

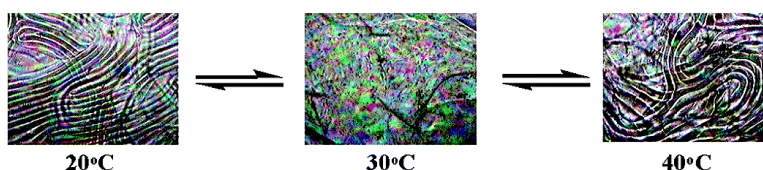
Article

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Chiral Conflict. The Effect of Temperature on the Helical Sense of a Polymer Controlled by the Competition between Structurally Different Enantiomers: From Dilute Solution to the Lyotropic Liquid Crystal State

Kai Tang, Mark M. Green,* Kap Soo Cheon, Jonathan V. Selinger,* and Bruce A. Garetz

Contribution from the Herman F. Mark Polymer Research Institute, Polytechnic University, 6 Metrotech Center, Brooklyn, New York 11201, and Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Code 6900, 4555 Overlook Avenue, SW, Washington, D.C. 20375

Received January 30, 2003; E-mail: mgreen@duke.poly.edu

Abstract: Helical polymers appended with paired structurally different enantiomers, which have opposing helical sense preferences, yield a new kind of relationship between optical activity and temperature, and also reveal unusual details of the nature of chiral interactions. Consistent with a statistical physical theory developed for these experiments, the proportion of the competing chiral groups, determined by synthesis, fixes the compensation temperature at which the helical senses are equally populated. The lyotropic liquid crystal state formed by these polymers yields therefore a nematic state at any chosen temperature over a very wide range, with a cholesteric state arising with tightening pitch as temperature deviates from this point. Far from the nematic temperature, the pitch reaches the nanometer scale and therefore the reflection of visible light. Before crossing zero at the nematic temperature, the optical activity becomes so large that it may be observed with the unaided eye through crossed polarizers.

Introduction

The helix forms a central motif among the wide variety of conformational states available to molecular and supramolecular organizations, with as many reasons for a system to fall into a helical energy well as there are examples of helical arrangements. Three Nobel Prizes have been awarded for demonstrations of this variable genesis of helical forms: the α -helix of proteins; the double helix of DNA; and the stereoregular synthesis of isotactic polypropylene, revealed by formation of a helical conformation in the crystal.

Helical structures play important roles across the whole spectrum of science and technology,¹ as evidenced by the extreme examples of viruses, which often form helical arrays from assembly of nucleic acid and protein components,² all the way to the other side of the structural spectrum to twisted nematic (cholesteric) states formed in liquid crystal displays.³ Chemists have been stimulated to construct helical arrays that mimic the helical structures in biological systems; thus, there is a large literature from which the wide variety of approaches can be accessed via leading and recent publications in this area.^{4–25}

There is a dichotomy in the literature of helical arrays. On one hand, there are the biological systems and their synthetic mimics that use biologically derived building blocks. Here, the given nonracemic chirality of the molecules forming the helical

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arrays leads invariably to a single helical sense under any single set of conditions. One could, in one way of thinking, see these systems of biological origin as disadvantaged because they block our observation of how helical sense is chosen. In many synthetic systems, in contrast, helical sense control can be addressed by using the power of chemistry, in its ability to incorporate nonracemic chirality, therefore opening the potential to observe the interplay of local chirality and helical sense.

In one synthetic polymer, this opportunity to observe how helical sense is controlled leads to quantitative insight into the cooperativity of helical systems.^{26,27} One aspect of this cooperativity is encountered in an experiment in which mirror-image-related moieties compete for control of helical sense, giving rise to a highly nonlinear relationship between the enantiomeric excess of the competing groups and the excess helical sense.^{28,29} This experiment, termed “majority rule,”²⁸ is altered in the work reported here to ask a new kind of question: What would happen if the information offered to a helical array arose from a conflict in which the chiral forces favoring left- and right-handed conformations arose from structurally different enantiomers?

In answering this question, we discover, as outlined in the work presented below, a new kind of relationship between temperature and optical activity in both dilute solutions and liquid crystals; this relationship can be described in quantitative detail by statistical physics and could be applied, in principle, to a wide variety of helical arrays.³⁰

Theoretical Background

An approximate algebraic solution (eq 1) to a one-dimensional Ising model, describing the effect of conflicting chiral information on choosing helical sense in a helical array, has been developed to understand the experimental results for a helical polymer appended with enantiomeric groups.^{28,31} The theory addresses

a polymer with a helical conformation that is interrupted *infrequently* by mobile helical reversal defects, allowing the chains to dynamically interconvert between left- and right-handed conformations. The appended competing enantiomeric groups, which may reside on all units of the chain or some fraction of the units, then respectively favor the mirror-related helical senses.

$$M = \operatorname{erf} \left[\sqrt{\frac{Lr}{2p^*(1-p^*)}} (p - p^*) \right] \quad (1)$$

In the theoretical expression (eq 1),³⁰ the excess of one helical sense is expressed by M , which varies from unity for a single helical sense, which would lead to the maximum chiral optical effect, to zero for a 50:50 mixture, for which all chiral optical measurements at all wavelengths would be zero. As shown in eq 1, M is related through an error function (erf) to four different variables. The term r measures the fraction of chiral groups appended to the chain, allowing therefore for the possibility that the competing chiral units are dispersed among achiral units. L measures the number of helical units along the chain between the interrupting helical reversal units and therefore is a measure of the cooperativity.^{26,27} Finally there is a term measuring the difference between the variables p and p^* . If the competing chiral units are C_a and C_b , then p measures the fraction of C_a , that is, $C_a/(C_a + C_b)$, which is determined by synthesis and therefore can be varied.

The variable p^* is defined by eq 2, where ΔG_a and $-\Delta G_b$ are the chiral bias energies by which the competing groups favor one or the other helical sense. If C_a and C_b are enantiomers of

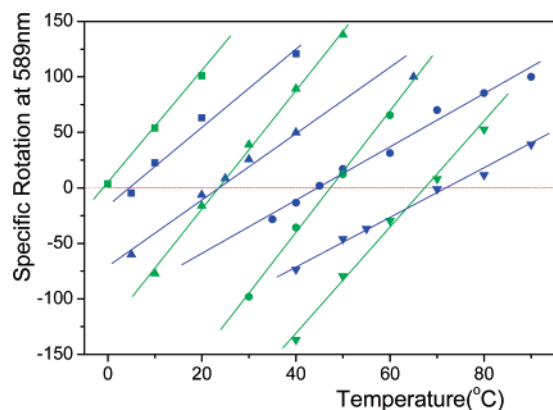
$$p^* = \left(\frac{\Delta G_a}{\Delta G_a + \Delta G_b} \right) \quad (2)$$

each other, then these free energies must be identical in magnitude, and therefore p^* must equal 1/2. This situation gives rise to the theoretical expressions originally derived for the majority rule experiments^{28,31} and informs us that, for a 1:1 mixture of C_a and C_b , for which $p = 1/2$, $p - p^*$ is zero and therefore, from eq 1, M must be zero and so must all chiral optical measures. This conclusion is independent of temperature, although the free energy terms in eq 2 may be temperature-dependent, because the temperature dependencies of ΔG_a and ΔG_b must be identical. In other words, p^* is independent of temperature when the competing chiral groups are mirror-related. For the latter situation, the theory has been shown to quantitatively fit experiment.³¹

In the current work, we are interested in the situation where C_a and C_b are structurally different enantiomers,³⁰ that is, not enantiomers of each other. It follows that ΔG_a and ΔG_b might have different temperature dependencies, and therefore p^* would change with temperature. This sets up an interesting experiment. If C_a and C_b are randomly distributed along the chain in a proportion corresponding to p , then there may be a temperature, T_c , at which p^* will be equal to p and therefore a temperature at which $M = 0$. However, above and below T_c , p and p^* will differ because p^* is a function of temperature while p is not, causing M to differ from zero.

