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# Side-Chain Liquid-Crystalline Copolymers Containing Spacers of Differing Lengths

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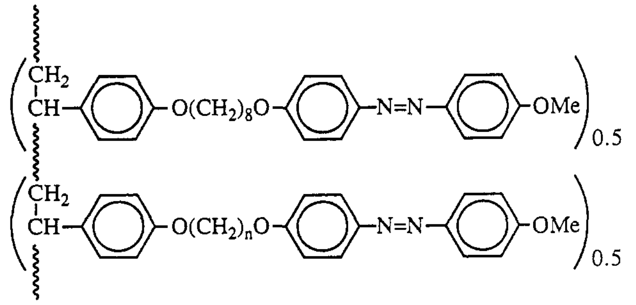
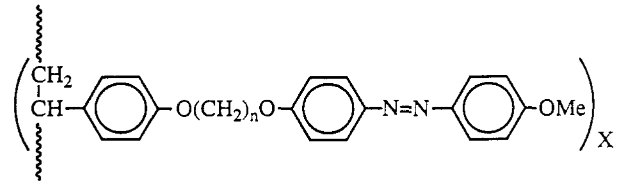
ABSTRACT: A series of side-chain liquid-crystalline copolymers, the poly[4-[1-(4-methoxy-4′-oxyazobenzene)-8-octyl]oxystyrene]-*co*-poly[4-[α-(4-methoxy-4′-oxyazobenzene)-ω-alkyl]oxystyrene]s, has been prepared in which the second spacer is varied in length from 3 methylene units up to 12. The properties of the copolymers are compared with those of the homopolymers, the poly[4-[α-(4-methoxy-4′-oxyazobenzene)-ω-alkyl]oxystyrene]s. All the polymers exhibit smectic behavior with the exception of the propyl homopolymer, for which no mesophase is observed. The transition temperatures of the copolymers are similar to the mean values of the homopolymers. The largest deviations from this behavior are observed for copolymers containing either propyl or butyl spacers. In contrast the transitional entropies exhibited by the copolymers show significant negative deviations with the exception of dodecyl–octyl copolymer, for which a small positive deviation is observed. We interpret these differences in terms of steric factors.

## Introduction

Side-chain liquid-crystalline polymers have aroused considerable interest in recent years, for they combine properties characteristic of polymers, most notably a glass transition, with the electrooptic properties of low molar mass mesogens. This duality of properties endows upon this class of materials application potential in numerous areas, for example, information storage and nonlinear optic devices. The operation of such devices imposes constraints on the polymer's properties, including a high glass transition in order to improve the long-term stability of the stored information, or the noncentrosymmetric distribution of dipoles, and also a low clearing point so that the possibility of dielectric breakdown is minimized during the processing of the polymer using high electric field densities. Side-chain liquid-crystalline polymers derived from poly(4-hydroxystyrene) appear to satisfy these criteria[1] and, furthermore, can be prepared using a phase-catalyzed reaction yielding polymers of high ionic purity—again of importance in avoiding dielectric breakdown. In addition, the monomers are derived from α,ω-dibromoalkanes, which are readily available from the propyl to the dodecyl homologues, so that a complete homologous series can be prepared and used to derive knowledge-based rules concerning the effects of the spacer on the mesogenic properties.[2] Indeed, there are very few examples in the literature describing complete homologous series, and instead conclusions are drawn from incomplete series. In this paper we describe the properties of a series of copolymers containing spacers of differing lengths, the poly[[[8-[[[(4-methoxyphenyl)azo]phenyl]oxy]octyl]oxy]styrene]-*co*-poly[[[ω-[[[(4-methoxyphenyl)azo]phenyl]oxy]alkyl]oxy]styrene] (hereafter called poly[4-[1-(4-methoxy-4′-oxyazobenzene)-8-octyl]oxystyrene]-*co*-poly[4-[α-(4-methoxy-4′-oxyazobenzene)-ω-alkyl]oxystyrene]s)



and compare these to the analogous homopolymers, the poly[4-[α-[4-methoxy-4′-oxyazobenzene)-ω-alkyl]oxystyrene]s.



