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Side-Chain Liquid-Crystalline Copolymers.[†] 2. Polystyrene-Based Side-Chain Polymers Containing Nitroazobenzene

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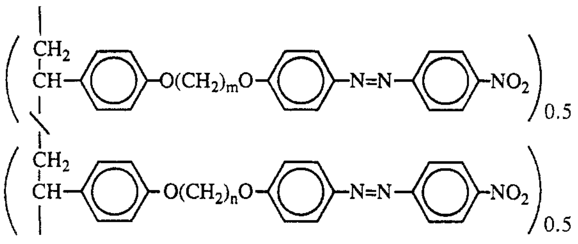
ABSTRACT: Two new series of side-chain liquid-crystalline copolymers, the poly[4-[1-(4-nitro-4′-oxyazobenzene)-8-octyl]oxystyrene]-*co*-poly[4-[α-(4-nitro-4′-oxyazobenzene)-ω-alkyl]oxystyrene]s and the poly[4-[1-(4-nitro-4′-oxyazobenzene)-9-nonyl]oxystyrene]-*co*-poly[4-[α-nitro-4′-oxyazobenzene)-ω-alkyl]oxystyrene]s, have been prepared in which the second spacer is varied in length from 3 to 12 methylene units. All the copolymers exhibit a smectic phase identified using polarizing microscopy. The thermal behavior of the copolymers has been investigated and is compared with that of the analogous homopolymers. To make such comparisons, we scale the transition temperatures of the copolymers with respect to the mean temperatures of the respective homopolymers. The deviations from ideal behavior in all cases are very small. By comparison, the entropy changes associated with the smectic–isotropic transition for the copolymers are more sensitive to changes in the molecular structure. We discuss these results in terms of the interaction parameters between the mesogenic cores and the formation of antiparallel dimers which serve to minimize the dipolar energy.

Introduction

The research activity in the area of side-chain liquid-crystal polymers has been driven largely by the promise of new advances in electrooptic technologies including optical information storage[1] and nonlinear optics.[2] These materials are suited to such applications because they possess a duality of properties, combining macromolecular characteristics, for example, ease of processibility and glassy behavior, with the electrooptic properties of low molar mass mesogens.[3] A critical stage in the processing of liquid-crystalline materials for use in electrooptic applications is the alignment of the mesophase directors by an electric field. This requires that the mesogenic unit has a positive dielectric anisotropy ($\Delta\epsilon$), as provided by, for example, a nitroazobenzene group. The thermal properties of low molar mass liquid crystals derived from such moieties are governed largely by the formation of antiparallel dimers which serve to minimize the dipolar energy of the system. A consequence of these associations is a reduction in the anticipated $\Delta\epsilon$ for the mesophase. In the development of devices incorporating low molar mass mesogens, mesogenic mixtures containing components of high and low $\Delta\epsilon$ were used in which the compounds possessing low $\Delta\epsilon$ values are thought to disrupt the formation of the antiparallel dimers.[4] We have explored this strategy for polymeric systems in which the different components are attached to the same backbone.[5,6] An alternative strategy to prevent the formation of the dimers is unique to side-chain polymers and results specifically from the attachment of the mesogen to the backbone. If we consider a side-chain random copolymer in which the spacer lengths are allowed to vary, then it may be assumed that the dipoles could not associate to the same extent as either in a low molar mass mixture or in a homopolymer. To explore this possibility and as part of a continuing program to develop materials for electrooptic applications, we have prepared *two* new random copolymer systems, based on atactic polystyrenes, in which one spacer length (m) was held constant (m = 8 or 9) while the other was systematically varied as shown:



m = 8, 9; n = 3-12

The acronyms we use to describe these two copolymer series are therefore n-8NO$_2$ and n-9NO$_2$, in which n denotes the number of methylene units in the variable-length flexible spacer. These particular structures were chosen for two reasons. First, polymers derived from polystyrene have relatively high glass transition temperatures coupled with low clearing points; these are important considerations in the development of materials suited to information storage or nonlinear optics. Second, the monomers used in the phase-transfer-catalyzed reaction with poly(4-hydroxystyrene) are derived from α,ω-dibromoalkanes which are readily available from the propyl to the dodecyl homologues. Consequently, a complete polymer series may be prepared and the effects of the length and parity of the spacers elucidated.[7-9] In fact, such an in-depth study has been performed for only one other system in which poly(vinyl ether)s were substituted with cyanobiphenyl-terminated side chains.[10-14] In this contribution, we also compare the properties of the two new copolymer series, n-8NO$_2$ and n-9NO$_2$, with those of an analogous series, n-8OMe, containing a methoxy rather than a nitro substituent.[7]

