]oxy]styrene]s, **1**.



The acronym nNO$_2$-8OMe is used to refer to series **1** in which n indicates the number of methylene units in the flexible spacer linking the 4-nitroazobenzene moiety to the polystyrene backbone. This particular series was chosen because the corresponding homopolymers[32,33] and the copolymers in which the mesogenic units are identical but the spacer lengths are varied[32,34] have been studied.

Experimental Section

Synthesis. The synthetic route taken to prepare the nNO$_2$-8OMe copolymer series is shown in Scheme 1. The syntheses of 1-bromo-8-[[[(4-methoxyphenyl)azo]phenyl-4]oxy]octane, **2**, and the α-bromo-*ω*-[[[(4-nitrophenyl)azo]phenyl-4]oxy]alkanes, **3**, have been described in detail elsewhere.[32,33]

Polymers. The copolymers were prepared by the phase transfer catalyzed reaction of **2** and **3** in equimolar amounts onto poly(4-hydroxystyrene) (M_w = 9000−11 000, PolySciences

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Scheme 1

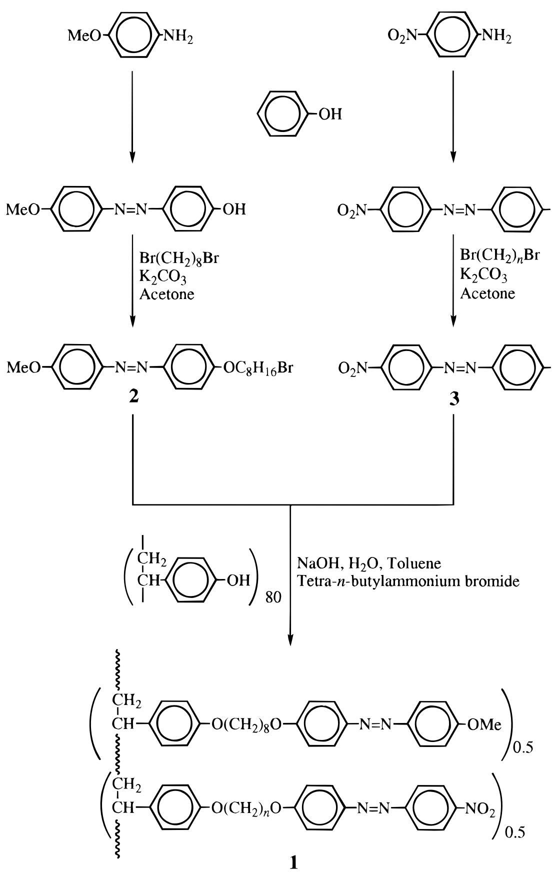

Table 1. Elemental Analyses for the nNO$_2$-8OMe Copolymer Series

			C		H		N	
n	formula	mol wt	calc	found	calc	found	calc	found
3	$C_{52}H_{55}N_5O_7$	862.0	72.45	71.62	6.43	6.29	8.13	7.88
4	$C_{53}H_{57}N_5O_7$	876.0	72.66	71.70	6.56	5.58	8.00	7.96
5	$C_{54}H_{59}N_5O_7$	890.0	72.87	72.13	6.68	6.54	7.87	8.12
6	$C_{55}H_{61}N_5O_7$	904.1	73.06	72.64	6.80	6.64	7.75	7.69
7	$C_{56}H_{63}N_5O_7$	918.1	73.26	72.80	6.92	6.59	7.63	7.68
8	$C_{57}H_{65}N_5O_7$	932.1	73.44	73.10	7.03	7.13	7.51	7.44
9	$C_{58}H_{67}N_5O_7$	946.2	73.62	73.73	7.14	7.35	7.40	7.11
10	$C_{59}H_{69}N_5O_7$	960.2	73.80	73.97	7.24	7.46	7.29	6.98
11	$C_{60}H_{71}N_5O_7$	974.2	73.97	73.31	7.35	7.33	7.19	7.06
12	$C_{61}H_{73}N_5O_7$	988.2	74.13	74.30	7.45	7.34	7.09	6.87

Inc.) as described in detail elsewhere.[27,32,35] The copolymers were purified by a single precipitation from dichloromethane into methanol followed by exhaustive Soxhlet extraction using methanol. These procedures ensured the complete removal of any unreacted side chains. The polymer modification reaction does not result in any detectable molecular weight degradation.[32] The degree of backbone derivitization was assessed using infrared spectroscopy[35] and within detection limits confirmed that 100% substitution had occurred. Copolymer composition was estimated using ^{1}H-NMR spectroscopy, data for 8NO$_2$-8OMe have already been described in detail,[28] and by elemental analysis; see Table 1.

