Mechanism of the Transformation of a Stiff Polymer Lyotropic Nematic Liquid Crystal to the Cholesteric State by Dopant-Mediated Chiral Information Transfer

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Abstract: In this work the lyotropic liquid crystal nematic state of poly(*n*-hexyl isocyanate) (PHIC) was converted to the cholesteric state by doping with a variety of chiral small molecules and with optically active polyisocyanates. Circular dichroism experiments in dilute isotropic PHIC solutions show that several of the small molecules used as dopants in the liquid crystal work cause an excess of one helical sense in the otherwise helically dynamically racemic PHIC. Both the helical sense and excess of this sense in dilute solution correlate to the cholesteric sense and twisting power of the same dopants in the concentrated PHIC liquid crystal solutions. The experimental results are consistent with a mechanism of cholesteric formation in which the chiral dopants displace slightly the otherwise equal population of the dynamically interconvertable mirror helical senses of the PHIC, which is then further amplified by the liquid crystal matrix. Direct evidence for the amplification of the intrinsic helical sense excess of the polyisocyanate by the liquid crystal state could be demonstrated by comparing the cholesteric properties of systems doped with polyisocyanates in which the ratio of the mirror helical senses of the dopants in two compared experiments are identical but in one experiment the helical senses could interconvert and in a separate experiment could not interconvert. The amplification mechanism is driven by the reduction in population of the mobile kinked helical reversals which likely act as "bad neighbors" to the local liquid crystal organization.

Introduction

The interplay between chirality and the liquid crystalline state is a subject of great interest from both the theoretical and the technological points of view.[1] Display technology based on thermotropic cholesteric and smectic C* liquid crystals is a well-established demonstration of the importance of chirality in the liquid crystal area.[2] From the first liquid crystal observed which was incidentally chiral, this area of study has generated a huge patent and journal literature, which has overwhelmingly focused on thermotropic liquid crystals. In the lyotropic polymer liquid crystal area we often encounter cholesteric states formed by chiral polypeptides,[3] polysaccharides and their derivatives,[4]

DNA,[5] chiral micellar systems,[6] and guanylic nucleotides[7] although one notes the interesting exception of Tobacco Mosaic Virus which forms a nematic lyotropic state. Early studies of Robinson[8] on lyotropic solutions of poly(γ-benzyl L-glutamate) (PBLG) yielded the first careful studies of cholesteric pitch and a precise correlation between experimental observations and theories of the extraordinary optical properties of the cholesteric state.[3] In PBLG the cholesteric lyotropic state arises from the chirality of the polymer which is known to take a fully right-handed helix.[9] There have been few studies on the lyotropic polymer liquid crystals to parallel the chiral doping experiments in thermotropic liquid crystals simply because most lyotropic polymer systems are intrinsically chiral and therefore form cholesteric states directly. In the nematic lyotropic micellar area, which exists in a narrow region of the phase diagram,[10] some limited number of studies on chiral doping have been carried out.[6]

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Table 1. Helical Twisting Power of Various Chiral Dopants

| dopant | in toluene solution of PHIC[a] | | in PCB[b] | in isotropic solution |
	w^c	$\beta_M/\mu m^{-1}$	$\beta_M/\mu m^{-1}$	$[\theta]_{257\ nm}/C_{dope}{}^d$
BN-1	0.30	-0.48 ± 0.02 (-0.46 ± 0.02)	$+85 \pm 4$	
BN-2	0.30	0.00 (0.00)		
BN-3	0.30	($+0.69 \pm 0.03$)	$+80 \pm 3$	
BN-4	0.32	$+0.22 \pm 0.02$ ($+0.57 \pm 0.04$)	$+79 \pm 4$	
cholesterol	0.30	$+0.32 \pm 0.01$	-5.6 ± 0.5	
cholesteryl chloride	0.29	$+0.28 \pm 0.02$	-3.5 ± 0.4	-64
cholesteryl propionate	0.30	$+0.20 \pm 0.01$	-9.7 ± 0.7	-62
cholesteryl nonanoate	0.23	$+0.027 \pm 0.001$	-9.6 ± 0.6	not detectable
cholestane	0.27	-0.055 ± 0.002		11
MPC	0.30	-0.26 ± 0.01		
camphor	0.28	$+0.062 \pm 0.002$		-24
HIC/NIC (85/15)	0.30	1.2 ± 0.1		
	0.40	1.7 ± 0.1		

