Effect of Backbone Flexibility on the Transitional Properties of Side-Chain Liquid-Crystalline Polymers

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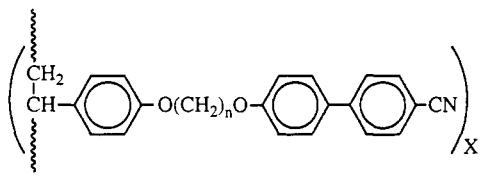
ABSTRACT: A new homologous series of side-chain liquid-crystalline polymers has been synthesized, the poly[4-[[α-(4-cyanobiphenylyl-4′-oxy)-ω-alkyl]oxy]styrene]s, and the thermal behavior of the series investigated. The homologues with butyl or longer spacers exhibit a smectic phase, whereas the propyl homologue does not exhibit liquid crystallinity. The properties of these polymers are compared with those containing other polymeric backbones to study the effect of flexibility on thermal behavior. We propose a new model to account for the liquid crystal properties of side-chain polymers.

Introduction

A side-chain polymer that exhibits liquid-crystalline behavior comprises three elements: a polymer backbone, a flexible spacer, and a mesogenic group. This class of polymers has generated considerable interest because of its unique combination of polymeric properties and the electrooptic characteristics of low molar mass materials, which makes these polymers candidates for use in advanced electrooptic technologies.[1] Such materials are also inherently interesting, because in principle the configurational entropy of the polymer is antagonistic to liquid-crystalline order. The transitional temperature for any given backbone depends largely on the molecular structure of the mesogenic group and on the length and parity of the flexible spacer. The effects of the molecular structure are, in general, in accordance with the empirical rules developed for low molar mass systems,[2] and the role of the spacer in modifying these temperatures is also reasonably well understood.[3] However, it has been shown that, for a given mesogenic group and spacer, varying the chemical nature of the backbone can have a profound effect on the transition temperatures,[4] although the molecular significance of this complex behavior is unclear.

To investigate the effect of backbone flexibility, we have prepared a new series of polystyrene-based liquid-crystal polymers, the poly[4-[[α-(4-cyanobiphenylyl-4′-oxy)-ω-alkyl]oxy]styrene]s (see 1). This particular series was



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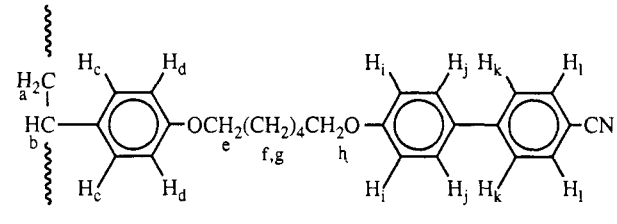
chosen for two reasons; first, polystyrene-based liquid crystals are attracting increasing attention because of their relatively high glass transition temperatures[3,5–8] and, second, cyanobiphenyl has been extensively studied as a mesogenic group in a range of systems. Indeed, cyanobiphenyl has become the benchmark in comparisons of differing polymer backbones.[4,9]

Experimental Section

Synthesis. Monomers. The preparation of the monomers, the α-bromo-ω-(4-cyanobiphenyl-4′-oxy)alkanes, has been described in detail elsewhere.[10]

Polymers. The phase-transfer-catalyzed reaction of the monomer onto poly(4-hydroxystyrene) (Polysciences Inc., M_w = 30 000) was performed according to the procedure described by Crivello et al.[5] The grafting reaction was allowed to proceed for 72 h, and the product was extracted from the reaction mixture with methylene chloride. The organic solvents were removed, and the polymer was redissolved in a small amount of methylene chloride and precipitated into methanol. To ensure the total removal of the monomer, the polymer was extracted with methanol in a Soxhlet apparatus for 48 h. The removal of the monomer from the polymer was monitored by thin layer chromatography and verified by elemental analysis. The substitution of the backbone was complete within our experimental limits. This result is particularly evident in the IR spectra of the polymers, which do not contain the very strong band associated with OH stretching that is present in the spectrum of poly(4-hydroxystyrene).[7] The elemental analyses for the polymers are listed in Table I, and representative spectroscopic data are given below for the hexyl homologue (see **A**).



A

Poly[4-[[1-(4-cyanobiphenylyl-4′-oxy)-6-hexyl]oxy]styrene]. ^{1}H NMR ($CDCl_3$, TMS): δ 1.52, 1.86 (m, 11H, H_f, H_g, H_a, H_b), 3.96 (m, 4H, H_e, H_h), 6.60, 6.95 (m, 6H, H_c, H_d, H_i), 7.46, 7.58 (m, 6H, H_j, H_k, H_l). IR (thin film, NaCl plate): ν 2225 cm^{-1} (CN stretch). UV–vis (methylene chloride solution): λ_{max} 295 nm.