Thermal Characterization. The thermal properties of the polymers were investigated using a Perkin-Elmer DSC-7 differential scanning calorimeter calibrated using an indium standard. For each copolymer two samples were run and the values quoted are the average values for the second heating cycle; the heating rate in all cases was 10 °C min^{-1}. Peak maxima are given as the smectic A–isotropic transition temperatures. The error associated with the smectic A–isotropic enthalpy is estimated to be ±5%. The optical textures of the mesophases were studied using a Zeiss polarizing microscope equipped with a Linkam hot stage.

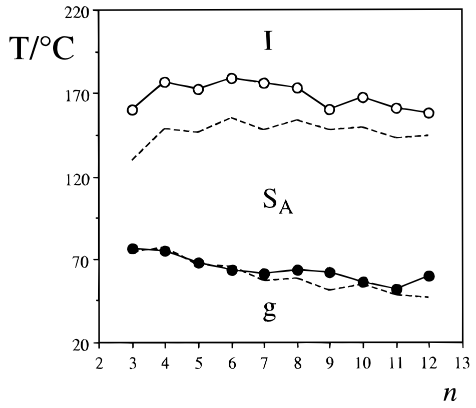

Figure 1. Dependence of the glass transition temperatures indicated by ● and the smectic A–isotropic transition temperatures denoted by ○ on the number of methylene units, n, in the flexible spacer linking the nitro-terminated side chains to the polystyrene backbone for the nNO$_2$-8OMe copolymer series. The broken lines represent ideal behavior calculated using the data for the homopolymers. Key: g, glass; S$_A$, smectic A; I, isotropic.

Table 2. Transitional Properties of the nNO$_2$-8OMe Copolymer Series

n	T_g/°C	T_{S_AI}/°C	ΔH_{S_AI}/J g^{-1}	$\Delta S_{S_AI}/R$
3	76	160	9.28	1.11
4	75	177	10.93	1.28
5	68	172	10.49	1.26
6	63	179	9.42	1.13
7	61	176	10.03	1.23
8	63	173	11.31	1.42
9	62	160	11.25	1.48
10	56	167	11.31	1.49
11	52	161	10.98	1.48
12	60	158	9.77	1.35

Results and Discussion

The poly(4-hydroxystyrene) used in this study yields final polymers of approximately 80 repeat units.[32] A recent investigation using 4-cyanoazobenzene as the mesogenic group suggested that polymers derived from this backbone are essentially in the regime in which transitional properties do not show molecular weight dependence.[36] The transition temperatures and associated enthalpies and entropies of transition for the nNO$_2$-8OMe copolymers are listed in Table 2. The DSC second heating trace for each member of the series contained two transitions: a step in the baseline at lower temperatures and an endotherm at higher temperatures. Using optical microscopy these were assigned as the glass and clearing transitions respectively. In order to obtain clear, characteristic optical textures to facilitate phase identification, each copolymer was heated to approximately 10 deg above the clearing temperature and allowed to cool at 0.2 °C min^{-1} into the mesophase. At the transition, bâtonnets developed which coalesced, yielding a well-defined focal-conic fan texture in coexistence with regions of homeotropic alignment. The observation of focal-conic defects implies a layered structure, while homeotropic alignment reveals an orthogonal arrangement of the director with respect to the layer planes. In consequence the mesophase exhibited by these copolymers is assigned as a smectic A phase. This view is supported by X-ray diffraction experiments using 8NO$_2$-8OMe.[28] The width of the endotherm associated with the smectic–isotropic transition was the same for both the homopolymers and copolymers.

Figure 1 shows the dependence of the transition temperatures on the number of methylene units, n, in

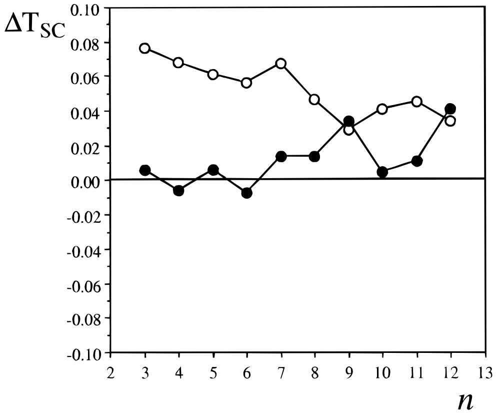

Figure 2. Dependence of ΔT_{SC} on the number of methylene units, *n*, in the flexible spacer linking the nitro-terminated side chains to the polystyrene backbone for the nNO$_2$-8OMe copolymer series. ● indicates glass transition temperatures, and ○ denotes the smectic A–isotropic transition temperatures.