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Table 1. Elemental Analyses for the *n*-8NO$_2$ Copolymer Series

			C		H		N	
n	formula	mol wt	calcd	found	calcd	found	calcd	found
3	$(C_{25.5}H_{26}N_3O_4)_x$	$(438.5)_x$	69.84	69.45	5.98	5.76	9.58	9.63
4	$(C_{26}H_{27}N_3O_4)_x$	$(445.5)_x$	70.09	69.37	6.11	5.90	9.43	9.60
5	$(C_{26.5}H_{28}N_3O_4)_x$	$(452.5)_x$	70.33	69.71	6.24	6.02	9.29	9.55
6	$(C_{27}H_{29}N_3O_4)_x$	$(459.5)_x$	70.57	69.86	6.36	6.18	9.15	9.03
7	$(C_{27.5}H_{30}N_3O_4)_x$	$(466.5)_x$	70.79	69.79	6.48	6.33	9.01	8.91
9	$(C_{28.5}H_{32}N_3O_4)_x$	$(480.6)_x$	71.23	71.03	6.71	6.50	8.74	8.85
10	$(C_{29}H_{33}N_3O_4)_x$	$(487.6)_x$	71.43	71.14	6.82	6.56	8.62	8.57
11	$(C_{29.5}H_{34}N_3O_4)_x$	$(494.6)_x$	71.63	70.97	6.93	6.64	8.50	8.54
12	$(C_{30}N_{35}N_3O_4)_x$	$(501.6)_x$	71.83	71.36	7.03	7.03	8.38	8.23

Table 2. Elemental Analyses for the *n*-9NO$_2$ Copolymer Series

			C		H		N	
n	formula	mol wt	calcd	found	calcd	found	calcd	found
3	$(C_{26}H_{27}N_3O_4)_x$	$(445.5)_x$	70.09	69.70	6.11	5.95	9.43	9.58
4	$(C_{26.5}H_{28}N_3O_4)_x$	$(452.5)_x$	70.33	69.80	6.24	6.10	9.29	9.31
5	$(C_{27}H_{29}N_3O_4)_x$	$(459.5)_x$	70.57	70.23	6.36	6.44	9.15	9.28
6	$(C_{27.5}H_{30}N_3O_4)_x$	$(466.5)_x$	70.79	70.04	6.48	6.27	9.01	8.69
7	$(C_{28}H_{31}N_3O_4)_x$	$(473.6)_x$	71.01	70.09	6.60	6.42	8.87	8.86
10	$(C_{29.5}H_{34}N_3O_4)_x$	$(494.6)_x$	71.63	70.81	6.93	6.91	8.50	8.26
11	$(C_{30}H_{35}N_3O_4)_x$	$(501.6)_x$	71.83	71.58	7.03	7.00	8.38	8.24
12	$(C_{30.5}H_{36}N_3O_4)_x$	$(508.6)_x$	72.16	71.90	6.95	6.99	8.28	8.24

Table 3. Thermal Properties of the *n*-8NO$_2$ Copolymer Series

n	T_g/°C	T_{Cl}/°C	ΔH/J g^{-1}	$\Delta S/R$
3	45	138	4.86	0.62
4	47	152	5.09	0.64
5	42	146	4.99	0.65
6	42	163	5.49	0.70
7	38	157	6.57	0.86
9	31	159	7.23	0.97
10	33	146	6.81	0.95
11	28	144	6.17	0.88
12	26	142	6.59	0.96

Table 4. Thermal Properties of the *n*-9NO$_2$ Copolymer Series

n	T_g/°C	T_{Cl}/°C	ΔH/J g^{-1}	$\Delta S/R$
3	52	122	4.06	0.55
4	55	148	4.90	0.63
5	45	139	4.89	0.66
6	39	158	5.02	0.65
7	35	137	3.89	0.54
10	27	137	4.91	0.71
11	23	135	5.39	0.80
12	22	136	6.27	0.94