The acronyms we use to describe these polymers are *n*-8OMe for the copolymers and *n*OMe for the homopolymers, in which *n* represents the number of methylene units in the flexible spacer. An azobenzene was chosen as the mesogenic moiety, as such groups have application potential in memory storage devices.[3,4]

## Experimental Section

**Synthesis.** The polymers were prepared using Scheme I consisting of three steps.

**4-Hydroxy-4′-methoxyazobenzene.** The coupling of phenol with a diazotized 4-substituted aniline is described in detail elsewhere.[5]

**α-Bromo-ω-(4-methoxyazobenzene-4′-oxy)alkanes.** The 4-hydroxy-4′-methoxyazobenzene was reacted with a 10-fold excess of an α,ω-dibromoalkane using potassium carbonate as base in dry acetone according to the method described by Crivello et al.[1] The products were purified by recrystallization at least twice from aqueous ethanol with hot filtration. This was necessary to ensure the total removal of any α,ω-bis(4-methoxyazobenzene-

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**Scheme I**

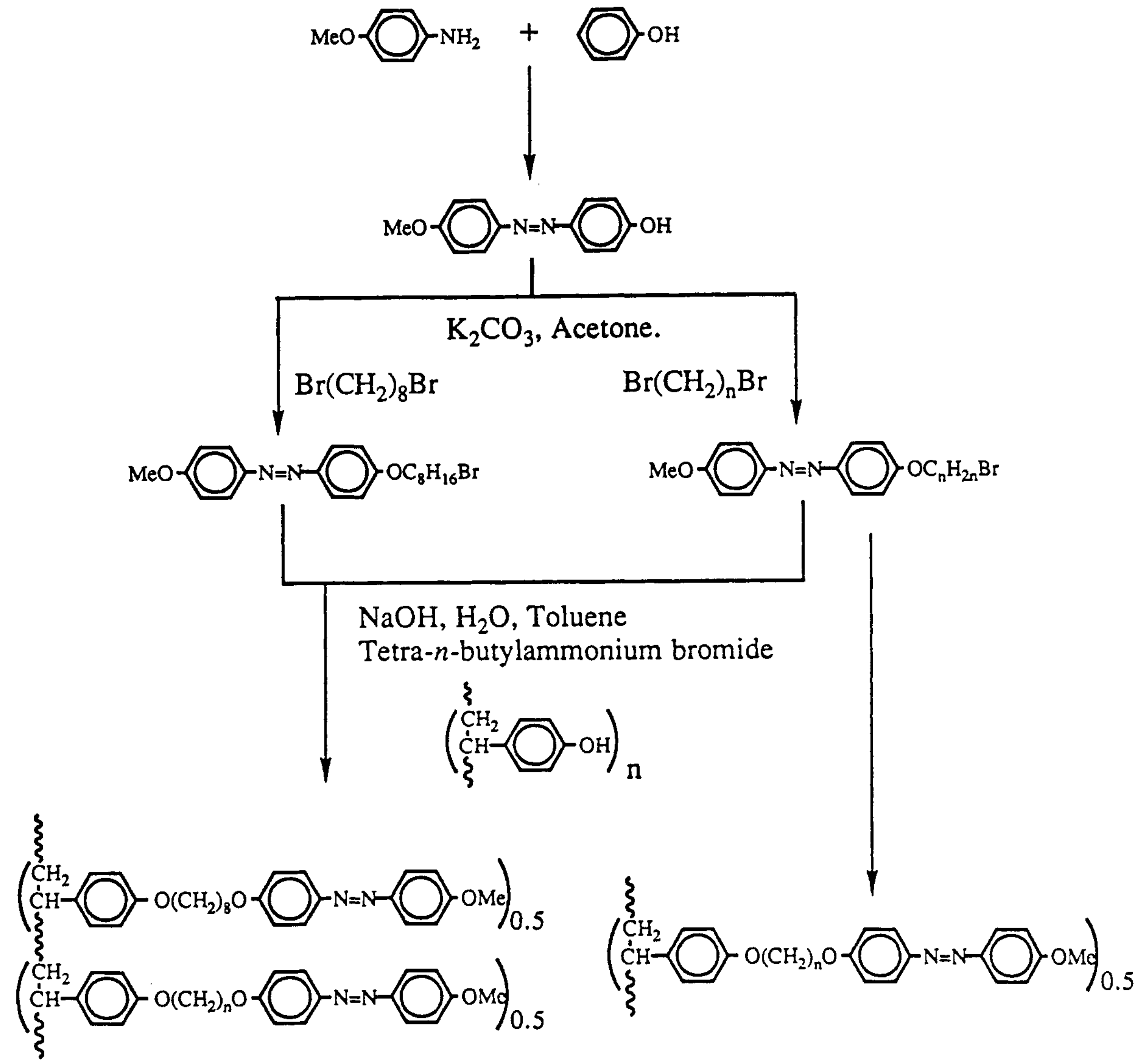


**Table I**
**Elemental Analyses for the $\alpha$-(4-Methoxyazobenzene-4'-oxy)-$\omega$-bromoalkanes**

| | | | C | | H | | N | |
|---|---|---|---|---|---|---|---|---|
| *n* | formula | mol wt | calc | found | calc | found | calc | found |
| 3 | $C_{16}H_{17}N_2O_2Br$ | 349.2 | 55.02 | 54.92 | 4.91 | 4.87 | 8.02 | 7.88 |
| 4 | $C_{17}H_{19}N_2O_2Br$ | 363.3 | 56.21 | 56.41 | 5.27 | 5.25 | 7.71 | 7.81 |
| 5 | $C_{18}H_{21}N_2O_2Br$ | 377.3 | 57.30 | 57.10 | 5.61 | 5.75 | 7.43 | 7.41 |
| 7 | $C_{20}H_{25}N_2O_2Br$ | 405.3 | 59.26 | 58.77 | 6.22 | 6.68 | 6.91 | 6.89 |
| 8 | $C_{21}H_{27}N_2O_2Br$ | 419.4 | 60.14 | 60.20 | 6.49 | 6.48 | 6.68 | 6.69 |
| 9 | $C_{22}H_{29}N_2O_2Br$ | 433.4 | 60.97 | 60.55 | 6.74 | 6.94 | 6.47 | 6.39 |
| 10 | $C_{23}H_{31}N_2O_2Br$ | 447.4 | 61.74 | 61.78 | 6.98 | 6.93 | 6.26 | 6.31 |