the flexible spacer linking the nitro-terminated side chain to the polystyrene backbone for the nNO$_2$-8OMe copolymers. Also shown in Figure 1 are the calculated transition temperatures for ideal equimolar copolymers obtained using the transition temperatures of the corresponding homopolymers;[32,33] ideal in this context is used to describe a system in which the transition temperatures vary linearly with composition. We note, however, that strictly if the molar volumes of the two components differ significantly, then the volume fraction of each component should be used instead of the mole fraction. The glass transition temperatures of the nNO$_2$-8OMe series show a small decrease on increasing *n* before reaching a limiting value at *ca.* 60 °C and exhibit excellent agreement with those predicted for ideal behavior, although the T_g's for 9NO$_2$-8OMe and 12NO$_2$-8OMe show somewhat larger positive deviations than the other copolymers. The smectic A–isotropic transition temperatures of the nNO$_2$-8OMe series also show only a weak dependence on *n*. However, in contrast to the glass transition temperatures, the smectic A–isotropic transition temperatures all exhibit a significant positive deviation from ideal behavior.

In order to assess the relative magnitudes of the deviations from ideal behavior observed for the glass transition and smectic A–isotropic transition temperatures (see Figure 1), we define a scaled deviation, ΔT_{SC}, as[18,34]

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

where T_{AB} is the transition temperature for the copolymer and T_A and T_B are those of the homopolymers; it is important to note that the homopolymers exhibit the same phase sequence as the copolymers. Thus, if the copolymer has a lower smectic A–isotropic or glass transition temperature than predicted by ideal mixing, ΔT_{SC} will be negative while a positive value of ΔT_{SC} indicates a higher than predicted T_g or smectic A–isotropic transition temperature for the copolymer. Figure 2 shows the dependence of ΔT_{SC} on *n* for both the glass transition temperature and the smectic A–isotropic transition temperature. The scaled deviations in T_g are small and exceed 1.5% only for 9NO$_2$-8OMe (3.4%) and 12NO$_2$-8OMe (4.1%). For two members of the series, 4NO$_2$-8OMe and 6NO$_2$-8OMe, a small negative deviation is observed. The small alternation observed initially ($n = 3-7$) in the reduced glass transition temperatures is also evident in the weighted averages of the T_g's of the corresponding homopolymers; see Figure 1. This observation strongly suggests, therefore, that the error associated with these scaled values is $<\pm 0.01$. If this was not the case, then this small alternation would be smeared out. This provides further evidence that the synthetic methodology developed to prepare mesogenic polystyrenes yields materials of high purity with reproducible thermal behavior. On increasing *n*, however, the regular alternation in the scaled glass transition temperature is no longer apparent, suggesting that the specific interaction is, in part, determining T_g of the copolymer. Small scaled deviations in T_g were also observed for other copolymer series containing electron rich and electron deficient groups[27−30] and also for copolymers containing spacers of differing lengths but only one type of mesogenic group.[30,32,34,37−40] By contrast, larger scaled deviations are observed for the smectic A–isotropic transition temperature (see Figure 2), which tend to decrease smoothly with increasing *n*. Two members of the series do not fall on this smooth curve: 7NO$_2$-8OMe for which ΔT_{SC} lies above the curve and 9NO$_2$-8OMe for which ΔT_{SC} falls below the curve. The maximum value of ΔT_{SC} for the smectic A–isotropic transition temperatures is observed for 3NO$_2$-8OMe (7.6%) and is comparable to ΔT_{SC} observed for other copolymer series containing potentially charge-transfer groups.[27−30] These scaled deviations are, however, considerably larger than those normally observed for copolymer series containing one type of mesogenic group but differing spacer lengths.[30,32,34,37−40]

The deviations in the smectic A–isotropic transition 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.[41] This theory requires three intermolecular interaction parameters to be defined: the interaction parameters between the like components, ϵ_{AA} and ϵ_{BB}, and the mixed interaction parameter between the unlike components, ϵ_{AB}. ϵ_{AA} and ϵ_{BB} are proportional to the smectic A–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.* $\Delta T_{SC} = 0$. Deviations from the geometric mean approximation give rise to a nonlinear dependence of the smectic A–isotropic transition temperature on composition, *i.e.* $\Delta T_{SC} \neq 0$.[41,42] If ϵ_{AB} is larger 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.* $\Delta T_{SC} < 0$. It is important to note that even small deviations in ϵ_{AB}, for example ±1.85%, give rise to curved boundaries in the phase diagrams. For many low molar mass systems, experimentally, ΔT_{SC} is found to be 0 and, hence, the geometric mean approximation appears to be valid. This is also the case for selected side-chain liquid crystal copolymers containing one type of mesogenic group but differing spacer lengths.[30,32,34,37−40] This implies that within the range of spacer lengths investigated, the ability of the mesogenic groups to interact appears to be the same in both the homo- and copolymers. In contrast, binary mixtures of low molar mass mesogens containing electron rich and electron deficient groups