[a] MW 73 000 (MW 133 000). [b] 4-Cyano 4′-*n*-pentylbiphenyl. [c] PHIC weight fraction in toluene solution. [d] Molar ellipticity of the PHIC monomer unit per unit molar concentration of the dopant in the units of deg/cm·M².

There is one very well studied class of macromolecules, the polyisocyanates, which consist of equal populations of dynamically interconverting left- and right-handed helical forms which yield a lyotropic nematic state in which both the local and dimensional characteristics of the chain and the conditions for forming the nematic liquid crystal phase are well understood and where the nematic state is stable over a wide concentration range in common solvents and is easily accessible.[11–14] In this polymer, as in the parallel work on PBLG, the cholesteric state has been carefully studied in the situation where the chain has been forced by intrinsically chiral units to take a single helical sense.[15] Here we have taken the unusual opportunity offered by poly(*n*-hexyl isocyanate) PHIC to obtain information on the use of chiral dopants, including bridged binaphthyls used for doping of thermotropic liquid crystals[16,17] and optically active polyisocyanates with interconverting and noninterconverting helical sense blocks,[18,19] to convert the lyotropic nematic state to its cholesteric counterpart. The results of this study support the hypothesis that the dopants act to favor one helical sense of the PHIC, which is further amplified by conformational changes imposed by the liquid crystal field, and which is then responsible for the formation of the cholesteric state. Parallel mechanisms are known in both thermotropic and micellar liquid crystals.

Results and Discussion

Small Molecule Dopants. According to the convention of doping experiments of thermotropic liquid crystals,[16,20] we express the helical twisting power (HTP) of a chiral dopant in

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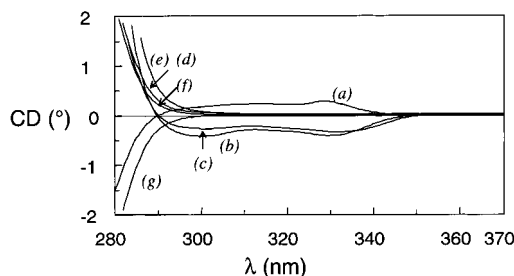(20) Finkelmann, H.; Stegemeyer, H. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 1302.

Figure 1. CD spectra (elipticity vs λ) of 10 μm planar samples of PHIC doped with BN-1 (a), BN-3 (b), BN-4 (c), cholesterol (d), cholesteryl chloride (e), cholesteryl propionate (f), and MPC (g). The optical rotations of these same samples are reported in Table 2.

terms of

$$\beta_M = 1/(PXr) \qquad (1)$$

where P is the cholesteric pitch, X is the mole fraction of the dopant in the mixture of the matrix PHIC and the dopant ((mole of the dopant)/[(mole of the PHIC monomer units) + (mole of the dopant)]), and r is the enantiomeric purity of the dopant. The sign of P and β_M is defined to be positive for the right-handed cholesteric helix, and vice versa.

Table 1 summarizes the results of β_M for all the small molecule dopants studied in toluene solutions of poly(*n*-hexyl isocyanate) (PHIC) at 30 °C.[21] The cholesteric pitch was measured by polarizing microscopy of the cholesteric solutions in a nonplanar texture where the classic fingerprint pattern appears, and the sign of β_M was determined by circular dichroism (CD) and optical rotation dispersion (ORD) of the solutions in a planar texture following standard procedures in this field.[22–24] The CD and optical rotation data for some of the investigated dopants are shown in Figure 1 and Table 2.