Experimental Section

The synthesis of polymers derived from poly(4-hydroxystyrene) has been discussed in detail elsewhere.[5,7,9,15] The poly(4-hydroxystyrene) ($M_w = 1.0 \times 10^4$, PolySciences Inc.) derivatized in this study was used as received. The copolymers were purified by a single precipitation followed by exhaustive Soxhlet extraction using methanol; this ensured the complete removal of any unreacted side chains. The absence of degradation in this derivatization procedure has been noted in part 1 (ref 7); thus, the degrees of polymerization of the copolymers are essentially identical to those previously listed. The elemental analyses, performed by the University of Massachusetts Microanalytical Laboratory, for the *n*-8NO$_2$ and *n*-9NO$_2$ copolymer series are listed in Tables 1 and 2, respectively. Typical NMR, IR, and UV–vis spectra for this class of polymers have been described in detail elsewhere.[8,16] IR spectroscopy is particularly useful in determining backbone derivatization, as has already been noted,[9] and confirmed that 100% substitution had occurred.

Thermal Characterization. The thermal properties of the copolymers were studied by differential scanning calorimetry using a Perkin-Elmer DSC-7 differential scanning calorimeter calibrated with indium. Each copolymer was treated in an identical manner, namely, heated into the isotropic phase, cooled to −30 °C, held at that temperature for 10 min, and then reheated into the isotropic phase. The values quoted are the average values for two different samples measured on the second heating cycle. In all cases, the heating and cooling rate was 10 °C min^{-1}. The clearing temperatures correspond to the peak maxima. The optical textures of the mesophases were studied using a Zeiss polarizing microscope equipped with a Linkam hot stage.

Results and Discussion

The thermal properties of the *n*-8NO$_2$ and *n*-9NO$_2$ copolymer series are listed in Tables 3 and 4, respectively. All the copolymers exhibited a single mesophase which was identified as a smectic A phase on the basis of its optical texture when viewed through the polarizing microscope. A small biphasic region was also typical; we could not, however, establish any correlation between the width of this regime and the molecular structure. To obtain a clear texture from which such an assignment was possible, the sample was cooled slowly from the isotropic phase into the mesophase as described in detail elsewhere.[5] This method revealed the presence of characteristic focal conic fans in coexistence with homeotropic regions, implying a smectic A phase.

The dependence of the transition temperatures on the length of the varied spacer for the *n*-8NO$_2$ copolymer series is shown in Figure 1. The glass transition temperatures decrease gradually on increasing *n*, due to the increasing plasticization effect of the second spacer. The clearing temperatures, by comparison, exhibit only an initial alternation with increasing *n* which attenuates on increasing *n* further. The *n*-9NO$_2$ copolymer series exhibits similar behavior (see Figure 2); the alternation in the clearing temperatures is somewhat larger.

To compare the transition temperatures of the copolymers with those of the analogous homopolymers,[8] we define reduced temperatures T_g^* and T_c^* as

$$T_j^* = [2T_j^{(AB)}/(T_j^{(A)} + T_j^{(B)})] - 1 \qquad (1)$$

where the subscript j refers to either the glass (J = g) or the clearing (J = c) temperature (K) of the homopolymers (superscripts A and B) or of the copolymer (superscript AB). The use of the reduced temperatures T_j^* is to provide comparisons of deviations from ideal mixing behavior in different copolymer structures. For example, if the

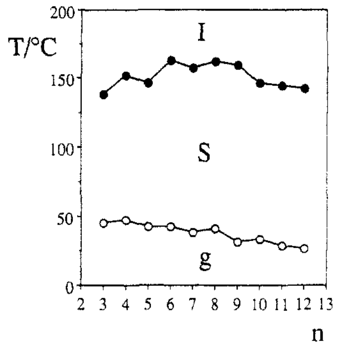


Figure 1. Dependence of the glass transition temperatures (○) and the clearing temperatures (●) on the number of methylene groups, *n*, in the variable-length flexible spacers for the *n*-$8NO_2$ copolymer series. I, S, and g (Figures 1 and 2) refer to isotropic, smectic, and glassy phases, respectively.