Characterization. The proposed structures for the polymers were verified by NMR spectroscopy on a Varian XL-300 NMR spectrometer, by IR spectroscopy on an IBM System 9000 FT-IR spectrometer, and by elemental analysis performed by the University of Massachusetts Microanalytical Laboratory. The UV–vis spectra of the polymers were recorded on a Perkin-Elmer Lambda 9 UV–vis–near-IR spectrophotometer interfaced to a Perkin-Elmer Laboratory Computer.

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Table I. Elemental Analyses of the Polymers

			C		H		N	
n	formula	mol wt	calcd	found	calcd	found	calcd	found
3	$(C_{24}H_{21}NO_2)_m$	$(355.4)_m$	81.10	80.05	5.96	6.03	3.94	3.74
4	$(C_{25}H_{23}NO_2)_m$	$(369.4)_m$	81.27	80.87	6.27	6.30	3.79	3.80
5	$(C_{26}H_{25}NO_2)_m$	$(383.5)_m$	81.43	81.21	6.57	6.43	3.65	3.68
6	$(C_{27}H_{27}NO_2)_m$	$(397.5)_m$	81.58	81.58	6.85	6.94	3.52	3.34
7	$(C_{28}H_{29}NO_2)_m$	$(411.5)_m$	81.72	81.96	7.10	6.96	3.40	3.45
8	$(C_{29}H_{31}NO_2)_m$	$(425.5)_m$	81.85	81.85	7.34	7.51	3.29	3.08
9	$(C_{30}H_{33}NO_2)_m$	$(439.6)_m$	81.97	81.97	7.57	7.58	3.19	3.13
10	$(C_{31}H_{35}NO_2)_m$	$(453.6)_m$	82.08	82.45	7.78	7.68	3.09	3.19
11	$(C_{32}H_{37}NO_2)_m$	$(467.6)_m$	82.19	81.94	7.98	8.20	3.00	2.93
12	$(C_{33}H_{39}NO_2)_m$	$(481.6)_m$	82.29	82.39	8.16	7.78	2.91	2.95

Table II. Thermal Properties of the Polymers

n	T_g/ °C	T_{Cl}/ °C	ΔH/ (J g^{-1})	ΔS/ R	n	T_g/ °C	T_{Cl}/ °C	ΔH/ (J g^{-1})	ΔS/ R
3	76				8	39	123	7.30	0.94
4	77	107	1.22	0.14	9	31	119	7.57	1.02
5	62	101	3.14	0.39	10	18	118	8.82	1.23
6	60	120	5.49	0.67	11	12	120	8.73	1.25
7	43	115	6.16	0.79	12	14	119	9.94	1.47

Thermal Characterization. The thermal properties of the polymers were investigated by polarizing light microscopy on a Zeiss polarizing microscope equipped with a Linkam hotstage. In addition, the polymers were characterized by differential scanning calorimetry with a Perkin-Elmer DSC-7 differential scanning calorimeter calibrated with an indium standard. Two samples were used for each polymer, and the values quoted are the average values for the second heating cycle; the heating rate in all cases was 10 °C min^{-1}. The transition temperatures listed for the polymers are those obtained from the calorimetry data.

Results and Discussion

The thermal properties of the polymers are listed in Table II. All the polymers exhibit liquid-crystalline behavior, with the exception of the propyl homologue, which is amorphous at all temperatures. The mesophase for each polymer was identified on the basis of the optical texture observed through a polarizing microscope. In preparation for this identification, the polymer was heated to approximately 10 °C above its clearing temperature and then cooled at 0.2 °C min^{-1} into the mesophase. For each polymer, bâtonnets developed and coalesced to produce a focal-conic fan texture, a result implying a layered structure. In addition it was possible to achieve homeotropic alignment, a result implying an orthogonal arrangement of the director with respect to the layer planes. In consequence, the phase producing this texture was assigned as a smectic A. The average molecular weight of the poly(4-hydroxystyrene) was 30 000 (number-average degree of polymerization, 250) and was chosen so that the thermal properties of the final polymers were not in the molecular weight-dependence regime.[11]

The dependence of the transition temperatures on the number n of methylene units in the spacer for the polymers is shown in Figure 1. The glass transition temperatures decreased as the length of the spacer increased and exhibited a small odd–even effect. The decreasing trend implies a plasticization of the backbone by the side chain, although the significance of the odd–even effect is unclear. As the spacer length increased, the heat capacity change associated with the glass transition became increasingly weaker and hence the uncertainty in the temperatures became larger. On increasing the spacer length, therefore, the size of the alternation in the glass transition temperatures becomes comparable to the experimental error. We note, however, that similar odd–even effects have been reported for other polystyrene-based side-chain polymers.[3,8]

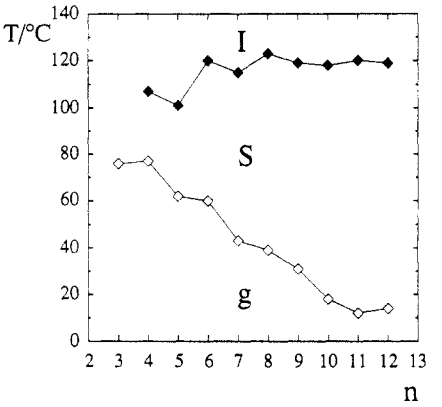


Figure 1. Dependence of glass transition temperatures (◇) and clearing temperatures (◆) on the number n of methylene groups in the spacer for the poly[4-[[α-(4-cyanobiphenylyl-4′-oxy)-ω-alkyl]oxy]styrene]s. I, isotropic phase; S, smectic phase; g, glass phase.