The sign of M will reflect the sign of the term $p - p^*$, and this sign will change above and below T_c . Therefore, the sense of the helix in excess will, as well, change above and below T_c .

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Molar percentage of designated competing chiral groups

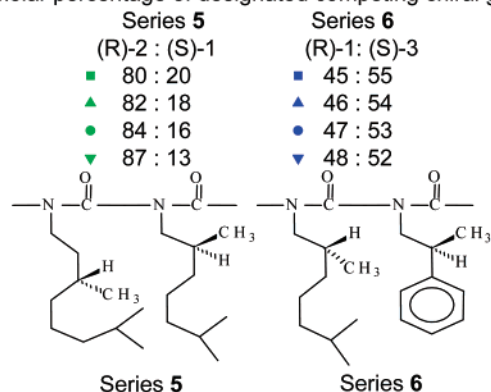
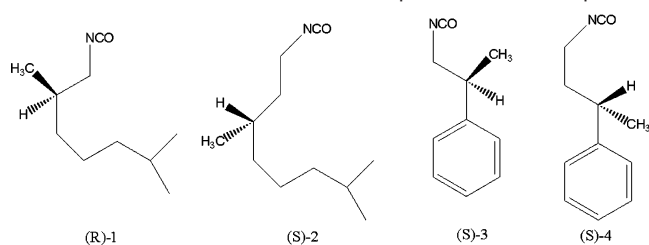


Figure 1. Specific rotation at 589 nm as a function of temperature for series 5 and series 6 in dilute solution in toluene ($c = 1$ mg/mL).

Scheme 1. Chemical Structures of Competitive Chiral Groups



It is of great interest that variation of p by synthesis can cause p^* to equal p at differing temperatures. In other words, and remarkably, the system can yield a series of polymers of variable composition, p , which will exhibit equal proportions of left- and right-handed helical conformations at continuously variable temperatures.

Results and Discussion

Dilute Solution. A successful test of the temperature-dependence concept outlined above has been made in model polyisocyanates by forming copolymers from the chiral molecules shown in Scheme 1.³⁰ The results in Figure 1 demonstrate the expected relationship between the composition, p , of the competing structurally different enantiomers and temperature, which is consistent with the theoretical ideas (eqs 1 and 2), and these results also reveal an aspect of the theory shown in eq 3.³¹

One competitive set of structures in Figure 1 exhibits a significantly steeper dependence of the helical sense excess (M from eq 1 as measured by the optical rotation $[\alpha]$) on tem-

perature, $d[\alpha]/dT$, near T_c , and a steeper dependence of T_c on p . As predicted by eq 3, the larger the temperature dependence of the free energy terms controlling the chiral interaction between the side groups and the backbone helix, dp^*/dT , the larger should be $d[\alpha]/dT$ at T_c . The temperature dependence of

$$\left. \frac{d[\alpha]}{dT} \right|_{p=p^*(T)} = -[\alpha]_{\max} \sqrt{\frac{2Lr}{\pi p^*(1-p^*)}} \frac{dp^*}{dT} \quad (3)$$

p^* can be expected to be greater for a more conformationally flexible structure, which fits the observation that a larger $d[\alpha]/dT$ is observed for the competition between **1** and **2** (series 5) compared to that between **1** and **3** (series 6; Figure 1, Scheme 1). Another opportunity for evaluation of the predictions in eq 3, including evaluation in a quantitative manner, arises from the relationship between $d[\alpha]/dT$ at T_c and L , which will be addressed after the discussion of further experimental work presented below.

The conclusion above concerning the relationship between $d[\alpha]/dT$ at T_c and the flexibility of the chiral competitors suggests that a competition among chiral groups with restricted conformational motions would reduce the temperature dependence of p^* , even to the extent that temperature could have little or no effect on the helical sense excess. It is valuable to test this hypothesis to judge our general understanding of the phenomenon.

NMR studies on the movement of helical reversals in the polyisocyanates as well as measures of chain stiffness demonstrate that branched side chains in this highly crowded structure²⁶ reduce conformational motion.³² One of the model branched side chains used is derived from 2-butylhexyl isocyanate, suggesting that dispersing the competitive chiral groups (Figure 1) among 2-butylhexyl side chains may lead to a reduced temperature dependence of p^* compared to dispersing the same chiral groups among linear side chains.

Figure 2 shows the differing temperature dependences of terpolymers **7** and **8**, synthesized from two of the competitive chiral entities shown in Scheme 1 with 2-butylhexyl isocyanate (series **7**) and alternatively with *n*-hexyl isocyanate (series **8**). The difference is striking. Changing the composition, p (eq 1), of the chiral units in series **7** strongly affects the optical activity, even reversing sign as a function of p , but with a weak temperature dependence for each composition p . In contrast, the terpolymers in series **8** exhibit the same kind of temperature dependence as seen for the copolymers in Figure 1. The sign of the optical activity and therefore the change of excess helical sense switch with temperature, with the switching temperature dependent on the composition, p .

The difference between these terpolymers, in series **7** and **8**, reasonably arises from the increased restrictions to conformational motion associated with the crowded branched side chains (series **7**).³² The observations for series **7** (Figure 2) can, however, still be interpreted in light of the theory presented in eqs 1 and 2. While p^* appears to take a value that has little temperature dependence, p varies with composition (Figure 2). The data reveal that the changing value of p falls above and below p^* , leading to a change in helical sense excess that

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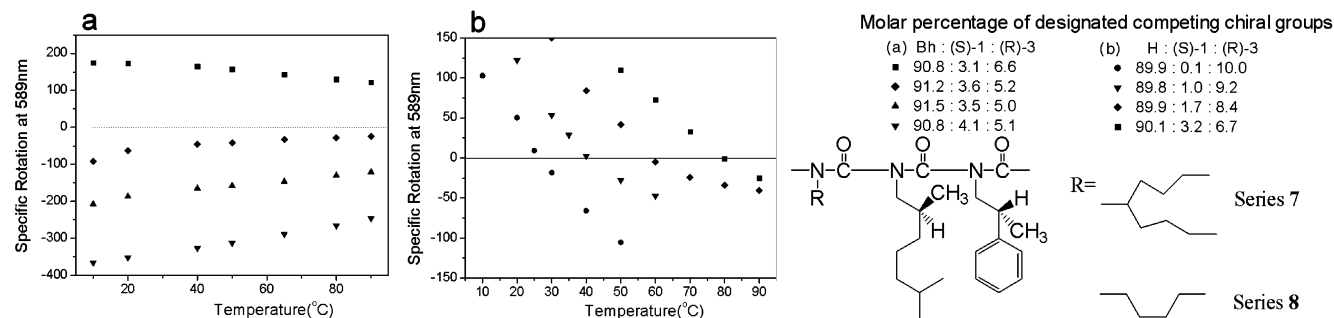


Figure 2. Specific rotation at 589 nm as a function of temperature in dilute solution in toluene ($c = 1$ mg/mL). (a) Series 7 terpolymers derived from (S)-1, (R)-3, and 2-butylhexyl isocyanate (Bh). (b) Series 8 terpolymers derived from (S)-1, (R)-3, and *n*-hexyl isocyanate (H).