| 11 | $C_{24}H_{33}N_2O_2Br$ | 461.4 | 62.47 | 62.43 | 7.21 | 7.21 | 6.07 | 6.07 |
| 12 | $C_{25}H_{35}N_2O_2Br$ | 475.5 | 63.15 | 63.02 | 7.42 | 7.41 | 5.89 | 5.92 |

4'-oxy)alkanes that may have been produced in the reaction. The $^1$H NMR and IR spectra of the hexyl member of this series have been reported elsewhere.[6] The elemental analyses of the nine new members of this series are listed in Table I.

**Homopolymers.** The homopolymers were prepared by the phase-catalyzed reaction of an $\alpha$-bromo-$\omega$-(4-methoxyazobenzene-4'-oxy)alkane with poly(4-hydroxystyrene) (Polysciences, $M_w$ = 9000–11 000) using sodium hydroxide as base and tetra-*n*-butylammonium bromide as catalyst in a toluene–water mixture.[1,6] The reaction mixture was refluxed for at least 24 h, and, for the dodecyl homologue, a reaction time of 72 h was required in order to obtain complete substitution of the polymer backbone. The crude polymers were dissolved in methylene chloride and precipitated from methanol. The precipitate was filtered off and extracted in a Soxhlet apparatus using methanol for up to 48 h. The removal of the monomer was monitored using thin-layer chromatography and further confirmed by elemental analysis. The coverage of the backbone was 100% within our detection limits; the very strong OH stretch in the IR spectra of the parent polymer is not present on that of the final polymers.[2] The $^1$H NMR and IR spectra for the hexyl homologue of this series have been reported elsewhere.[6] The elemental analyses for the nine new polymers of the series are given in Table II.

**Copolymers.** The copolymers were prepared using the method described for the homopolymers employing a 1:1 feed ratio of the monomers. The elemental analyses, listed in Table III, and the $^1$H NMR spectra of the copolymers confirm that their compositions are in good agreement with the feed ratios.