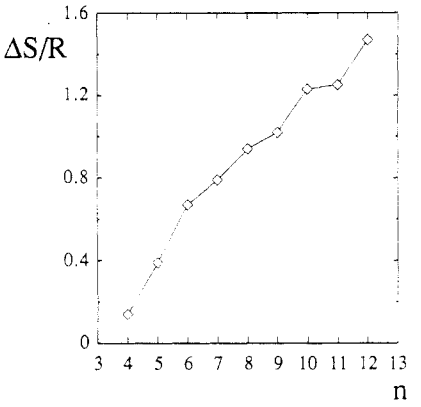


Figure 2. Dependence of the entropy change associated with the clearing transition on the number n of methylene groups in the flexible alkyl spacer for the poly[4-[[α-(4-cyanobiphenylyl-4′-oxy)-ω-alkyl]oxy]styrene]s.

The clearing temperatures exhibited a more pronounced odd–even effect, which was attenuated as the spacer length increased (Figure 1). This curve is rather flat for longer spacer lengths and is in accord with the behavior observed for low molar mass mesogens having clearing temperatures in the region of 100 °C.[2] Figure 2 shows the dependence of the entropy change associated with the clearing transition, expressed as the dimensionless quantity $\Delta S/R$, on the length of the spacer; these values increased with little or no odd–even effect. This result also is in accord with the behavior observed for low molar mass mesogens.[12]

Comparison of Different Backbones. Four different backbones for which homologues have been prepared are shown in Figure 3 (this figure also lists the abbreviation used for each system). The reaction scheme used to prepare the polystyrene-based liquid crystal polymers enables the synthesis of a full homologous series,[3,7] whereas

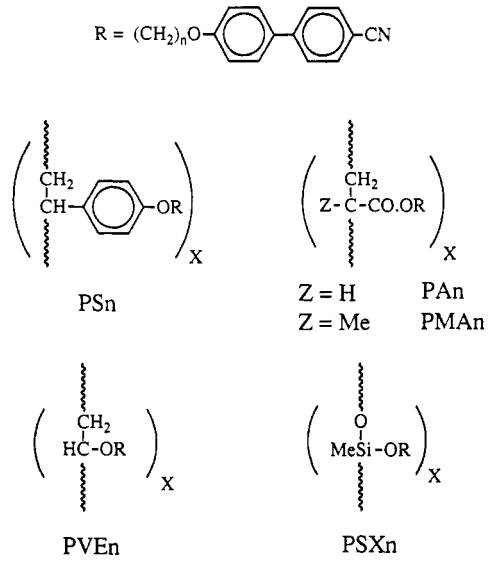


Figure 3. Structures of the polymers and corresponding abbreviations. In each case *n* refers to the number of methylene groups in the spacer. PA, polyacrylates; PMA, polymethacrylates; PS, polystyrenes; PSX, polysiloxanes; PVE, poly(vinyl ether)s; X, one repeat unit.

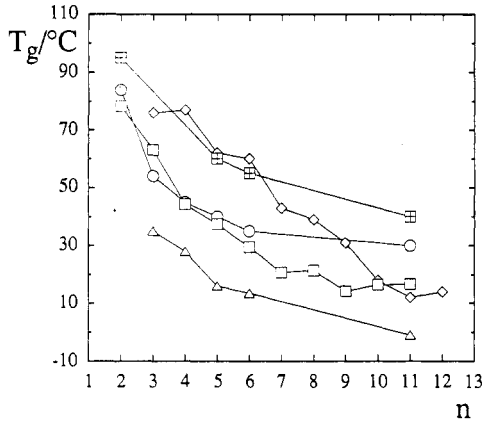


Figure 4. Glass transition temperatures for the PS*n* (◇), PA*n* (○), PMA*n* (□), PVE*n* (□), and PSX*n* (△) series. *n*, number of methylene units in the spacer. See Figure 3 for meanings of the abbreviations.

the methods used to synthesize, for example, the polysiloxanes limit the number of homologues that can be readily obtained. We have collated the data describing the polyacrylate,[13-23] polymethacrylate,[9,15,17,20,22] poly(vinyl ether),[24-34] and polysiloxane[35-42] series from the literature and selected the examples having the highest molecular weights for use in these comparisons.[43] If such information was not available, then the polymers having the higher transition temperatures were selected. We should note that, for examples for which the enthalpies of transition for the highest molecular weight polymers were not given, then the comparison of the entropies draws upon the available information for lower molecular weight polymers. This substitution should, however, make little difference, because the enthalpies of transition exhibit only a small or no molecular weight dependence.[11,44-47]