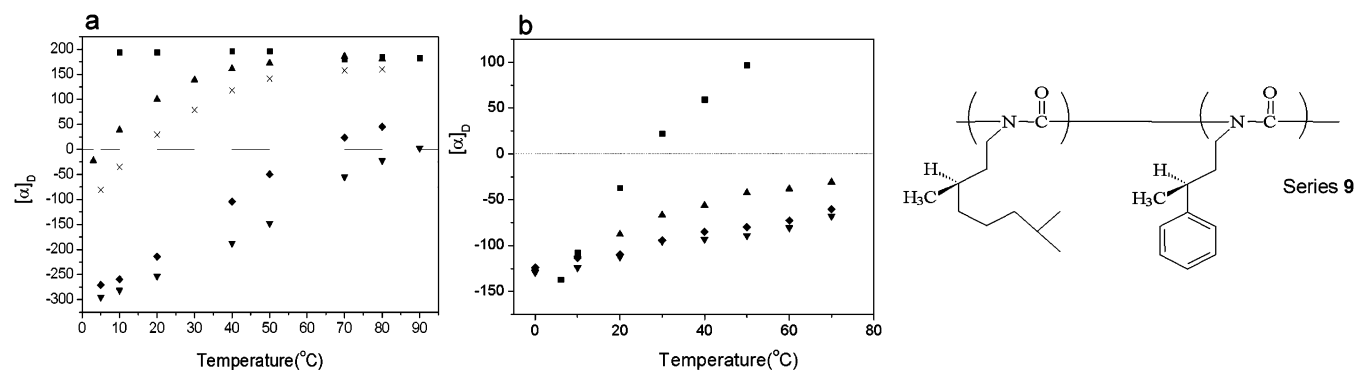


Figure 3. Optical rotation at 589 nm as a function of temperature for series 9 copolymer derived from (R)-2 and (S)-4 in dilute solution in different solvents ($c = 1$ mg/mL): (a) in toluene and (b) in chloroform. Molar percentage of designated competing chiral groups, (R)-2:(S)-4: ■, 50:50; ▲, 53:47; ×, 60:60; ◆, 65:35; ▼, 70:30.

depends on p . But since the temperature dependence of p^* is weak, the optical activity shows little dependence on temperature for any one of the compositions.

Looking at the temperature dependence of the competition between the chiral groups for helical sense control in still another way yields more information about the interplay between the chiral groups and helical sense preference. Figure 1 (series 5 and 6) and Figure 3a (series 9) demonstrate that the chiral group controlling the helical sense at temperatures above T_c is 1 over 2, and 3 over 1, and 4 over 2. This information arises simply from the sign of the optical activity as a function of temperature (Figures 1 and 3a) and the sign of the optical activity arising from each of the competing chiral units forming a polymer in the absence of the competing chiral moiety. Inspection of the structures of the chiral groups noted above indicates that the less conformationally mobile chiral group in each matched pair gains increasing control over the helical sense as temperature increases. The data are consistent with the notion that the chiral influence of the more flexible chiral competitor is more strongly temperature-dependent, with the ΔG term (eq 2) for this term diminishing in magnitude as temperature increases.

Another interesting aspect of the competition between the chiral competitors for helical sense control can be seen by comparing the data in Figure 3a with those in Figure 3b, in which chloroform has been substituted for toluene. As noted above, the positive optical rotation above T_c in the series 9 copolymers, and for that matter the tendency toward positive optical rotations as temperature increases seen in both parts a and b of Figure 3, arises from the predominant influence of 4.

The results for series 9 copolymers in chloroform (Figure 3), while also exhibiting increasing control of the helical sense by 4 as temperature increases (tendency toward positive optical

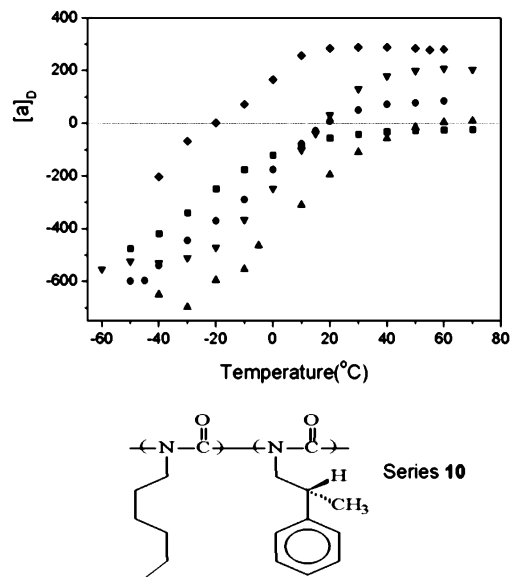


Figure 4. Specific rotation at 589 nm for series 10 copolymers derived from hexyl isocyanate (H) and (S)-3 as a function of temperature in dilute solution in toluene ($c = 1$ mg/mL). Molar percentage of designated competing chiral groups, H:(S)-3: ■, 99:1; ▲, 95:5; ●, 90:10; ▼, 85:15; ◆, 80:20.

rotations with increasing temperature), are, however, greatly changed (compare parts a and b of Figure 3). Only the copolymer with the highest proportion of 4 exhibits a detectable T_c . All others show negative optical activities at all temperatures studied, with a tendency to switch to a positive optical activity at far higher temperatures than seen for the same copolymers in toluene (Figure 4). A reasonable explanation for the difference between the data in parts a and b of Figure 3 is that chloroform

increases the net helical sense influence of the aliphatic competitor, **2**, at all temperatures, while toluene has a similar effect on the aromatic competitor, **4**.

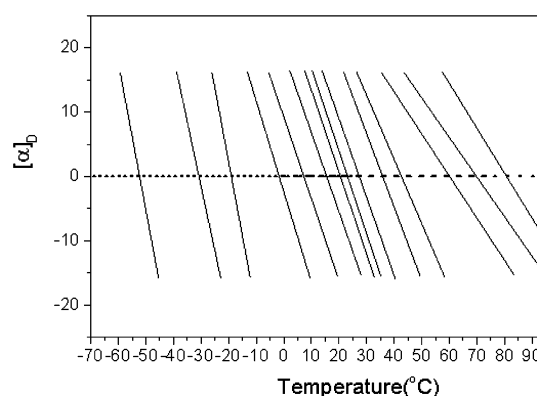
Another interesting aspect of the nature of the chiral competition arises from comparing the data in Figures 1 and 2b for **1** vs **3**. Incorporating the chiral competitive groups **1** and **3** in a terpolymer with *n*-hexyl side chains (series **8**) (Figure 2b) demonstrates that higher proportions of the aromatic chiral group **1** are necessary in the terpolymers of series **8** in order to switch helical sense in the same temperature range as for the copolymers in series **6** (Figure 1). Note that the enantiomers are opposite in the two experiments, so that the change in optical activity is opposite in the compared systems. Apparently, the net influence of the aliphatic chiral moiety, **1**, over the aromatic chiral group, **3**, increases under the influence of the aliphatic side chains in the terpolymer **8**.

Although the relationships between the structure and the environment of the chiral groups and the temperature dependence of helical sense discussed above are certainly interesting, and would likely make interesting grist for theoretical calculations³⁵ and for further experiments to gain detailed knowledge of the nature of the chiral forces at work, in the current effort, as discussed below, we have focused elsewhere.

It would appear from the T_c data in Figure 2b and from the change in T_c with composition in the copolymers in series **6** (Figure 1) that simply reducing the proportion of **1** in competition with **3** for the series **8** terpolymer would move T_c to increasingly lower temperatures. In fact, we discovered that removing the aliphatic group, **1**, entirely and forming a copolymer of **3** and *n*-hexyl isocyanate (series **10**) caused the helical sense to switch near 20 °C in the copolymer with 90% *n*-hexyl pendant groups. Figure 4 shows this effect and, in addition, that the proportion of *n*-hexyl pendants greatly influences the helical inversion temperature.