From the data in Table 1 we see the generally smaller HTP values in the lyotropic liquid crystal formed from PHIC than

(21) Except in the case of cholestane and camphor which were studied at $X = 0.15$ because of their very small helical twisting powers, all other dopants were used at $X = 0.03$, which is in the range where the relationship between X and inverse pitch is known to be linear. See ref 15 above.
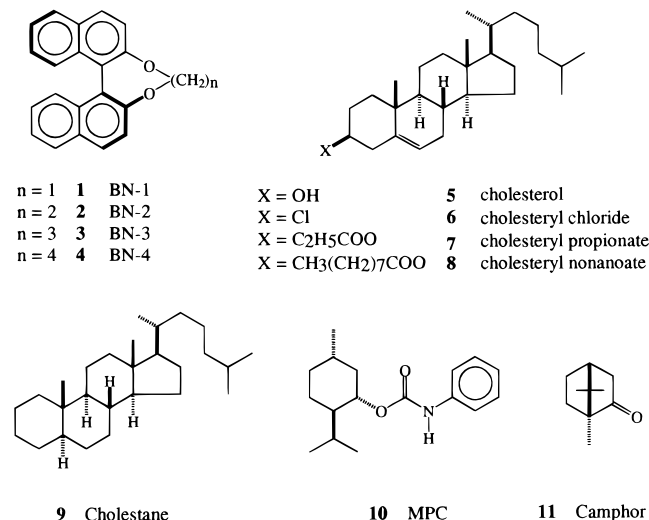
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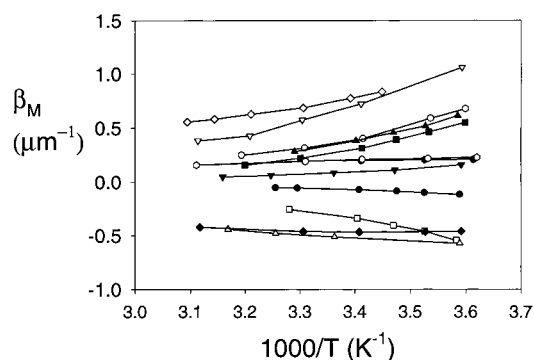
Table 2.   Optical Rotations Φ (rad/cm) of 10 μm Planar Samples of PHIC Doped with BN-1 (a), BN-3 (b), BN-4 (c), Cholesterol (d), Cholesteryl Chloride (e), Cholesteryl Propionate (f), and MPC (g)[a]

λ (nm)	(a)	(b)	(c)	(d)	(e)	(f)	(g)
589					26.8		−46.77
577	−27.3	48.7	372.2	209.0	27.0	26.2	−48.00
546	−24.3	56.9	413.5	220.7	29.5	31.5	−59.52
435	−49.0	121.0	771.3	277.9	72.5	63.6	−95.82
405	−61.7	133.0	941.7	300.9		80.1	−198.97

[a] The CD spectra of these samples are reported in Figure 1.

Chart 1

n = 1   **1**   BN-1
n = 2   **2**   BN-2
n = 3   **3**   BN-3
n = 4   **4**   BN-4

X = OH   **5**   cholesterol
X = Cl   **6**   cholesteryl chloride
X = C₂H₅COO   **7**   cholesteryl propionate
X = CH₃(CH₂)₇COO **8**   cholesteryl nonanoate