Glass Transition Temperatures. Figure 4 shows the glass transition temperatures of the five series. It is immediately apparent that the polysiloxane (PSX*n*) series has the lowest T_g's. For small values of *n*, the polystyrene (PS*n*) and polymethacrylate (PMA*n*) series have comparable T_g's, as do the polyacrylates (PA*n*) and the poly(vinyl ether)s (PVE*n*). These observations are in accord with the T_g's of the unsubstituted parent polymers:[48] polystyrene has a T_g of 100 °C; poly(methyl methacrylate), 105 °C; poly(methyl acrylate), 10 °C; poly(methyl vinyl ether), −31 °C; and poly(dimethylsiloxane), −127 °C. As spacer length increases, however, the T_g order, for the undecyl homologues, changes to

$$\text{PMA11} > \text{PA11} > \text{PVE11} \approx \text{PS11} > \text{PSX11}$$

As *n* increases, each series of polymers shows decreasing T_g's, a result caused by the plasticizing effect of the side chain. The shapes of the curves shown in Figure 4 differ, and in particular the T_g's of the PMA*n* and PA*n* series appeared to reach a limiting value more quickly than did those of the other series. This asymptotic behavior results in the change in the T_g order noted for the undecyl members and may be the result of specific dipole–dipole interactions in the PMA*n* and PA*n* series. It should be noted, however, that the changed order may also be a consequence of molecular weight effects or specific end-group interactions. This is not a general behavioral trend for poly(methyl methacrylate)s. Leslie et al.[49] reported the properties of the analogous polymers containing 4-nitrobiphenyl, and the T_g's for this series exhibited the same behavior as did those of the PS*n* series. The nitro substituent is more electronegative than the cyano group,[50] so the interaction between the backbone and nitrobiphenyl may be greater than that between the backbone and cyanobiphenyl. Therefore, nitrobiphenyl would disrupt the specific interactions to a greater extent and be a more effective plasticizer. We note that Figure 4 illustrates two types of behaviors that are dependent on substituting the parent polymer backbones: for the more rigid backbones (polystyrene and polymethacrylate), attaching a side chain reduced the T_g, whereas for the more flexible backbones (polyacrylate, poly(vinyl ether), and polysiloxane), the attachment of the side chain increased T_g. The molecular significance of this observation will be discussed later.

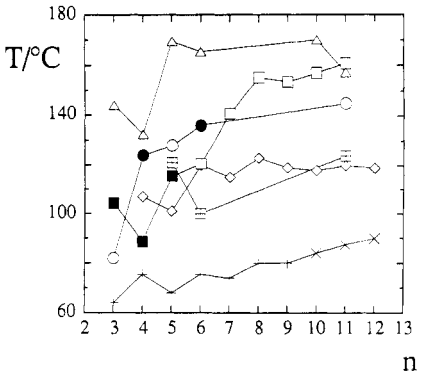


Figure 5. Clearing temperatures for the PS*n* (◇), PA*n* (○), PMA*n* (⊞), PVE*n* (□), and PSX*n* (△) series. Filled symbols denote nematic–isotropic transitions; open symbols represent smectic–isotropic transitions. Also shown are the nematic–isotropic (+) and smectic–isotropic (×) transition temperatures for the 4-cyano-4-*n*-alkoxybiphenyls.

Comparison of the Clearing Temperatures. Figure 5 shows the clearing temperatures for the five series. The PA*n* series exhibited unusual phase behavior as *n* increased; namely, PA3 was purely smectic,[14] whereas PA4 exhibited only a nematic phase.[14,23] The authors did not comment on this unusual behavior.[14] The general trend in Figure 5 is clearly that increasing the flexibility of the backbone tended to increase the clearing temperature.

Comparison of the Clearing Entropies. Figure 6 shows the entropy changes associated with the clearing transition for each series. It should be noted that the values for PA5, PA6, and PVE5 are for the combined smectic–nematic–isotropic transitions.[14,34] For each series, the entropies increase as *n* increases, a finding that, as we

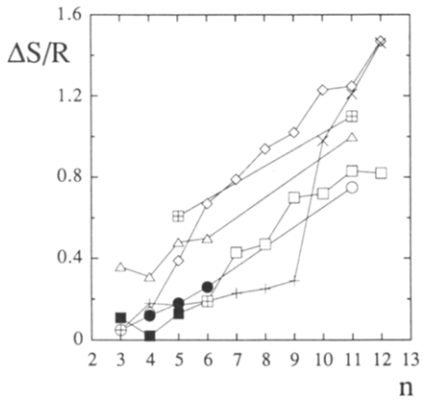


Figure 6. Clearing entropies for the PS*n* (◇), PA*n* (○), PMA*n* (□), PVE*n* (□), and PSX*n* (△) series. Filled symbols denote nematic–isotropic transitions; open symbols represent smectic–isotropic transitions. Also shown are the entropy changes associated with the nematic–isotropic (+) and smectic–isotropic (×) transitions for the 4-cyano-4-*n*-alkoxybiphenyls.