The observations in Figure 4 form a counterpoint to the focus of the work presented above in that they are *unrelated* to the helical inversion effect arising from the competition between chiral groups (Figures 1, 2b, and 3). Rather, the data in Figure 4 can be attributed to conflicting helical sense choices sometimes encountered in a variety of studies and often ascribed to same-signed enthalpic and entropic terms, therefore causing the sign of the free energy term for the chiral influence to invert with temperature. Alternatively, temperature-dependent helical sense inversions can arise from less defined aggregation-associated phenomena.^{37–40}

Using the chiral competition information gathered above, one can design polymers with a wide range of switching temperatures, as shown in Figure 5 for terpolymers of series **11**. The limitation on T_c at low temperature would reside only in the



The molar percentage of designated competing chiral groups and the corresponding switch temperature (T_c)

X	Y	Z	T_c (°C)
4.0	0	6.0	-53
3.0	0	7.0	-31
2.0	0	8.0	-19
1.5	0	8.5	-2
1.0	0	9.0	6
0.5	0	9.5	15
0	0	10	20
0	0.06	10	22
0	0.14	10	27
0	0.49	9.6	36
0	0.95	9.2	43
0	1.7	8.4	60
0	2.4	7.6	70
0	3.2	6.7	80

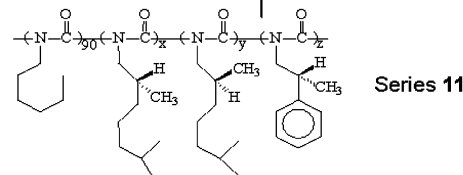


Figure 5. Optical rotation at 589 nm in dilute solution in toluene for series **11** terpolymers derived from hexyl isocyanate (H) and (*R*)-**3** and (*R*)-**1** or (*S*)-**1** as a function of temperature.

solubility of the polymer or the crystallization of the solvent, while on the high-temperature side the limitation would rest only on the stability of the polymer, which in the case of the polyisocyanates extends to about 100 °C.

The data over the wide temperature range seen for series **11** in Figure 5 make it obvious that the slope of the change of optical activity with temperature grows far steeper as temperature decreases, finally attaining a steady value for temperatures approximately below 0 °C. This result is associated with another aspect of the theory involved with the L term in eqs 1 and 3. Equation 4 shows the dependence of the cooperative length, L ,

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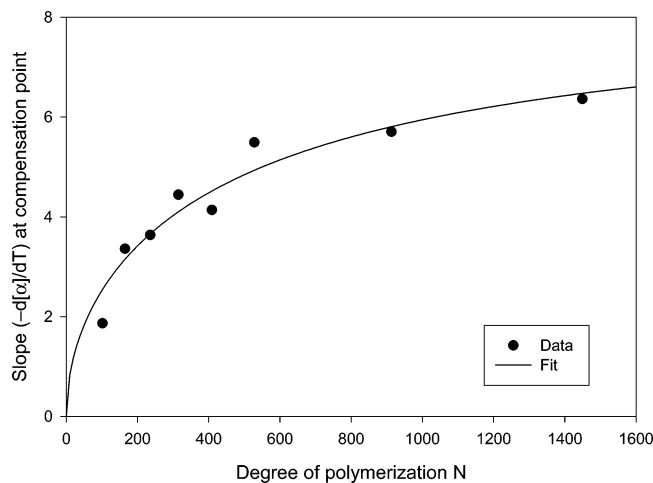


Figure 6. Slope ($-d[\alpha]/dT$) [measured in dilute solution in toluene] at optical switch temperature (T_c) as a function of degree of polymerization N for one of the series **5** copolymers derived from 82.3% (*S*)-**2** and 17.7% (*R*)-**1**.

on three terms, N , L_{rf} , and L_{th} .^{28,31} While N , the degree of

$$\frac{1}{L} = \frac{1}{L_{rf}} + \frac{1}{L_{th}} + \frac{1}{N} \quad (4)$$

$$L_{rf} = \left(\frac{\Delta G_r}{2\Delta G_h} \right)^2 \quad (5)$$

polymerization, is independent of temperature and L_{rf} , which is a ratio of free energies (eq 5),⁴¹ will depend only weakly on temperature, L_{th} designates the number of units along the chain between thermally activated helical reversals. L_{th} will therefore be exponentially related to both the temperature and the excess energy of a helical reversal along the chain, ΔG_r , that is, $e^{\Delta G_r/T}$.²⁷

Thus, L_{th} will greatly increase as temperature decreases, causing the overall limiting term L to increase (eq 4), which is the source of the change in the slope of $d[\alpha]/dT$ (eq 3) with decreasing temperature (Figure 5). Moreover, as L_{th} grows very large compared to the other cooperative terms in eq 4, its influence on L will diminish (eq 4), accounting for the leveling off of the change in $d[\alpha]/dT$ at the lowest temperatures in Figure 5.

Although the theory makes only a qualitative prediction of the effect of temperature on the slope $d[\alpha]/dT$ at T_c , it makes a quantitative prediction of the effect of degree of polymerization on this slope. Equation 3 shows that this slope scales with the square root of the domain size L . Equation 4 further shows that the domain size is limited by the degree of polymerization N for short chains and becomes independent of N for long chains. Hence, $d[\alpha]/dT$ should increase as $N^{1/2}$ for short chains and then saturate for long chains. To test this concept, Figure 6 shows experimental data for $d[\alpha]/dT$ as a function of N , as well as a fit to the theoretical prediction. In the samples of low N , the slope is low. In the higher- N samples, the slope increases and then saturates, consistent with the theoretical fit. The saturation occurs at a chain length N of approximately 1,000, which corresponds to a molecular weight of approximately 130 000.

(40) Reversal of sign of optical activity in helical polymers and related materials may arise from the effects of aggregation that do not necessarily arise from changes in helical sense of the component entities: Reidy, M. P.; Green, M. M. *Macromolecules* **1990**, *23*, 4225. Tabei, J.; Nomura, R.; Masuda, T. *Macromolecules* **2003**, *36*, 573.

The optical and switch consequences⁴² of the ability to vary T_c over a wide range, as demonstrated in Figure 5, could be greatly enhanced if incorporated in a liquid crystal. A nematic phase might be expected to form when the temperature equals T_c , which would transform to cholesteric phases of opposite sense and tightening pitch as T varied from T_c in either direction. As we will see below, this transformation of the dilute solution effects, discussed above, to a liquid crystal can be accomplished, and such cholesteric liquid crystals have extraordinary chiral optical properties.

Although reversal of the helical sense of cholesteric liquid crystals with temperature is well known in thermotropic liquid crystals, these reversals occur for reasons that are complex and not defined in terms of changes occurring, if any, in the mesogenic molecules.⁴³ In the work presented below, however, the inversion of the sense of the cholesteric liquid crystal arises from the inversion of the helical sense of the polymers forming the liquid crystal, the kinds of polymers described above (Figure 5). We shall also see below that the polymer that switches helical sense with temperature can act either as a dopant in a liquid crystal matrix or as the mesogen itself.

Doping the Lyotropic Liquid Crystal with the Helical Switchable Polymers. Lyotropic liquid crystal solutions⁴⁴ have a special advantage for temperature-dependent work because the phase boundaries of liquid crystals formed from solutions of rodlike objects are unaffected by temperature, except insofar as temperature affects the axial dimensions of the mesogenic object.^{3,45–47} Poly(*n*-hexyl isocyanate) forms such a liquid crystal when dissolved in an excellent solvent such as toluene,⁴⁸ allowing use of the switchable polyisocyanates (Figure 5) as chiral dopants in the lyotropic state formed by poly(*n*-hexyl isocyanate).