**Table II**
**Elemental Analyses for the Homopolymers**

| | | | C | | H | | N | |
|---|---|---|---|---|---|---|---|---|
| *n* | formula | mol wt | calc | found | calc | found | calc | found |
| 3 | $(C_{24}H_{24}N_2O_3)_n$ | $(388.5)_n$ | 74.20 | 73.59 | 6.22 | 6.01 | 7.21 | 7.35 |
| 4 | $(C_{25}H_{26}N_2O_3)_n$ | $(402.5)_n$ | 74.60 | 74.15 | 6.51 | 6.51 | 6.96 | 7.05 |
| 5 | $(C_{26}H_{28}N_2O_3)_n$ | $(416.5)_n$ | 74.97 | 74.62 | 6.77 | 6.57 | 6.73 | 6.64 |
| 7 | $(C_{28}H_{32}N_2O_3)_n$ | $(444.6)_n$ | 75.64 | 75.29 | 7.26 | 7.17 | 6.30 | 6.19 |
| 8 | $(C_{29}H_{34}N_2O_3)_n$ | $(458.6)_n$ | 75.95 | 75.66 | 7.47 | 7.38 | 6.11 | 6.03 |
| 9 | $(C_{30}H_{36}N_2O_3)_n$ | $(472.6)_n$ | 76.24 | 76.15 | 7.68 | 7.70 | 5.93 | 5.85 |
| 10 | $(C_{31}H_{38}N_2O_3)_n$ | $(486.6)_n$ | 76.51 | 76.44 | 7.87 | 7.86 | 5.76 | 5.59 |
| 11 | $(C_{32}H_{40}N_2O_3)_n$ | $(500.7)_n$ | 76.76 | 76.29 | 8.05 | 8.04 | 5.60 | 5.44 |
| 12 | $(C_{33}H_{42}N_2O_3)_n$ | $(514.7)_n$ | 77.00 | 76.01 | 8.23 | 7.67 | 5.44 | 5.55 |

**Table III**
**Elemental Analyses for the Copolymers**

| | | | C | | H | | N | |
|---|---|---|---|---|---|---|---|---|
| *n* | formula | mol wt | calc | found | calc | found | calc | found |
| 3 | $(C_{26.5}H_{29}N_2O_3)_n$ | $(423.5)_n$ | 75.15 | 74.55 | 6.90 | 6.72 | 6.62 | 6.59 |
| 4 | $(C_{27}H_{30}N_2O_3)_n$ | $(430.5)_n$ | 75.32 | 74.88 | 7.02 | 6.91 | 6.51 | 6.62 |
| 5 | $(C_{27.5}H_{31}N_2O_3)_n$ | $(437.5)_n$ | 75.48 | 75.04 | 7.14 | 6.81 | 6.40 | 6.23 |
| 6 | $(C_{28}H_{32}N_2O_3)_n$ | $(444.6)_n$ | 75.64 | 74.97 | 7.26 | 7.12 | 6.30 | 6.31 |
| 7 | $(C_{28.5}H_{33}N_2O_3)_n$ | $(451.6)_n$ | 75.80 | 75.79 | 7.37 | 7.39 | 6.21 | 6.10 |
| 9 | $(C_{29.5}H_{35}N_2O_3)_n$ | $(465.6)_n$ | 76.10 | 76.18 | 7.58 | 7.69 | 6.02 | 6.07 |
| 10 | $(C_{30}H_{36}N_2O_3)_n$ | $(472.6)_n$ | 76.24 | 76.52 | 7.68 | 7.70 | 5.93 | 5.77 |
| 11 | $(C_{30.5}H_{37}N_2O_3)_n$ | $(479.6)_n$ | 76.37 | 75.78 | 7.78 | 7.60 | 5.84 | 5.69 |
| 12 | $(C_{31}H_{38}N_2O_3)_n$ | $(486.6)_n$ | 76.51 | 76.24 | 7.87 | 7.83 | 5.76 | 5.69 |

**Table IV**
**Transitional Properties of the Homopolymers**

| *n* | $M_w$ | $T_g$/°C | $T_{CI}$/°C | $\Delta H_{SI}$/(J g$^{-1}$) | $\Delta S_{SI}/R$ |
|---|---|---|---|---|---|
| 3 | 31 100 | 62 | | | |
| 4 | 27 200 | 89 | 144 | 11.8 | 1.37 |
| 5 | 33 800 | 72 | 110 | 6.54 | 0.86 |
| 6[a] | 29 200 | 81 | 144 | 14.2 | 1.76 |
| 7 | 36 100 | 75 | 138 | 14.1 | 1.84 |
| 8 | 37 000 | 76 | 145 | 18.9 | 2.50 |
| 9 | 33 200 | 74 | 146 | 17.0 | 2.31 |
| 10 | 36 900 | 71 | 141 | 17.5 | 2.48 |
| 11 | 37 100 | 71 | 139 | 16.6 | 2.43 |
| 12 | 37 200 | 62 | 140 | 15.5 | 2.15 |