have noted already, is in accord with increasing the length of the terminal chain in monomeric low molar mass liquid crystals. A surprising feature of Figure 6 is the absence of a large entropy increase on passing from nematic to smectic behavior in the PA*n* and PVE*n* series. For early members, there were no clear trends, whereas for larger spacers the order became

$$\text{PS}n > \text{PMA}n > \text{PXS}n > \text{PVE}n \approx \text{PA}n$$

It appears, therefore, that for this particular set of polymers there is no simple relationship between backbone flexibility and the clearing entropy, although in general increasing flexibility tended to decrease the entropy change. It should be noted, however, that these values are small and in some instances may be within experimental error. Percec et al. reported similar relations between backbone flexibility and the transition temperatures and entropies for different mesogenic groups,[51,52] although Shibaev and Platé found that, for polymers containing methoxyphenylbenzoate groups, increasing backbone flexibility decreased the clearing temperature.[9] This result appears, however, to be an exception to a very general rule and is presumably a consequence of molecular weight effects.

New Model of the Behavior of Side-Chain Polymers. A useful model for side-chain polymers must be able to adequately explain the effects of backbone flexibility on transitional properties, namely, that increasing flexibility decreases T_g but enhances the clearing temperature while having a much smaller effect on the clearing entropy. In addition, the changes in the thermal properties of the monomer on attachment to a polymer backbone should also be considered. Figure 5 shows the clearing temperatures for the 4-cyano-4-*n*-alkoxybiphenyl (*n*OCB) series of monomers. It is clear that when the monomeric liquid crystals were attached to polymer backbones, the clearing points of the resulting macromolecules were substantially enhanced compared with those of the monomers. In addition the polymers tended to be smectogenic, whereas the *n*OCB series up to the nonyl homologue exhibited nematic behavior. Figure 6 shows the clearing entropies for the *n*OCB series.[53] A large increase is evident on passing from the nematic–isotropic transition exhibited by 9OCB to the smectic–isotropic transition shown by 10OCB. The values of $\Delta S_{NI}/R$ for the early members of the *n*OCB series are comparable to the smectic–isotropic transition entropies of the PA*n*, PS4, and PVE6 polymers. For PS4, the proximity of the glass transition may result

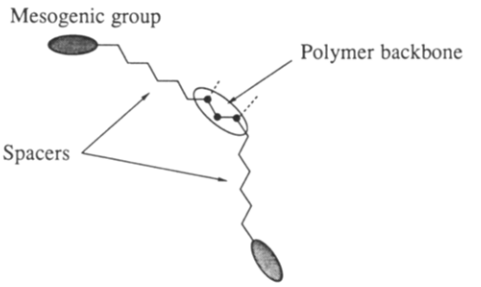
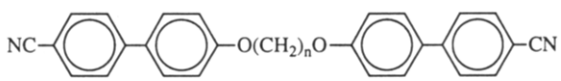


Figure 7. Schematic representation of a virtual trimer.

in an underestimation of this value. As the length of the alkyl chain increases, the $\Delta S_{NI}/R$ values of the *n*OCB series are smaller than the values exhibited by the polymers. On increasing the chain length further, the $\Delta S_{SI}/R$ values of the *n*OCB series are comparable to those of the PS*n* series.

If we assume that the limiting condition of an infinitely flexible backbone that is the potential barrier to rotation about the bonds is zero, then by extrapolating our results, the clearing temperature of such a polymer would represent the maximum possible for a side-chain polymer. In addition it would be considerably higher than that of the monomer. We suggest that this outcome is the result of the formation of virtual trimers in which a backbone segment links two side chains (see Figure 7). According to this model, it is not the side chain alone that represents the mesogenic unit; instead it is this trimeric species that readily explains the increased transition temperatures of the polymers relative to that of the monomer. In a rigid polymer the formation of these virtual trimers is obviously restricted, and hence lower clearing temperatures would be anticipated.

To test this prediction, we compared the clearing temperatures of the polymers 1 and the *n*OCBs with those of the analogous dimers, the α,ω-bis(4-cyanobiphenylyl-4′-oxy)alkanes[54] (**2**), which are hereafter denoted BCBO*n*,



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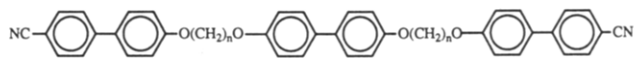
and the trimeric 4,4′-bis[[α-(4-cyanobiphenylyl-4′-oxy)-ω-alkyl]oxy]biphenyls[55] (**3**), which are hereafter referred



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to as TCBO*n* (Figure 8). The clearing temperatures of the polymers lie between those of the *n*OCB and BCBO*n* series. The BCBO*n* and TCBO*n* series both exhibit a very dramatic odd–even effect, an effect not observed for the polymers. At the root of this effect is the change in the average molecular shape as the parity of the spacer is varied (see Figure 9). If, for the sake of simplicity, we consider a spacer chain in the all-*trans* conformation, then the mesogenic cores are coparallel for an even-membered dimer but subtend an angle of about 108° for an odd-membered spacer. For trimers, the all-*trans* conformation of the even-membered spacers keeps the three mesogenic groups coparallel, whereas only two of the three cores are coparallel for the odd-membered spacers.