Our first results were based on the terpolymer **12** of *n*-hexyl isocyanate with the competitive chiral groups **2** and **3** in a proportion causing a T_c near 30 °C. Addition of **12** to a nematic solution of poly(*n*-hexyl isocyanate) in toluene maintained at close to 20 °C, over a period of a day or two, slowly gave rise to a typical fingerprint texture, which is a signature for the

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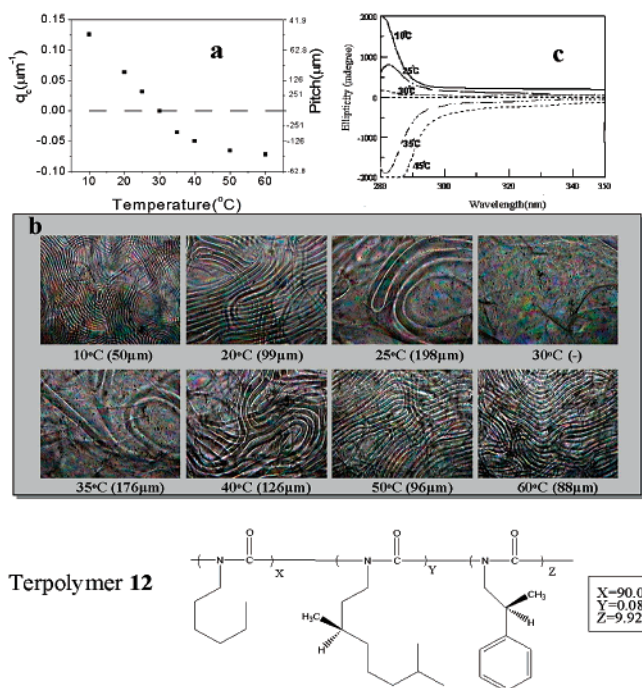


Figure 7. (a) Temperature dependence of the pitch and pitch wavenumber, q_c [measured from the fingerprint texture in a 1-mm-path glass cell], of 2 wt % [percentage of weight of dopant/(weight of dopant + weight of poly(*n*-hexyl isocyanate))] of terpolymer **12**, derived from hexyl isocyanate (H), (*R*)-**2**, and (*S*)-**3**, used as a dopant in the liquid crystal formed from a 40% [percentage of (weight of dopant + weight of poly(*n*-hexyl isocyanate))/(weight of dopant + weight of poly(*n*-hexyl isocyanate) + weight of toluene)] solution of poly(*n*-hexyl isocyanate) in toluene. (b) Temperature dependence of the fingerprint texture [measured from the fingerprint texture in a 1-mm-path glass cell] of the corresponding liquid crystal. (c) Circular dichroism spectra [measured in a water-jacketed quartz cell (path length = 0.01 cm)] of the planar texture of the corresponding liquid crystal.

cholesteric liquid crystal phase. Changing the temperature around the T_c value in dilute solution in a similarly slow fashion gave rise to changing pitch values, which are summarized in Figure 7a, which presents the pitch directly in micrometers and as the pitch wavenumber, $2\pi/\text{pitch}$.

The fingerprint textures associated with the observations reported in Figure 7a are shown in Figure 7b, which clearly show the pitch increasing as temperature falls from 60 °C, until the pitch grows so large as to be undetectable near 30 °C. On further reduction of the temperature, the fingerprint texture reappears, and the pitch tightens.

Confirmation that the senses of the cholesteric twisting that gives rise to the fingerprint textures in Figure 7b are opposite, and in particular left-handed above and right-handed below 30 °C, was provided by measurement of the circular dichroism spectra shown in Figure 7c. These spectra were determined by incorporating the liquid crystal solution in a narrow path cell, in the range of 50 μm. Under these conditions, the propensity of the stiff polymers to lie parallel to the cell surfaces is maintained throughout the solution, giving rise to a planar texture. Such textures are well understood and have optical properties that can be translated to the helical sense properties of the cholesteric phase.^{3,49} The observation that the helical sense

(49) For application of CD for the study of cholesteric mesophases, see: Gottarelli, G.; Spada, G. P. In *Circular Dichroism—Principles and Application*, 2nd ed.; Berova, N., Nakanishi, K., Woody, R. W., Eds.; Wiley-VCH: New York, 2000; Chapter 19.

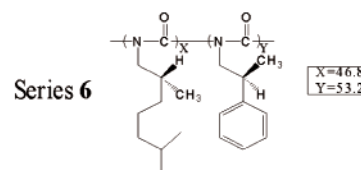
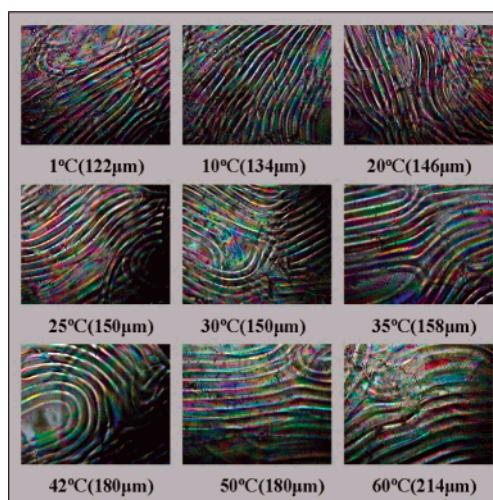


Figure 8. Temperature dependence of the fingerprint texture [measured in a 1-mm-path glass cell] of 2 wt % [percentage of weight of copant (weight of dopant + weight of poly(*n*-hexyl isocyanate))] of one of the copolymers from series **6**, derived from 46.8% (*R*)-**1** and 53.2% (*S*)-**3**, used as a dopant in the liquid crystal formed from a 30 wt % [percentage of (weight of dopant + weight of poly(*n*-hexyl isocyanate))/(weight of dopant + weight of poly(*n*-hexyl isocyanate) + weight of toluene)] solution of poly(*n*-hexyl isocyanate) in toluene.

of **12** in dilute solution is opposite to the helical twisting of the cholesteric formed on using **12** as a dopant is consistent with the literature reports on “sergeant and soldier” copolyisocyanates acting as dopants in the lyotropic phase of poly(*n*-hexyl isocyanate).⁴⁷

The pitch values shown in Figure 7a, even at temperatures far removed from T_c , are quite large, in the range of many tens of micrometers, and this fact contributes to the very slow response of the liquid crystal to form the equilibrium fingerprint texture and the slow response of this texture, once formed, to changes in temperature.

In an attempt to tighten the pitch, we considered that removing the “chiral diluting” *n*-hexyl pendants and using a copolymer of entirely chiral groups as the dopant added to the liquid crystal phase of poly(*n*-hexyl isocyanate) would accomplish this objective. For this purpose, a copolymer from series **6** with a composition of **1** and **3** yielding a dilute solution T_c near 40 °C (Figure 1) was dissolved in a concentrated solution of poly(*n*-hexyl isocyanate) similar to the solution used for the results in Figure 7a. To our surprise, as shown in Figure 8, the cholesteric pitch of the resulting liquid crystal solution showed no evidence of passing through the nematic state within a wide temperature range around the T_c observed in dilute solution (Figure 1). This was confirmed by observation of the circular dichroism of the planar texture of this cholesteric phase, which showed no reversal of the sign under conditions identical to those used to obtain the data in Figure 7c.

A clue to the mysterious difference between the behaviors of the copolymer of series **6** and terpolymer **12** as dopants to the lyotropic nematic state of poly(*n*-hexyl isocyanate) arises

from investigation of the properties of a copolymer of the competitive chiral groups in series **5** (Figure 1), which on use as a dopant in the liquid crystal phase of poly(*n*-hexyl isocyanate) behaves in parallel to the behavior observed when terpolymer **12** was used as a dopant (Figure 7).

Apparently, both the copolymer from series **6** and terpolymer **12** can transmit chiral information to the mesogenic matrix consisting of poly(*n*-hexyl isocyanate) chains, as evidenced by the formation of a cholesteric phase, but the data demonstrate that this chiral information is connected to a property of the helical backbone in terpolymer **12** but disconnected from this source in the series **6** copolymer. The chiral information apparently available to the liquid crystal matrix from the series **6** copolymer derives from the pendant groups associated with the structures of **1** and **3** rather than from the helical characteristics of the chain as in terpolymer **12** and the copolymer from series **5**.