9   Cholestane   **10**   MPC   **11**   Camphor

what is known for the same dopants in thermotropic liquid crystals. Table 1 also shows that the HTP values of the bridged binaphthyls **1**−**4** (Chart 1) are comparable to those of the other small molecular chiral dopants in the lyotropic solvent. This is in contrast with the strong HTP values of these dopants in the thermotropic nematogen 4-cyano-4′-*n*-pentylbiphenyl (PCB) (cf. the fourth column in Table 1). Gottarelli et al.[16,25] interpreted the strong HTP values of the bridged binaphthyls in the mesogen PCB by a mechanism in which the bridged binaphthyls are involved in a steric interaction with the biphenyl groups of the mesogen, introducing a preference for one of the mirror twist states. The findings in Table 1 suggest another mechanism is at work here which is supported by the finding of an inversion of the cholesteric sense of the lyotropic liquid crystal with a change in the number of methylene units in the binaphthyl bridge and by the temperature dependence of the cholesteric data (Figure 2). The data in Figure 2 are also in conflict with the idea[15] that the temperature dependence of the pitch data would correlate to the structures of the dopants and act thereby as a means to quantify the chirality[26] of these materials. This approach would not have been possible with thermotropic liquid crystals because of the temperature dependence of their phase boundary.[1]

So how do the dopants affect the transformation of the lyotropic nematic phase of PHIC to the cholesteric? It is known that the helical sense ratio of the dynamically racemic PHIC can be displaced from unity by chiral solvation, a phenomenon which has been used as a new way to measure preferential solvation.[27] To test if the chiral dopants are acting directly on the PHIC as the source of the cholesteric twisting is virtually

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Figure 2. Helical twisting powers, β_M, vs 1000/T for toluene solutions of PHIC, MW 73 000 (30%), doped with BN-1 (open triangle up), BN-4 (filled square), cholesterol (open circle), cholesteryl chloride (filled triangle up), cholesteryl propionate (filled hexagon), cholesteryl nonanoate (open hexagon), cholestane (filled circle), MPC (open square), and camphor (filled triangle down) and for toluene solutions of PHIC, MW 133 000 (30%), doped with BN-1 (filled diamond), BN-3 (open diamond), and BN-4 (open trangle down).
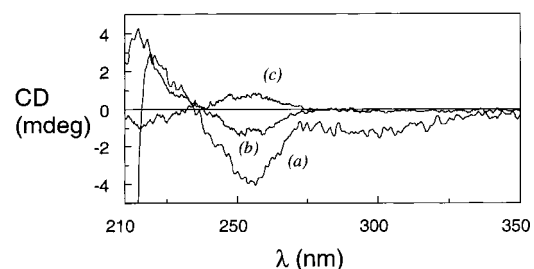
Figure 3. CD spectra (elipticity vs λ) of isotropic dilute solutions of PHIC (2.5 mg/mL) dissolved in hexane containing 50 mg/mL camphor (a), 50 mg/mL cholesteryl chroride (b), and 150 mg/mL cholestane (c) in a 0.01 cm quartz cell.

impossible in the cholesteric state since the strong CD of the mesogenic state precludes direct chiral optical probing of the PHIC macromolecule. Second best, we can study dilute solutions of PHIC with the same chiral dopants as used in the liquid crystal experiments. This can only be done with a few select dopants since among the chiral dopants in Table 1 only cholesteryl chloride, cholesteryl propionate, cholesteryl nanoate, cholestane, and camphor are both transparent at the wavelength necessary to measure the circular dichroism signal associated with the helical character of the PHIC, about 250 nm, and soluble in an appropriate UV transparent solvent, hexane, for this experiment.

Figure 3 shows examples of the CD spectra for isotropic dilute solutions of PHIC dissolved in *n*-hexane containing three of the chiral dopants, camphor, cholesteryl chloride, and cholestane. The signs of the CD bands near 257 nm, for all the dopants studied in this way, and their intensities expressed in molar ellipticity are presented in Table 1. When this CD band is negative, predicted to correspond to an excess of the left-handed helix sense of the PHIC,[28] the cholesteric sense, when using these dopants, is positive or right-handed and vice versa for the dopant with the positive CD band. In addition, the intensities of the CD bands in the dilute solution experiments (Table 1) are approximately correlated with the HTP values; that is higher molar ellipticity valued dopants in dilute isotropic solution correspond to higher HTP values in the liquid crystal state