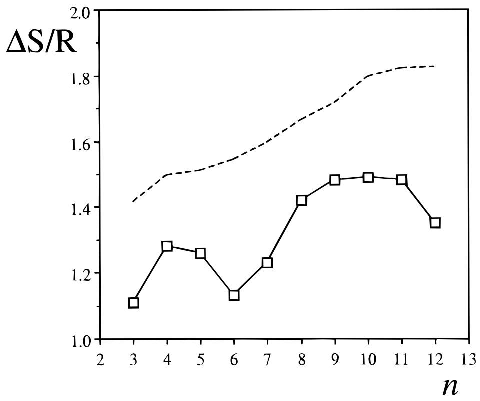

Figure 3. Dependence of the entropy associated with the smectic A–isotropic transition on the number of methylene units, *n*, in the flexible spacer linking the nitro-terminated side chains to the polystyrene backbone for the *n*NO_2-8OMe copolymer series. The broken line represents the weighted average of the smectic A–isotropic entropies of the corresponding homopolymers.

exhibit enhanced liquid crystal behavior, *i.e.* $\Delta T_{SC} > 0$. This is normally interpreted in terms of a favorable specific interaction between the unlike mesogens such that ϵ_{AB} is greater than the geometric mean of the like interaction parameters. The same approach can be used to account for the scaled deviations in the smectic A–isotropic transition temperatures for the *n*NO_2-8OMe series which are indicative, therefore, of the occurrence of a specific interaction between the unlike mesogenic groups in the polymer. The average value of ΔT_{SC} observed for the *n*NO_2-8OMe series is significantly higher than that observed for the equimolar mixture of the analogous low molar mass mesogens containing hexyloxy terminal chains.[27] This observation suggests that the specific interaction responsible for the enhancement in the smectic A–isotropic transition temperatures is maximized in the side-chain copolymers. Furthermore, the decreasing trend in ΔT_{SC} on increasing the length of the spacer, *n*, attached to the nitro-substituted mesogen reflects that increasing the flexibility of the system dilutes the specific interaction. However, the combination of spacer lengths present in 7NO_2-8OMe promotes the interaction and ΔT_{SC} is higher than expected while in 9NO_2-8OMe the interaction is presumably hindered and ΔT_{SC} is correspondingly lower.

The dependence of the entropy associated with the smectic A–isotropic transition on *n* for the *n*NO_2-8OMe copolymer series is shown in Figure 3; also shown are the average values of $\Delta S/R$ for the respective homopolymers.[32,33] All the copolymers exhibit smectic A–isotropic entropies which are significantly smaller than those predicted on the basis of ideal mixing. This may be accounted for by the packing of the side chains in the smectic phase. For the methoxy-substituted homopolymer the side chains overlap almost completely[28] and the resulting interaction between the mesogenic units and the flexible spacers tends to order the latter. Thus at the smectic A–isotropic transition there is an enhanced conformational contribution to the overall entropy resulting in high values of $\Delta S/R$.[32] In contrast, the nitro-substituted homopolymers[28,43] and 8NO_2-8OMe[28] exhibit partially interdigitated smectic phases in which the interaction between the mesogenic units and spacers is considerably reduced. Thus the associated smectic A–isotropic entropies are lower. Hence, the calculated smectic A–isotropic entropies reflect the differing phase structure exhibited by the methoxy-substituted homopolymer and are, therefore, somewhat higher than observed.

The proposed interpretation of the phase behavior of the copolymers has not considered the effect of the mesogenic group sequence distribution on the thermal behavior. A comparison of the thermal behavior of copolymers containing a regularly alternating mesogenic group sequence with those containing the same groups but in random sequencing revealed that the randomization of the mesogenic groups gave rise to small but definite increases in both the smectic A–isotropic transition temperature and entropy.[44] In that study the mesogenic groups did not exhibit a specific interaction. It is unwise, therefore, to speculate about the relative magnitude of this effect for the copolymers under consideration here, but work is in progress to prepare regularly alternating copolymers in which the mesogenic groups exhibit a specific interaction.

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