An interesting collection of literature concerned with the properties of chiral liquid crystals, including smectic C* phases^{50,51} and cholesteric phases,⁵² and consistent with studies on the polyisocyanates focused on here,⁴⁷ may be summarized by the idea that enhanced communication of dopant chiral information to liquid crystals depends on structural similarity between the dopant and the mesogen. That these ideas are at work in the observations discussed above is confirmed by the data in Table 1.

A quantitative measure of the relationship between the pendant group structure and the changing helical sense characteristics of the polymer on the pitch properties of the liquid crystal is found in Table 1, which presents the ratio S_{T_c} of the slope of $d[\alpha]/dT$ in the dilute solution to the slope of $d[\text{pitch}]/dT$ in the liquid crystal, both measured near T_c for the series **5** and **6** copolymers and for terpolymer **12**.

Because the optical activity in dilute solution of these helical-switching polymers is almost entirely determined by the helical characteristics, which contribute overwhelmingly to the optical activity at all wavelengths,²⁶ $d[\alpha]/dT$ measures the changing helical sense ratio with temperature. The effect of these helical sense changes on the cholesteric state is then measured by dq_c/dT . The difference in slopes in dilute solution versus the liquid crystal, S_{T_c} , is then a measure of the translation of the helical sense changes of the polymer to the helical twisting of the liquid crystal. The difference in S_{T_c} between the two copolymers from series **5** and **6**, which are generally structurally similar, means that the translation of the dilute solution to the liquid crystal is greater by a factor of 36 for series **5** compared to series **6**. The data further show that terpolymer **12** acts to enhance the connection between its helical sense changes and the liquid crystal matrix by an additional factor of 2 (Table 1).

The structural feature of the poly(*n*-hexyl isocyanate) chain, which forms the liquid crystal matrix in the experiments discussed above, is overwhelmingly aliphatic, arising from the *n*-hexyl pendant groups. In the two polymers that communicate their changing helical properties to the liquid crystal matrix (smaller values of S_{T_c}), the pendant groups in one, the series **5** copolymer, are entirely aliphatic and those in the other,

Table 1. Comparison of Different Dopant Systems^a

liquid crystal	chemical structure of dopant	T_{c1}/T_{c2}	S2	S1	S_{T_c}
A	series 6 copolymer	42/—	−0.000351	2.66	-7.6×10^4
B	terpolymer 12	60/~30	−0.00605	6.40	-1.1×10^3
C	series 5 copolymer	25/~20	−0.00306	6.56	-2.1×10^3

^a Liquid crystal A, 2 wt % of one copolymer from series **6** in a 30 wt % solution of poly(*n*-hexyl isocyanate) in toluene; liquid crystal B, 2 wt % of terpolymer **12** in a 40 wt % solution of poly(*n*-hexyl isocyanate) in toluene; liquid crystal C, 2 wt % of one copolymer from series **5** in a 40 wt % solution of poly(*n*-hexyl isocyanate) in toluene. T_{c1} , optical switch temperature (°C) in dilute solution in toluene; T_{c2} , optical switch temperature (°C) in lyotropic liquid crystal matrix. S1, slope of the curve of $[\alpha]_D$ vs temperature (degree·L/dL·g·°C) near T_{c1} in dilute solution in toluene; S2, slope of the curve of q_c vs temperature ($\mu\text{m}^{-1}\cdot\text{°C}^{-1}$) near T_{c2} in the liquid crystal matrix; S_{T_c} , $(d[\alpha]_D/dT_{T_{c1}})/(dq_c/dT)_{T_{c2}}$.

terpolymer **12**, are overwhelmingly aliphatic. In further detail, there is an exact structural match between 90% of the side groups of the helical-switching polymer and the matrix polymer only in terpolymer **12**. Thus, the structural match between the mesogenic matrix *n*-hexyl pendant groups and the helical switchable polymers acting as chiral dopants follows the trend, from best to least match, terpolymer **12** > series **5** > series **6**. Apparently, the helical characteristics of the backbone of the polymer are transferred to the liquid crystal matrix via the aliphatic side groups.

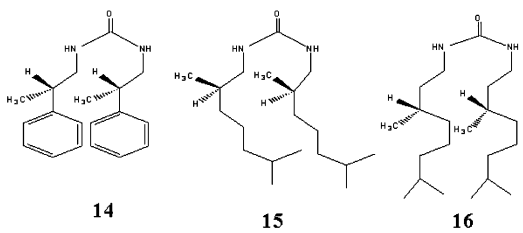
This interpretation of the failure of the series **6** copolymer to transfer the helical sense changes to the liquid crystal matrix must mean that the cholesteric state arises from chiral information inherent in the chiral pendant groups of the series **6** copolymer. It must follow, then, that the competitive helical twisting powers of the chiral groups constituting **1** and **3** should control the cholesteric properties encountered on doping poly(*n*-hexyl isocyanate) with the series **6** copolymer. To test this hypothesis, we synthesized the ureas **14**, **15**, and **16** shown in Table 2 and used these molecules as dopants for the lyotropic liquid crystal of poly(*n*-hexyl isocyanate). Measurement of the pitch of the resulting cholesteric state then allowed evaluation of the helical twisting power (HTP) of each urea and therefore an estimate of the influence of the polymer pendant groups, in the absence of the helix, on the poly(*n*-hexyl isocyanate) liquid crystal matrix.

From the HTP data in Table 2, it is apparent that urea appended with the chiral group of **1** has approximately twice

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Table 2. Chemical Structures and Properties of Ureas Derived from (*R*)-1, (*S*)-2, and (*S*)-3


structure	urea source	$[\alpha]_{25}^D$ of urea (100 mg/mL in toluene)	HTP ^a
14	(<i>S</i>)-3	-67.3	-0.230
15	(<i>R</i>)-1	+4.59	+0.377
16	(<i>S</i>)-2	-0.41	~0

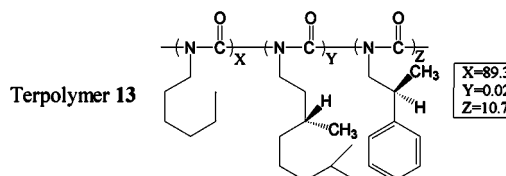
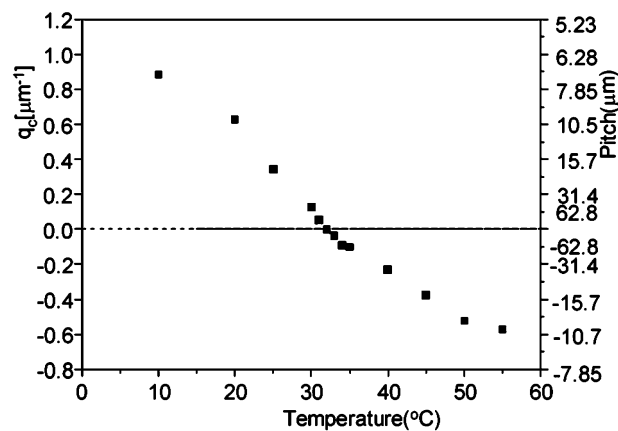
^a HTP, helical twisting power, determined by doping the urea into a 40 wt % solution of poly(*n*-hexyl isocyanate) in toluene and measuring the pitch from the fingerprint texture at 30 °C in a 1-mm-thick glass cell. HTP = $1/rxp$, where r is the enantiomeric excess of the starting material, x is equal to weight of urea/(weight of urea + weight of poly(*n*-hexyl isocyanate)), and p is the resulting pitch value in micrometers. The sign of the cholesteric pitch values is determined from the circular dichroism spectra.

the HTP of the urea appended with the chiral group of **3** and of opposite sign. Because the two competitive groups in the series **6** copolymer are present in nearly equal proportions (Table 1), the result on the comparison of the two ureas noted above (Table 2), if translatable to the properties of the series **6** copolymer, would lead to a right-handed cholesteric when poly(*n*-hexyl isocyanate) is doped with the series **6** copolymer, which is the observed twist sense as determined by CD measurements of the planar texture.⁴⁹ Following this view of the experimental results, the cholesteric properties of the liquid crystal doped with the series **6** copolymer are oblivious to any change of backbone helical sense of the series **6** copolymer which is shown to be taking place in the dilute solution measurements (Figure 1). The cholesteric twist sense is rather responding to the competition between the two chiral side-chain groups.