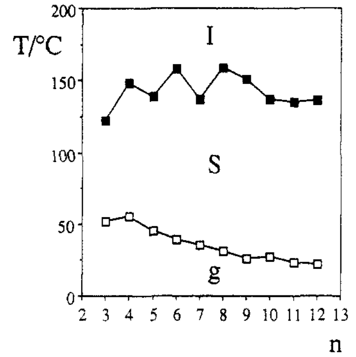


Figure 2. Dependence of the glass transition temperatures (□) and the clearing temperatures (■) on the number of methylene groups, *n*, in the variable-length flexible spacers for the *n*-$9NO_2$ copolymer series.

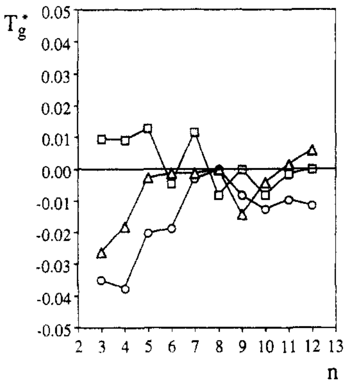


Figure 3. Dependence of the reduced glass transition temperatures on the number of methylene groups, *n*, in the variable-length spacers for the *n*-$8NO_2$ (○), the *n*-$9NO_2$ (□), and the *n*-8OMe compolymer[7] series (△).

copolymer has a lower clearing (or glass transition) temperature than predicted by ideal mixing, T_j^* will be negative. Figure 3 shows the dependence of the reduced glass transition temperature, T_g^*, on *n* for all the copolymers studied. It is noted that the deviations from ideality are small ($T_g^{(AB)}$ is within 97% of the arithmetic mean of $T_g^{(A)}$ and $T_g^{(B)}$) and probably within experimental error except for the *n*-$8NO_2$ copolymer series for $n \leq 6$. This behavior can also be seen for the *n*-8OMe copolymer series[7] (Figure 3). This reflects the difficulty experienced by randomly located shorter side chains in packing efficiently.

Figure 4 shows the dependence of the reduced clearing temperatures, T_c^*, on *n* for the *n*-$8NO_2$ and the *n*-$9NO_2$ copolymer series; also shown for comparison are the values for the *n*-8OMe copolymer series.[7] Again it can be seen that the deviations of $T_c^{(AB)}$ from ideality are small, less

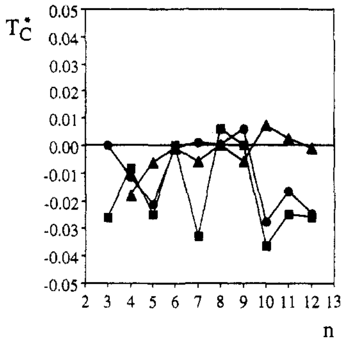


Figure 4. Dependence of the reduced clearing temperatures on the number of methylene groups, *n*, in the variable-length flexible spacers for the *n*-$8NO_2$ (●), the *n*-$9NO_2$ (■), and the *n*-8OMe copolymer[7] series (▲).

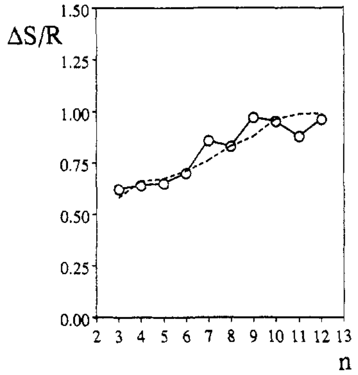


Figure 5. Dependence of the reduced entropy change associated with the clearing transition on the number of methylene groups, *n*, in the variable-length spacer for the *n*-$8NO_2$ copolymer series. The broken line represents the arithmetic mean of $\Delta S/R$ for the respective homopolymers.[8]

than ±4%, and generally negative, suggesting that the formation of antiparallel dimers has been somewhat disrupted. The homologues of the *n*-$8NO_2$ copolymer series for which $n = 6$, 7, and 9 behave in essentially an ideal manner. As the difference in length between the two spacer chains increases, the deviations from ideal behavior become more negative with the exception of 3-$8NO_2$. Similar behavior is observed for the *n*-$9NO_2$ copolymer series; as the difference in length between the two spacers becomes larger, the deviations from ideal behavior become more negative. For this series, the copolymers with $n = 6$ and 8 behave essentially in an ideal fashion, i.e., $T_c^* \approx 0$, but 7-$9NO_2$ exhibits a significant negative deviation. This may reflect a specific unfavorable dipole interaction which occurs for this particular combination of spacer lengths. For the *n*-$8NO_2$ and the *n*-$9NO_2$ copolymer series, the magnitude of T_c^* tends to be larger than for the *n*-8OMe copolymers. The transitional properties of the *n*-8OMe copolymers are not dependent on a specific dipolar interaction between the mesogenic groups as they are for nitroazobenzenes, and hence, the effect of differing length spacers would be anticipated to be smaller.