[a] The data for 6OMe are from Imrie et al.[6]

$^1$H NMR (CDCl$_3$) for 6–8OMe: δ 1.7, 1.9, 2.3 (m, alkyl, benzylic, 13 H), 3.9 (alkyloxy, 7 H), 6.8, 7.0, 7.9 (m, aromatics 12 H).

**Characterization.** The structural characterization of the polymers and their intermediates was performed by IR spectroscopy using an IBM System 9000 FTIR spectrometer and by $^1$H NMR spectroscopy using a Varian XL200 NMR spectrometer; elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory. The molecular weights of the polymers were determined by gel permeation chromatography using a Waters 590 GPC chromatograph equipped with a Waters 410 differential refractometer, calibration being performed using polystyrene standards.

**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 polymer 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 clearing temperatures. The optical textures of the mesophases were studied using a Zeiss polarizing microscope equipped with a Linkam hot stage.

## Results and Discussion

The transitional properties of the homopolymers are listed in Table IV. We should note that, although these polymers are composed of approximately 80 repeat units, recent research using cyanoazobenzene as the mesogenic moiety suggests that the transitional properties are still in the molecular weight dependence regime.[7] This, however, does not prevent a comparison of the transitional properties of the polymers here, as they all are derived from the same parent polymer. With the exception of the propyl homologue, the polymers exhibit two transitions, a glass transition, and a clearing transition (see Figure 1). In contrast, only a glass transition is observed for the propyl homologue. The DSC trace for the dodecyl homologue shows a second transition at a temperature slightly higher than the glass transition although there was no apparent textural change when viewed through the polarizing microscope.

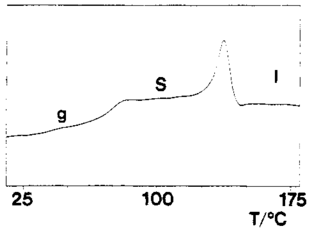


**Figure 1.** Heating DSC trace for the homopolymer with a seven-membered spacer.

On cooling the polymers from the isotropic phase, a birefringent texture develops when viewed through the polarizing microscope. In order to obtain clear characteristic optical textures for phase identification, the polymer was cooled slowly, 0.2 °C min$^{-1}$, from approximately 20 °C above its clearing point into the mesophase. It should be noted that annealing the polymer at a temperature slightly below its clearing point failed to produce well-defined textures, and this was found to be true for other polystyrene-based polymers.[6] Thus, on cooling slowly from the isotropic phase, bâtonnets develop at the transition temperature that coalesce to form a focal–conic fan texture indicative of a layered structure; a typical texture is shown in Figure 2. In addition, several preparations exhibited homeotropic regions implying the director to be orthogonal to the layer planes. In consequence, we assign the mesophases exhibited by the polymers to be smectic A phases, and detailed structural studies of the mesophase ultrastructure are currently in progress to confirm this.

Figure 3 shows the dependence of the transition temperatures on the length of the flexible alkyl spacer for

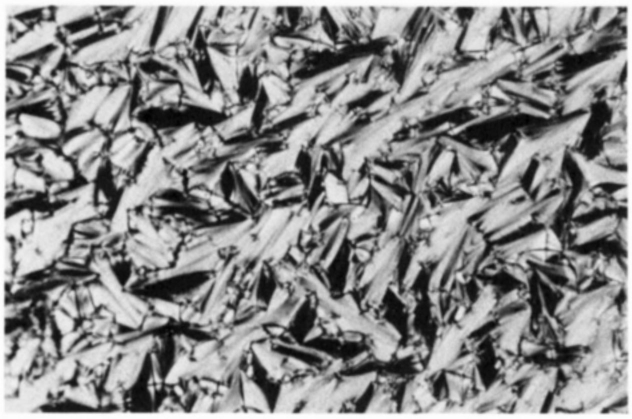


**Figure 2.** Focal–conic fan texture exhibited by the smectic phase of 7OMe.

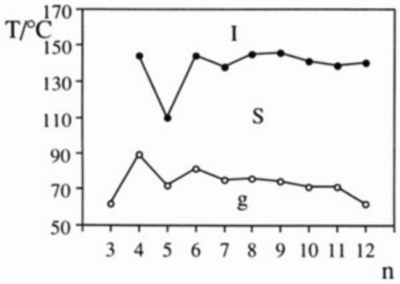
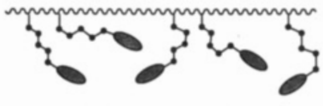