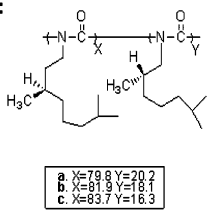
Forming the Lyotropic Liquid Crystal Directly from the Helical-Switching Polymers. Using the helical-switching polymer directly as the mesogen would likely decrease the pitch compared to using the helical-switching polymer as a dopant, because every macromolecule in the solution would now be contributing to the cholesteric liquid crystal properties. A smaller pitch would likely speed the response of the liquid crystal to temperature changes; perhaps small enough pitch values could be attained to allow reflection of visible light.³

Driven by these expectations, we synthesized⁵³ a series of polymers that switch helical sense as a function of temperature in dilute solution and were of appropriate molecular weight and polydispersity to be used to form the liquid crystal directly.⁴⁷ When the switching polymers are used as dopants, the molecular weight characteristic is less critical.

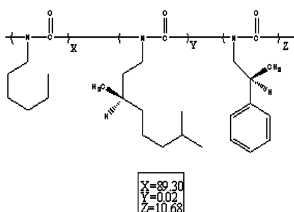
Figure 9 presents the liquid crystal pitch as a function of temperature for terpolymer **13**, which is closely related to the terpolymer studied as a dopant reported in Figure 7. Comparison of Figures 7a and 9 demonstrates the strong tightening of the

**Figure 9.** Temperature dependence of the pitch and pitch wavenumber, q_c [measured from the fingerprint texture in a 1-mm-path glass cell], of terpolymer **13** dissolved in toluene to make a 40 wt % solution.**Table 3.** Comparisons among Four Different Polyisocyanates Used To Form Liquid Crystals in Concentrated Solution^a

a, b, c:



d:



liquid crystal	chemical structure of the mesogen	T_c1/T_c2 (°C)	S1	S2	S_{T_c}
A	a	0/-25	5.018	-0.0349	-143.8
B	b	25/-5	4.894	-0.0359	-136.3
C	c	45/25	4.902	-0.0373	-109.7
D	d	20/32	5.855	-0.0451	-129.8

^a Liquid crystal A, 40 wt % of **a** in toluene; liquid crystal B, 40 wt % of **b** in toluene; liquid crystal C, 40 wt % of **c** in toluene; liquid crystal D, 40 wt % of **d** in toluene. T_c1 , optical switch temperature (°C) in dilute solution in toluene; T_c2 , optical switch temperature (°C) in the lyotropic liquid crystal matrix. S1, slope of curve of $[\alpha]_D$ vs temperature (degree/L·dL·g·°C) near T_c1 in dilute solution in toluene; S2, slope of curve of q_c vs temperature ($\mu\text{m}^{-1}\cdot^\circ\text{C}^{-1}$) near T_c2 in the liquid crystal matrix; S_{T_c} , $(d[\alpha]_D/dT)_{T_c}/(dq_c/dT)_{T_c}$.

pitch arising from using the helical-switching polymer directly as the mesogen. In addition, studies of the CD spectra of the planar texture, as for the doped system (Figure 7a), demonstrate that the sense of the cholesteric helix is opposite to the sense of the helix for the mesogenic terpolymer **13**.

In a parallel fashion, several series **5** copolymers, which were studied as dopants previously (Table 1), were used directly to form the lyotropic liquid crystal, also with very large reductions in the pitch. These results can be summarized by comparison of the data in Table 3 with those in Table 1. Whereas in Table 1 the change of optical activity in dilute solution as a function of temperature near T_c divided by the change in pitch wavenumber as a function of temperature, S_{T_c} , which measures the sensitivity of the change in cholesteric pitch properties to the

(53) Okamoto, Y.; Nagamura, Y.; Hatada, K.; Khatri, C.; Green, M. M. *Macromolecules* **1992**, *25*, 5536. Other approaches are available to control molecular weight and polydispersity in the polyisocyanates. See: Patten, T. E.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 5065. Shin, Y. D.; Kim, S. Y.; Ahn, J. H.; Lee, J. S. *Macromolecules* **2001**, *34*, 2408.

change in helical sense ratio of the component polymers, is a very large number, the comparable number in Table 3 is far smaller. Using the helical-switching polymer directly as the mesogenic entity leads to a far greater sensitivity of the cholesteric twisting to the helical sense changes in the polymers responsible for that twisting.

An interesting difference is seen in the liquid crystals formed from doping poly(*n*-hexyl isocyanate) (Figure 7, Table 1) compared to using the helical-switching polymer directly as the mesogen (Figure 9, Table 3). In the doped systems, the T_c in dilute solution is close to the T_c observed in the liquid crystal, whereas when the helical-switching polymer is used directly as the mesogen, as shown in Table 3, the liquid crystal T_c value can differ significantly from the T_c observed in dilute solution.

In dilute solution, because the optical activity is overwhelmingly determined by the helical backbone, the observed T_c is close to the temperature at which the left- and right-handed helical senses of the polymer are equally populated. However, as we have seen above in the discussions concerned with using the ureas as dopants (Table 2), the side-chain chirality can play a role in the liquid crystal properties. The “concentration” of the side chains in the undoped systems (Figure 9, Table 3) is far higher than in the doped systems, making a role for the side chains likely in the differences observed in T_c between the dilute solution and the liquid crystal. In qualitative terms, because the helical twisting powers of the chiral side groups are unbalanced (Table 2), it follows that when the left- and right-handed helices of the backbone are equally populated, as revealed by the dilute solution T_c , the pitch would not go to infinity (q_c would not reach zero). The ratio of helical senses within the polymer would have to change away from the 1/1 state, requiring a deviation from the dilute solution T_c to compensate for the contribution of the chiral side group to the cholesteric twisting as observed experimentally.

As we expected, the steeper slope for the pitch change with temperature (Table 3 compared to Table 1) is found to correspond to a faster response of the cholesteric pitch properties with temperature change. In the doped systems (Figure 7, Table 1), the change in pitch in the planar texture with temperature is very slow on a laboratory time scale, so that there is a delay of hours or even days in the change of the liquid crystal pitch following temperature changes. In contrast, when the helical-switching polymer is used as the mesogen, the pitch change in the planar texture occurs as quickly as the temperature can be changed.⁵⁴

In addition to the increased response speed with temperature change, the smaller pitch attained when the helical-switching polymer was used directly as the mesogen (Figure 7, Table 1) translates into reflection of visible light at temperatures far removed from T_c . This effect, which is further enhanced when the concentration of the lyotropic solution is increased to 50 wt %, is shown in Figure 10. When the pitch reaches dimensions corresponding to visible wavelengths, light of this wavelength, modulated by the index of refraction, is reflected from the planar texture.³ For the liquid crystal T_c at 32 °C shown in Figure 10a, the liquid crystal in the temperature range from about –25 to –60 °C exhibits variable reflected colors in the wavelength range from about 600 to 400 nm.