The virtual trimers we propose do not exhibit this dramatic odd–even effect, and the reason lies in the

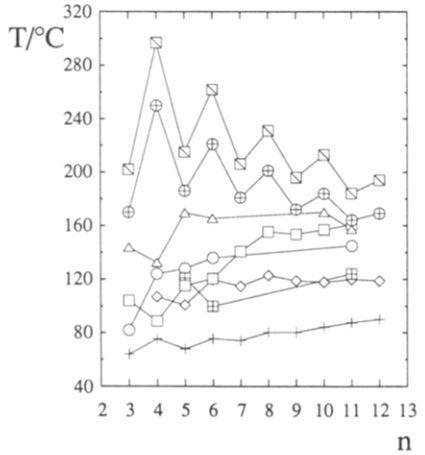


Figure 8. Clearing temperatures for the PS*n* (◇), PA*n* (○), PMA*n* (⊞), PVE*n* (□), PSX*n* (△), *n*OCB (+), BCBO*n* (⊕), and TCBO*n* (⧅) series.

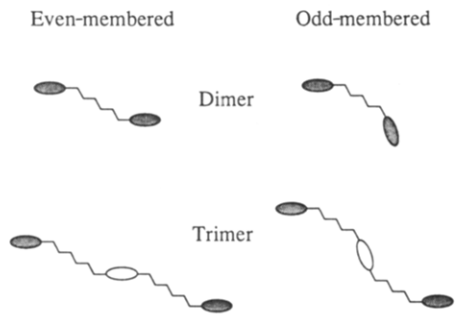
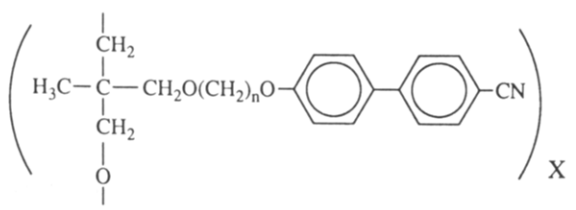


Figure 9. Schematic representations of odd- and even-membered dimers and trimers.

molecular shape. As can be seen in Figure 7, the polymer segment twists the trimeric structure because it contains an odd number of atoms. Therefore, for both odd- and even-membered spacers, the mesogenic cores are not coparallel in the virtual trimers and can be considered to be similar to the odd-membered dimers. Indeed, as the spacer length increased, the transition temperatures of the more flexible backbones approached those of the odd-membered dimers.

This model opposes a concept that has gained considerable popularity in which the side chain serves to decouple the backbone from the mesogenic group. In our virtual trimer model, however, it is clear that the backbone is not a passive component in the system but instead plays an important role in determining the transitional behavior. Attard et al. developed a mean-field model to describe side-chain polymers in which the conformational statistics of the spacer chain and polymer backbone are shown to be interrelated.[7] Decoupling only occurs in the sense that there is an increasing number of conformations available to the spacer as its length increases.

An apparent exception to this relation between backbone flexibility and clearing temperatures is the polyoxetane series[56,57] (**4**). The glass transition temperatures of these



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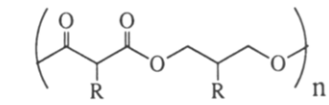
polymers are approximately equal to those of the corresponding polysiloxanes, whereas their clearing temperatures are lower than those of the polystyrenes. This apparent anomaly is caused by two factors; first, the backbone has side chains attached in a 1,5 sense such that the mesogens are diluted by a factor of 2 relative to the 1,3-disubstituted backbones, and, second, the 1,5 oxygen atoms are known to stabilize the formation of gauche linkages,[58] which will affect the shape of the virtual trimers. The effect of switching from a 1,3- to a 1,5-disubstituted backbone is discussed in more detail later. It should be noted, however, that the analogous propyl- and butylfluorobiphenyl-substituted polymers have higher clearing temperatures, results that are not in accord with the general observation for both low molar mass[2] or side-chain liquid crystal polymers[7] that changing a fluorine terminal substituent to a cyano group enhances the liquid crystal–isotropic transition temperature.

Another apparent anomaly is found in the transition temperatures of the side-chain polyesters reported by McRoberts et al.[59] (**5**). These T_g's are approximately equal



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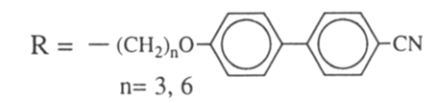
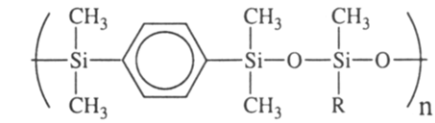


to those of the corresponding members of the PA*n* series, but the clearing temperature of the propyl homologue lies between those of PVE3 and PSX3 and that for the hexyl homologue is lower than that of PS6. These polyesters are, however, of relatively low molecular weight, and the properties quoted probably lie in the molecular weight-dependence regime.