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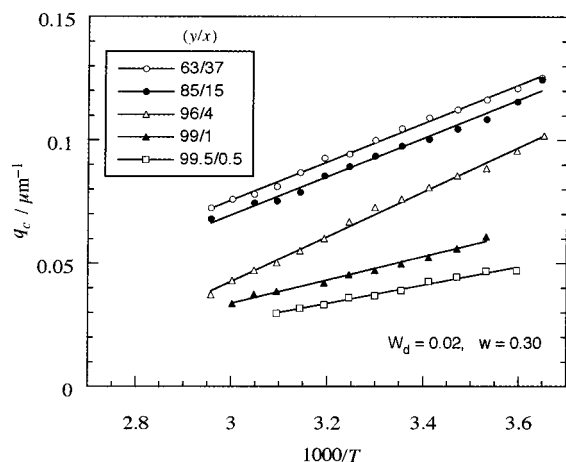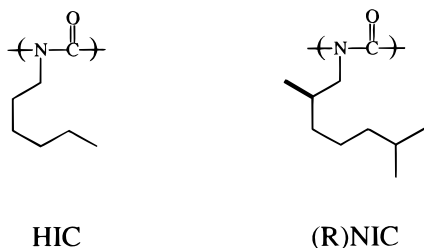
Figure 4. Absolute values of cholesteric wavenumber, q_c, vs $1000/T$ for toluene solutions of PHIC doped with 2% of the specified with y = HIC and x = NIC.

Chart 2

including the case of cholesteryl nonanoate where the HTP is very small and the CD band is undetectable.

The liquid crystal experiment is conducted in toluene while that in dilute solution takes place in hexane, and the concentration of the PHIC in the liquid crystal is far higher than that of the chiral dopant while in the isotropic CD experiment the opposite is the case. The latter is necessary in order to detect any CD signal which, as it is, corresponds to only a tiny excess of one helical sense of the PHIC.[27] Although these facts make it surprising that the experiments in the isotropic phase could be connected to the observations in the liquid crystal, the sign and intensity correlation shown in Table 1 strongly indicate a role for the effect of the dopant on the helical sense population in the PHIC mesogen. Is it possible that the effect of the chiral dopants on the ratio of the left- and right-handed helical senses of the PHIC mesogen in the isotropic solutions (as shown by the sign and intensity of the CD bands for the helical backbone chromophore (Table 1)) may be further magnified in the liquid crystal state? The experiments to be discussed below bear on this point.

Optical Active Polyisocyanate Dopants. Figure 4 shows the plot of the cholesteric wavenumber q_c (equal to 2π divided by the pitch) vs $1000/T$ for toluene solutions of PHIC doped with random copolymers constructed of hexyl isocyanate units and varying proportions of the chiral nonracemic unit (*R*)-2,6-dimethylheptyl isocyanate ((*R*)-NIC) (Chart 2). In these sergeants-and-soldiers copolymers the helical sense ratio within each chain, from studies in isotropic dilute solution, is known to vary in a highly nonlinear manner with the proportion of the chiral comonomer within the chain.[18,19] In the copolymers, HIC/(*R*)-NIC(*y/x*), HIC corresponds to hexyl isocyanate and (*R*)-NIC to (*R*)-2,6-dimethylheptyl isocyanate with an HIC composition (mol %) of y and an (*R*)-NIC composition of $x = 100 - y$. In Figure 4, the total polymer concentration including

therefore the mesogenic PHIC and the chiral dopant copolymer described above was fixed to 0.30 (w, the weight fraction in toluene) and the ratio of the weights of the dopant to the PHIC, W_d, was fixed at 0.02. The q_c value of the doped PHIC solutions increases (more tightly wound cholesteric) with increasing (*R*)-NIC composition x in the dopant copolymer as is expected.