**Figure 3.** Dependence of the transition temperatures on the length of the flexible spacer for the homopolymers. The glass transitions are denoted by ○, and the clearing points are represented by ●.

(a) Even Spacer



(b) Odd Spacer

**Figure 4.** Schematic representation in two dimensions of the effect of introducing a single gauche defect into the flexible spacer of a side-chain liquid-crystalline polymer.

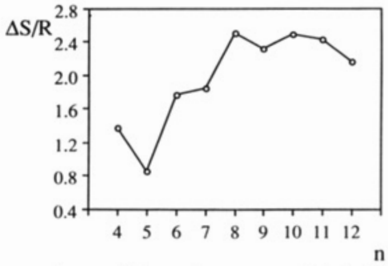


**Figure 5.** Dependence of the entropy associated with the clearing transition on the length of the flexible alkyl spacer for the homopolymers.

the homopolymers. The glass transition temperature and the clearing point both exhibit a large alternation that attenuates rapidly on increasing the spacer length. The alternation in the clearing temperatures has been observed for many systems and is often rationalized in terms of the all-trans conformation of the flexible spacer. Thus, for an even-membered spacer, the mesogenic unit is orthogonal with respect to the backbone whereas for an odd-membered spacer the mesogenic unit forms some angle with respect to the backbone. Clearly this assumes that the backbone lies in a plane orthogonal to the director, and this is supported to some extent by experimental studies using techniques including X-ray diffraction,[8] neutron scattering,[9] and $^2$H NMR.[10] This explanation should be extended, however, to consider a conformational distribution rather than just a single conformation, for the spacer and backbone are flexible. Figure 4 shows the effect of introducing a single gauche defect into a flexible spacer. It is clear that for the even spacer (Figure 4a) there exist more conformations for which the mesogenic units are coparallel, and thus the interactions between them are maximized. Also, these more elongated conformers are more favored in a liquid-crystalline environment, and hence at the clearing point there is a greater conformational entropy change for the even-membered spacer than there is for the odd-membered spacer. Figure 5 shows the dependence of the transitional entropies on the length of the flexible spacer, and for early members these do exhibit the alternation predicted by this explanation. We should stess that the clearing entropy for a smectic phase has many important contributions including changes in orientational and translational ordering as well as in conformational distributions. This interpretation of the alternation in clearing temperatures accounts only for transition temperatures that increase with spacer length, and in order to rationalize either falling transition temperatures or temperatures that are approximately constant with increasing spacer length, the chain flexibility, which acts to reduce transition temperatures, has also to be considered. This dual role of the spacer can be considered to be analogous, therefore, to the role of terminal alkyl chains in determining the properties of low molar mass mesogens.[11] We have formalized this approach recently in a molecular field theory that describes side-chain liquid-crystalline polymers.[2] It should be noted that the values of $\Delta S/R$ listed in Table IV are similar to those observed for low molar mass mesogens.

The alternation in the glass transition temperatures is unusual and can be explained in terms of the specific free volume. The largest difference in $T_g$ is between the third and fourth homologues. The third homologue does not exhibit liquid crystallinity whereas the fourth member exhibits smectic behavior. A smectic phase possesses less specific free volume than the isotropic phase, and hence a higher glass transition temperature would be anticipated for the fourth member. The transitional entropy for the fifth member is significantly lower than that of either the butyl or hexyl homologues; this implies that the degree of ordering within the phase is almost certainly lower and hence the specific free volume higher. The alternation in the glass transition temperature attenuates quickly, and this attenuation is exhibited also by both the clearing temperatures and entropies of transition. The decreasing trend in the glass transition temperatures can be rationalized in terms of the plasticizing effect of the side chain on the backbone.