The dependence of the entropy change associated with the clearing transition on the length of the variable spacer for the *n*-$8NO_2$ copolymer series is shown in Figure 5. Also shown are the calculated weighted entropy averages for the respective homopolymers; the agreement between the experimental and calculated values is mostly within the experimental error of ±5%. For the *n*-$9NO_2$ copolymer series (Figure 6), the measured entropy values are in general less than the calculated ones and for $n = 7$, 10, and 11 these deviations are significantly greater than the experimental error.

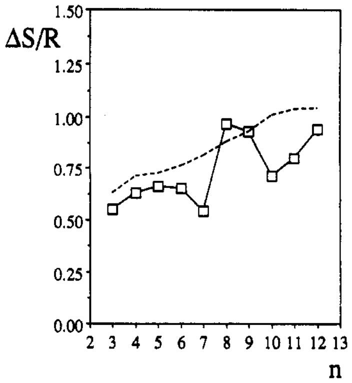
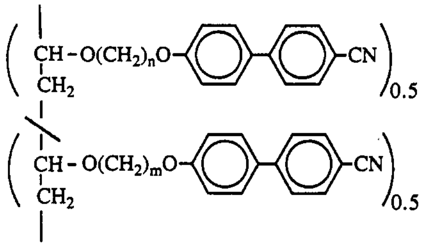


Figure 6. Dependence of the entropy change associated with the clearing transition on the number of methylene groups, *n*, in the variable-length spacer for the *n*-9NO$_2$ copolymer series. The broken line represents the arithmetic mean of $\Delta S/R$ for the respective homopolymers.[8]

Table 5. Difference, ΔT, between the Transition Temperatures of the *n–m* Cyanobiphenyl Copolymers and the Arithmetic Means of the Respective Homopolymers, and the Reduced Temperatures, T_j^* [17–20]

n–m	ΔT_g/°C	T_g^*	ΔT_{Cl}/°C	T_c^*
2–8	−10.7	−0.034	−4.2	−0.011
2–11	−16.5	−0.052	−8.1	−0.021
3–5	−2.2	−0.007	−1.1	−0.003
3–11	−14.5	−0.047	−0.7	−0.002
5–11	−6.6	−0.022	−3.6	−0.009
6–11	−6.9	−0.023	6.1	0.015

In a similar study, Percec et al.[17–20] studied the thermal properties of copolymers based on poly(vinyl ethers)s containing cyanobiphenyl as the mesogenic group:



The acronym we use to describe these copolymers is *n–m* where *n* and *m* refer to the number of methylene units in the respective alkyl spacers. The reduced transition temperatures for these copolymers are listed in Table 5; all the values are small, in accord with our results. It is interesting to note that for binary mixtures of low molar mass mesogens whose structures are analogous to the pendant groups, such small deviations from ideal behavior have been interpreted in terms of a deviation of the mixed interaction parameter, ϵ_{12}, from the geometric mean of the interaction parameters of the pure components, $(\epsilon_{11}\epsilon_{22})^{1/2}$.[21,22] However, to account for such small deviations in the clearing temperatures, ϵ_{12} has to deviate from the geometric mean by ≤5%. This modest deviation cannot be interpreted at a molecular level, but our results imply that if dipole–dipole interactions are indeed important in determining the homopolymer clearing temperatures, then such interactions have not been significantly disrupted in these copolymers. This result suggests that the polymer backbone must reside in essentially an *isotropic* conformation which permits the formation of antiparallel dimers. By comparison, if the chain backbone is confined by the smectic density field to lie between layers, then it is difficult to propose a microscopic arrangement of the nonequivalent side chains which would allow the preservation of the antiparallel dimers. Further speculation awaits structural and dielectric studies which probe the extent of dipole correlations in these copolymers.

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