If we take into account only the chirality coming from the chiral monomer units in the dopant copolymers, then X in eq 1 would be equated to the moles of the chiral monomer units in the copolyisocyanate divided by the moles of the total HIC monomer units in PHIC and in the copolyisocyanate. Under this assumption the plot of q_c vs X constructed from the data shown in Figure 4 is nonlinear and from the initial slope yields an inappropriately high value of the helical twisting power. This result comes from the fact that the HTP in fact arises not only from the chiral NIC units in the chain but also from the fact that these chiral units are cooperatively influencing large domains of the helical backbone, and therefore the achiral units, to take an excess of one helical sense. In such a case, we must choose the mole fraction of all monomer units on the optically active copolyisocyanate chain as X ((mole of the monomer units in the optically active copolyisocyanate)/[(mole of the monomer units in PHIC) + (mole of the monomer units in the optically active copolyisocyanate)]), and the excess of one helical sense of the chiral dopant copolyisocyanate by r in eq 1. The latter can be related to the mole optical rotation [m] (per the monomer unit) of the chiral copolymer in dilute solution by

$$r = [m]/[m]_m \qquad (2)$$

where [m]$_m$ is the molar optical rotation of the polyisocyanate with a single-handed helical conformation. As we will see below though this equation can be shown not to hold under certain circumstances.

In the situation where x, the proportion of the chiral comonomer, is about 15%, the chiral influence is adequate to force the entire chain to take a single helical sense while when x is smaller than this value any single chain will consist of domains of left- and right-handed regions as discussed above.[18,19] This allows us to construct an experiment to explore the possibility that the helical sense ratio of the polyisocyanates in dilute solution may not reflect the helical sense ratio in the liquid crystal state and therefore to ask if there is a further amplification of the chiral influence on the chain in the liquid crystal over that in the isotropic state. To carry this out, we first synthesized the HIC/(*S*)-NIC copolymer with x equals 15%. This copolyisocyanate will take a fully one-handed helical sense opposite to that of the HIC/(*R*)-NIC copolyisocyanate discussed above. We then mixed these enantiomeric copolyisocyanates in various proportions to yield various dilute solution optical activities representing varying ratios of the left- and right-handed helical chains. In these mixtures the ratios of the helical senses are invariant since they arise from mixtures of chains which are fully one or the other handed. Alternatively, the dilute solution optical activities of the copolyisocyanates HIC/(*R*)-NIC with variable values of x below 4% correspond to single chains with dynamically interconvertable left- and right-handed helical sense domains within each chain.

In Figure 5, we show the results of using the polyisocyanates discussed above as dopants to transform the nematic to cholesteric phase of the lyotropic PHIC liquid crystal. The ordinate q_c is the cholesteric wavenumber while the abscissa, Xr, is the product of the mole fraction of the dopant and the ratio of the helical senses as determined by the dilute solution optical activity (eq 2). Here the enantiomer mixtures of the
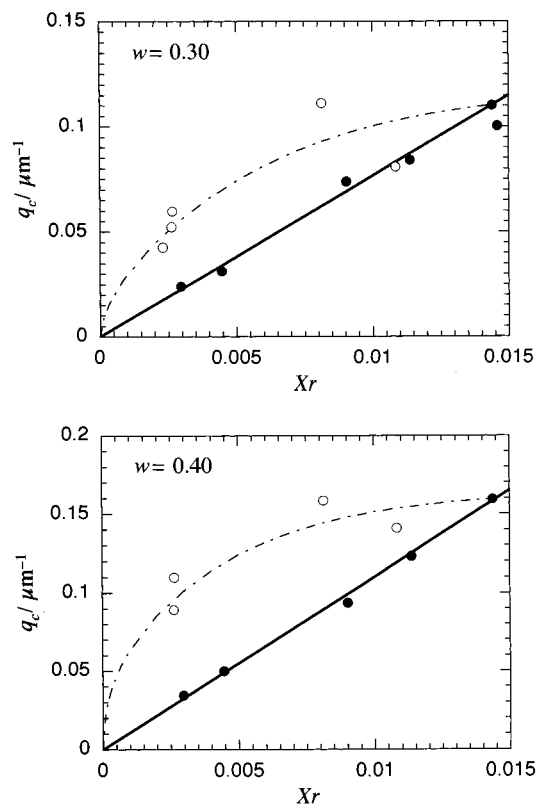
Figure 5. q_c vs Xr for the chiral−achiral random copolyisocyanates: filled circles, mixtures of HIC/(R)-NIC (85/15) and HIC/(S)-NIC (85/15); unfilled circles, copolymers HIC/(R)-NIC (y/x) with x equal to or less than 0.04; r, calculated from eq 2 with $[m]_m = -706$ (the value for HIC/NIC (85/15) at −20 °C at 589 nm). (a) and (b) show the results for total polymer concentrations of 30% and 40%, $w = 0.30$ and 0.40, respectively.