The transitional properties of the copolymers are listed in Table V. All the copolymers exhibit a smectic phase, which was identified using the criteria described for the homopolymers. Figure 6 shows the dependence of the transition temperatures on the length of one of the flexible spacers for the copolymers. The behavior of the glass transition temperature and clearing point is very similar to that observed for the homopolymers, namely, a pro-

**Table V**
**Transitional Properties of the Copolymers**

| $n$ | $M_w$ | $T_g$/°C | $T_{CI}$/°C | $\Delta H_{SI}$/(J g$^{-1}$) | $\Delta S_{SI}/R$ |
|---|---|---|---|---|---|
| 3 | 35 000 | 60 | 92 | 3.20 | 0.45 |
| 4 | 37 000 | 76 | 137 | 13.63 | 1.72 |
| 5 | 36 800 | 73 | 125 | 9.27 | 1.23 |
| 6 | 42 700 | 78 | 144 | 15.88 | 2.04 |
| 7 | 34 900 | 75 | 139 | 13.76 | 1.81 |
| 9 | 39 900 | 70 | 143 | 15.28 | 2.06 |
| 10 | 41 100 | 72 | 146 | 16.65 | 2.26 |
| 11 | 39 200 | 74 | 143 | 16.32 | 2.26 |
| 12 | 42 900 | 71 | 142 | 17.64 | 2.49 |

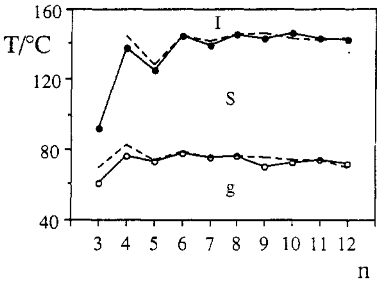


**Figure 6.** Dependence of the transition temperatures on the length of the flexible spacer for the copolymers. The glass transitions are denoted by ○, and the clearing points are represented by ●. The dashed lines join the average values for the respective homopolymers.

nounced alternation that attenuates with increasing spacer length. Figure 6 shows also the averaged transition temperatures of each $n$OMe homopolymer with 8OMe. It can be seen that the glass transition temperatures of the copolymers are similar to the calculated values, with the largest deviation being exhibited by 3-8OMe and 4-8OMe. These negative deviations are presumably a consequence of the difficulty experienced by the side chains of differing lengths in packing efficiently. Indeed, it is interesting to note that the $T_g$ of 3-8OMe, which is liquid-crystalline, is actually lower than that of 3OMe, which is amorphous.

The clearing points of the copolymers are also very similar to the calculated values. The largest deviation is again observed for the butyl spacer and is presumably indicative of steric difficulties arising from the differing spacer lengths. It is interesting to note that, if we assume a linear dependence of the transition temperatures on the composition for the 3-8OMe copolymer, then the virtual transition temperature for the 3OMe homopolymer is 39 °C. It is reasonable to assume, however, that a negative deviation away from such behavior occurs at least as great as that observed for 4-8OMe, and thus a more reasonable estimate of the virtual clearing point of 3OMe is 55 °C. This is approaching the $T_g$ of this polymer, and it is possible that liquid crystallinity is not observed for kinetic rather than thermodynamic considerations.

In contrast to the largely anticipated behavior of the transition temperatures of the copolymers, the transitional entropies show significant deviations away from a linear dependence on composition, and this is shown in Figure 7. For copolymers with $n$ less than 8, the odd members show larger negative deviations and, in consequence, the alternation is more pronounced than would be anticipated. For values of $n$ greater than 8, negative deviations are observed also except for the dodecyl homologue, for which a small positive deviation is observed. These differences are difficult to interpret unambiguously, although in part they must be a result of the introduction of the entropically unfavorable mesogenic unit–spacer interaction resulting from the differing spacer lengths. Indeed, it is the analogous interaction between mesogenic units and terminal alkyl chains in low molar mass systems that drives the formation of smectic phases.