We noted earlier that the attachment of side chains onto the polymer backbone increases the T_g for a flexible polymer while decreasing it for a rigid backbone. A flexible backbone facilitates the formation of the virtual trimers, which increases the rigidity of the backbone. Thus, an increase in T_g is anticipated and observed. For rigid backbones, the side chains have a greater tendency to act independently, and thus the plasticization effect is dominant and we see a decrease in T_g. For example, we may compare the behavior of PSX3, which has a T_g of 35 °C and a clearing point of 144 °C,[35] with the behavior of the silphenylene–siloxane analogue (**6**). Although the main chain of **6** is more rigid, it is an amorphous polymer with a T_g at 22 °C.[60] The amorphous behavior is a result of the dilution of the side chains.



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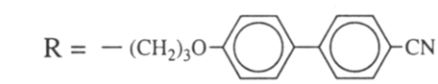
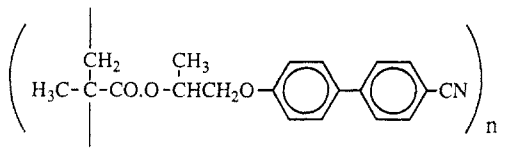


Cowie and Hunter[61] reported the properties of a chiral homopolymer (**7**) and copolymers containing up to 75% of this side chain. The homopolymer was amorphous, whereas the copolymers exhibited liquid crystallinity, and the clearing temperature appeared to increase as the chiral content increased. The authors offered no comment on



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the amorphous nature of the homopolymer. If we apply the virtual trimer model to this polymer, then we can see that each timer contains two methyl branches. It is known that a single methyl branch in dimeric systems results in a large decrease in transition temperatures;[62] consequently, the homopolymer does not exhibit liquid crystallinity. When a second side chain is added, it dilutes the methyl branches; consequently, an increase in transition temperatures is anticipated. The addition of small amounts of the branched side chain to the other homopolymer would tend to decrease the clearing temperatures; this behavior was also observed. The behavior of the copolymers having between 25 and 75% of the branched side chain is more difficult to understand, because the clearing temperatures pass through a maximum and a minimum. It should be noted, however, that in this case the side chains have different lengths, and this complicates the situation further.[3]

We consider now the entropy change associated with the clearing transition. Figure 10 compares the clearing entropies of the polymers with those of the monomers, dimers, and trimers. Again it is clear that the very pronounced alternation exhibited by the entropies for the dimers and trimers is not seen for those of the polymers. This difference can be explained in terms of the bent shape of the virtual trimers. The alternation in the nematic–isotropic entropies of the dimers has been interpreted recently in terms of the alternation in the long-range orientational order,[63] and such an alternation has been found in the second-rank order parameter for the long axis of the cyanobiphenyl group in the BCBO*n* series.[64] It can be seen in Figure 10 that the smectic–isotropic entropies of the polymers are similar to those of the nematic–isotropic entropies of the odd-membered dimers. There are three main contributions to the smectic–isotropic entropy change, namely, the conformational, the orientational, and the translational components. It is the subtle interplay of these three contributions that will determine the total entropy change.

Consider first a flexible polymer, for which we would expect the conformational component to dominate. As model calculations have shown, however, the conformational contribution to the total entropy of transition for an odd-membered dimer is very small.[63] The virtual trimer model can explain therefore the tendency of flexible backbones to exhibit lower clearing entropies than anticipated. When we consider a rigid backbone, we would expect the orientational order to dominate. But again, because we are dealing only with odd-membered virtual trimers, this contribution would also be a small value, similar to that of the monomer. Again this prediction agrees very well with the experimental observations. The translational contribution to the entropy change is presumably small, and this fact would explain the lack of a large increase in the entropies exhibited by the PA*n* and PVE*n* series on passing from nematic–isotropic to smectic–isotropic transitions. A structural feature of side-chain polymers that receives little attention is the molecular geometry in the vicinity of the atom attached to the backbone. If we consider either monomeric or dimeric mesogens, then changing from an ether to a methylene

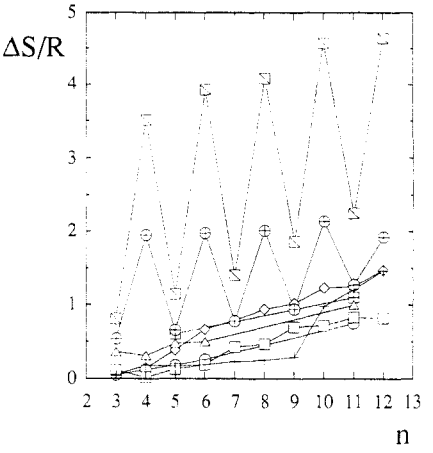
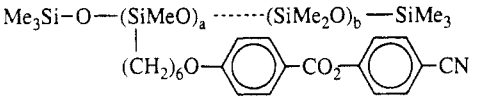