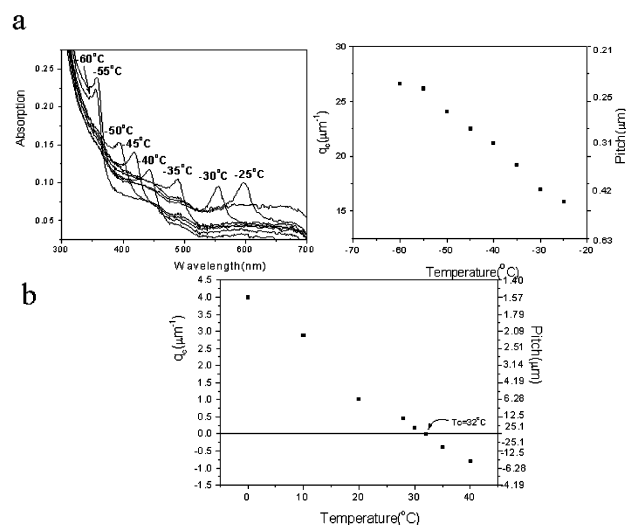


Figure 10. Reflection band and pitch wavenumber, q_c , as a function of temperature from a 50 wt % solution of terpolymer **13** in toluene. (a) Reflection band [measured in a 100- μm -path water-jacketed quartz cell at low temperature] and the corresponding pitch wavenumber [calculated from wavelength of reflective band by correction of refractive index] as a function of temperature at temperatures far from T_c in the planar texture. (b) Pitch wavenumber, q_c [measured from the fingerprint texture in a 1-mm-thick glass cell], as a function of temperature at temperatures near T_c .

Although commercial devices are available that allow temperature measurements using the reflected colors of liquid crystals, such thermotropic liquid crystals are formed from empirically discovered mixtures of liquid crystal materials and are bound by the temperature-dependent phase boundaries of such liquid crystals. For the lyotropic liquid crystals based on the helical-switching polymers discussed here, such a relationship between temperature and reflected colors can be tuned by choosing differing values of T_c via changing composition of the competing chiral groups, as discussed throughout this work. In addition, as noted above,⁴⁵ there will be no theoretical limit on the temperature range studied because of the absence of a temperature-dependent phase boundary for lyotropic liquid crystals formed from stiff polymers.⁵⁵

Figure 10 shows not only the pitch changes at temperatures far removed from T_c (Figure 10a), which are then responsible for the color reflections, but also the pitch changes around T_c (Figure 10b). The latter pitch changes, in bracketing the nematic phase where the pitch is infinite, open an opportunity for still another manner of correlating temperature changes to a rationally tunable liquid crystal property.

When the pitch, P , of a cholesteric liquid crystal in the planar texture is large compared to the wavelength, λ , of the probing light, there are two important limiting regimes to be considered, depending on how the pitch compares with the length parameter $2\lambda/\delta n$, where δn is the birefringence of the nematic phase corresponding to an infinite pitch of the cholesteric.³

For pitches greater than the wavelength but much smaller than $2\lambda/\delta n$, the cholesteric exhibits an optical rotation, ρ , in degrees, given by

$$\rho = 90(\delta n)^2 Pl/\lambda^2 \quad (6)$$

where l is the path length of the sample.³ In this well-known “pure rotation” regime, the rotatory power is proportional to

(54) Precise measurements on the speed of this change in pitch will be made in collaboration with Professor P. J. Collings of Swathmore College.

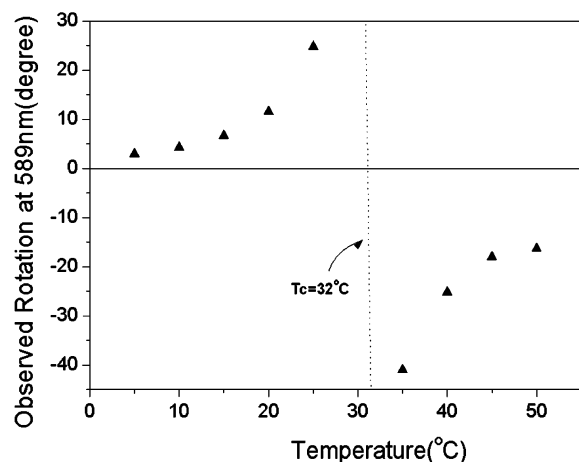


Figure 11. Observed optical rotation [measured from the planar texture in a 100 mm path water-jacketed quartz cell] as a function of temperature at 589 nm for a 40 wt % solution of terpolymer **13** in toluene.

the pitch and has the same sign as the pitch.⁵⁶ The optical rotation data presented in Figure 10 are well-fit to eq 6 using the pitch data presented in Figure 9, and with $\delta n \approx 0.01$, in which case $2\lambda/\delta n \approx 120 \mu\text{m}$. For pitches much larger than $2\lambda/\delta n$, a cholesteric liquid crystal exhibits “adiabatic following”, in which the plane of polarization of the incident light remains parallel to the local director of the helical cholesteric as the light propagates through the sample.⁵⁷ This regime is the basis of twisted liquid crystal displays and applies to our samples in the vicinity of the compensation temperature T_c , as is shown in Figure 11 in the optical activity changes occurring just above and below 32 °C.

At precisely T_c , the pitch becomes infinite, and the polarization of the incident light entering the nematic with plane of polarization parallel to the nematic director remains unchanged after the light has passed through the sample. Measuring optical rotations in samples as thick as ours (100 μm) in this regime, however, is extremely difficult because the plane of polarization is changing very rapidly as a function of temperature.⁵⁸ In addition, the cholesteric goes through an intermediate regime when the pitch is comparable to $2\lambda/\delta n$, in which the light becomes elliptically polarized with a rapidly changing major axis as a function of pitch.⁵⁹

The observed rotations of the plane of polarized light shown in Figure 11 as the temperature approaches T_c are large enough (for example, the observed rotation of 40° in Figure 11 corresponds to an $[\alpha]_D$ of 40 000°) that we were able to place the 100- μm -path-length cell between cross polarizers and easily observe, with the naked eye, the light from a laser pointer growing brighter as the temperature increased from below T_c to then extinguish at T_c . As the temperature further increases, the light quickly grows to maximum brightness and then dims again as the temperature increases above T_c . Rotation of the

second polarizer would reveal if the temperature is above or below T_c , because the sense of rotation in the pure rotation regime, as shown above, is opposite on either side of T_c .

Following the nature of the polymeric material discussed in this work, these correlated changes in light intensity with temperature (Figure 11) can be made to occur at any temperature over a wide temperature range, as demonstrated by the variation in T_c values shown in Figure 5.

These ideas of chiral conflict may be applied to any helical array subject to the general characteristics of the model helical polymer discussed in this work.^{26,27}

Summary

Randomly distributing structurally different enantiomers as pendants to a helical polymer, in which the helical senses form interconverting blocks, allows a correlation to be made between the composition of the enantiomers and the temperature at which the left and right helical senses of the polymer become equally populated, T_c . The system can be theoretically described by a variation of the same quenched random field one-dimensional Ising model used to understand the majority rule concept in the experiment in which the competing chiral groups are enantiomers of each other. Variation of the chemical characteristics of the competing chiral pendants, and variation of their macromolecular and solvent environment, yields insight into the nature of the chiral forces at work in choosing helical sense and its temperature dependence.

The helical-switching polymers were first incorporated as chiral dopants in a lyotropic liquid crystal formed by poly(*n*-hexyl isocyanate) and then used as the mesogenic entities themselves in forming the lyotropic liquid crystal. This allowed translation of the macromolecular helical properties to the supramolecular helical properties of the resulting cholesteric liquid crystal. Change of temperature, therefore, allowed changing between cholesteric states of opposite twist sense, with the liquid crystal passing through the nematic state formed near the temperature at which the macromolecular helical senses were equally populated. In this manner, temperatures far removed from T_c allowed pitch values to be reached that corresponded to reflection of visible light, while studies at temperatures near T_c showed very large observed rotations, so large in fact as to allow observation of temperature changes with the naked eye using crossed polarizers in real time.

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Supporting Information Available: Experimental Section (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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