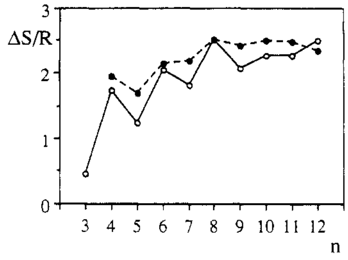
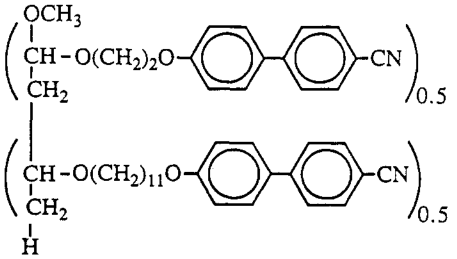


**Figure 7.** Dependence of the entropy of transition represented by ○ on the length of the flexible spacer for the copolymers. Also shown are the average values of the homopolymers, denoted by ●.

It is of interest to compare our results with those of Percec et al.,[12] who reported recently the phase behavior of poly[11-[(4-cyano-4′-biphenyl)oxy]undecanyl vinyl ether-*co*-2-[(4-cyano-4′-biphenyl)oxy]ethyl vinyl ether] as a function of the composition. The disparity in spacer length for this copolymer is greater than for those we report, and if, as we suggest, the transitional behavior of the copolymers is at least in part governed by packing considerations, then these should be even greater for this system. This is indeed the case: for the 50:50 copolymer a negative deviation of 16.5 °C is observed for $T_g$, and for the clearing transition a negative deviation of 8.7 °C is recorded. These are both larger than those observed for the $n$-8OMe copolymers. In addition the transitional entropy shows also a significant deviation, as we would anticipate from our interpretation. It should be noted that the two homopolymers in this case exhibit differing smectic phases, making a comparison of the entropies more difficult. Lee et al.[13] reported recently homopolymers and a 60:40 copolymer in which the mesogenic unit, 4′-cyano-4-biphenylyl 4-(octyloxy)benzoate, was attached laterally to a siloxane backbone. Again negative deviations from a linear dependence on composition are observed for the glass transition temperature, clearing point, and transitional entropy. This behavior is attributed to reduction in the antiparallel association of the cyano groups.



It appears, therefore, that, for a range of copolymer systems containing spacers of differing lengths, the transitional properties exhibit negative deviations from linear behavior. We should note, however, that the mesophase structure is almost certainly different for these systems, and this will play a role also in determining transitional properties. In order to investigate this, detailed structural studies of the mesophase ultrastructure formed by the $n$-8OMe copolymers are currently in progress.

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## References and Notes

(1) Crivello, J. V.; Deptolla, M.; Ringsdorf, H. *Liq. Cryst.* **1988**, *3*, 235.

(2) Attard, G. S.; Dave, J. S.; Wallington, A.; Imrie, C. T.; Karasz, F. E. *Makromol. Chem.* **1991**, *192*, 1495.

(3) Ikeda, T.; Hasegawa, S.; Sasaki, T.; Miyamoto, T.; Lin, M.-P.; Tazuke, S. *Makromol. Chem.* **1991**, *192*, 215.

(4) Ikeda, T.; Horiuchi, S.; Karanjit, D. B.; Kurihara, S.; Tazuke, S. *Macromolecules* **1990**, *23*, 42–48.

(5) *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Furniss, B. S., Hannaford, A. J., Rogers, V., Smith, P. W. G., Tatchell, A. R., revisors; Longman Scientific and Technical: New York, 1987.

(6) Imrie, C. T.; Karasz, F. E.; Attard, G. S. *Liq. Cryst.* **1991**, *9*, 47.

(7) Imrie, C. T.; Karasz, F. E.; Attard, G. S., in preparation.

(8) Davidson, P.; Keller, P.; Levelut, A. M. *J. Phys.* (*Les Ulis, Fr.*) **1985**, *46*, 939.

(9) Keller, P.; Carvalho, B.; Cotton, J. P.; Lambert, M.; Moussa, F.; Pépy, G. *J. Phys. Lett.* (*Les Ulis, Fr.*) **1985**, *46*, L1065.

(10) Boeffel, C.; Spiess, H. W. *Macromolecules* **1988**, *21*, 1626.

(11) Imrie, C. T.; Taylor, L. *Liq. Cryst.* **1989**, *6*, 1.

(12) Percec, V.; Lee, M. *Polym. Bull.* (*Berlin*) **1991**, *25*, 131.

(13) Lee, M. S. K.; Gray, G. W.; Lacey, D.; Toyne, K. J. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 109.