Figure 10. Clearing entropies for the PS*n* (◇), PA*n* (○), PMA*n* (⊞), PVE*n* (□), PSX*n* (△), *n*OCB (+), BCBO*n* (⊕), and TCBO*n* (⊠) series.

link between the mesogenic core and chain affects both the transition temperatures and the entropies. Emerson and Luckhurst[65] have shown recently, using a molecular field theory for flexible molecules, that these changes can be accounted for solely in terms of the molecular geometry. Within the framework of our virtual trimer model, such considerations are important and may account for the behavior of the entropies of transition. To test this, we are currently investigating model compounds.

A surprising feature of side-chain liquid crystal polymers is that diluting the mesogenic group by, for example, the statistical copolymerization of a mesogenic monomer with a nonmesogenic monomer results in polymers whose transition temperatures are not as depressed as might be anticipated. An example of this is the polysiloxane (8),



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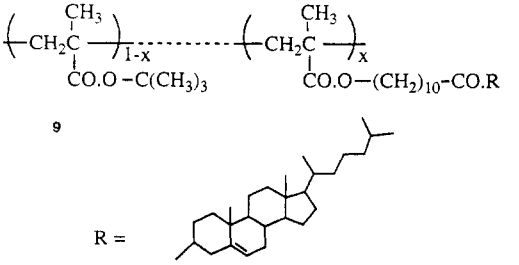
for which an *a*:*b* ratio of 3.2:1 yields the same transition temperature as the homopolymer.[66] Within the framework of our virtual trimer model, this surprising result is readily explained. On diluting the mesogenic cores, the backbone segment in the trimer is increased from three groups to five. This change results in a more elongated shape for the trimer, thereby enhancing the clearing temperature. The shape change is offset, however, by the dilution of the mesogenic cores, so the result is little change in the transition temperature. This model is supported further by studies of the copolymers prepared by Yamaguchi et al.[67] (9). The homopolymer containing the cholesteryl side



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chain has a lower clearing entropy than does the 80(chol):20 copolymer. The authors interpret this result in terms of the difference in the order of the polymers at temperatures slightly higher than the clearing temperature. An

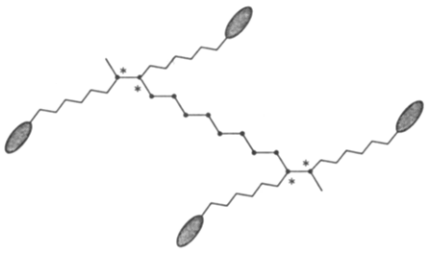
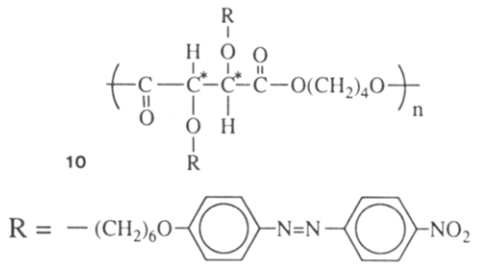


Figure 11. Schematic representation of a polytartrate.

alternative explanation is that the introduction of the nonmesogen creates a given number of 1,5 virtual trimers for which, by comparison with dimers,[63] the transitional entropies are anticipated to be higher.

Our model can account also for the high spontaneous polarization values measured for ferroelectric polytartrate[68] (**10**). The authors rationalize the high P_s values in



terms of the proximity of the polar ether oxygen and carbonyl groups. An alternative explanation considers that the chiral centers are in the core of an even-membered virtual trimer (see Figure 11), and it is well-known that the P_s value increases as the chiral center is moved toward the center of the molecular core.[69]

Movement of the chiral center is one of the several design implications suggested by the virtual trimer model, and we are currently investigating the properties of 1,4-disubstituted polymers in which the virtual trimers may be considered to be even-membered. In addition, to test this model, we are preparing realistic trimeric model compounds in which the central unit is kinked. Our model does not predict the relative orientations of the director of the phase and the polymer backbone, and this will clearly depend on the system in question. Both perpendicular and parallel arrangements of the mesogenic groups with respect to the backbone are readily incorporated into the model. Recent developments in computer software also allow for a realistic modeling of polymeric systems, and we plan to use such software packages to determine whether, by imposing correlations between side chains, i.e., virtual trimers, we can achieve both situations.

Conclusions

We have proposed a new model with which to explain the stabilization of liquid-crystalline behavior in side-chain polymers. Our virtual trimer model accounts successfully for the effects of backbone flexibility on the clearing temperatures and entropies as well as for the dilution of the mesogenic cores by nonmesogens. It differs from the existing models in that for the first time the backbone is considered to be a component of the mesogenic unit and as such plays an important role in determining the transitional properties.

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