random copolymers, HIC/(R)-NIC (85/15) and HIC/(S)-NIC (85/15), that is where each chain is fully of one helical sense, are designated by the filled circles. The total polymer concentration w is fixed to 0.30 and 0.40 as designated, and the total dopant fraction W_d is 0.02. The filled circles show a beautiful correlation with eq 1 in following an excellent straight line, which importantly passes through zero. From the slope of this straight line, the HTP for this dopant was estimated to be 1.2 μm^{-1} for $w = 0.30$ and 1.75 μm^{-1} for $w = 0.40$. The former value is larger than the β_M of the small molecular chiral dopants for $w \approx 0.3$ listed in Table 1. This is in accordance with the rule obtained in the thermotropic liquid crystal area that twisting powers are higher when the chiral molecule dopant has a structure similar to the nematic mesogenic phase.[16]

The unfilled circles in Figure 5 represent the data for the HIC/(R)-NIC copolymers with x equal to or less than 4%, that is where each chain has interconverting domains of left- and right-handed helical segments. Within the scatter, and including the points for the highest Xr value for the filled circles (corresponding to a single helical sense using either of the enantiomers of the HIC/NIC (85/15)), and for Xr equals zero (corresponding to a 50/50 mixture of the enantiomers of the HIC/NIC (85/15) which must be nematic), the unfilled circles trace lines deviating upward from the straight lines formed by the filled circles, with this deviation strongly increasing in the more concentrated PHIC liquid crystal; that is, w equals 0.40 over 0.30.

The results in Figure 5 demonstrate that the copolyisocyanate dopants in which the left- and right-handed helices are interconvertible within a single chain are, for the same helical sense ratio in dilute solution, capable of enforcing a smaller pitch on

the liquid crystal formed from the PHIC than for the dopants in which the helices are fixed within a single chain. In addition, this factor is stronger with increasing concentration of the lyotropic phase. Since a smaller pitch must be related to a higher ratio of one helical sense over the other in the dopant copolyisocyanate, as in fact the data for the filled circles in Figure 5 demonstrate, the results point to an increase in this helical sense ratio in the liquid crystal phase over that measured for the dopant in dilute solution.[29]

It must follow from the results above that in the dopant polyisocyanates where the left- and right-handed regions are interconvertible within single chains (open circles in Figure 5) the population of helical reversals,[19,30] which limit the cooperativity, must be reduced in the liquid crystal state compared to that in the isotropic solution. In a possibly interesting parallel, a reduction in the population of the helical reversal state compared to that in isotropic solution in the polyisocyanates has also been observed in the formation of thermally reversible gels from these polymers. The kinked helical reversal[28] was hypothesized to interfere with the known close parallel packing of the aggregate leading to the gel,[31] and this factor may be at work as well in the liquid crystals studied here. This general question of the effect of liquid crystals on conformational states which are "bad neighbors" to the liquid crystal arrangement in polymer liquid crystals is of longstanding and still current interest.[32,33] Along different lines, an interesting "ferrochirality" proposal has been made for the exclusion of helical reversals in the polyisocyanates under certain conditions where homochiral chain−chain interactions are favored over heterochiral interactions.[34] The work discussed below on the absolute sense of the cholesteric twisting in the lyotropic PHIC doped with the optically active polyisocyanates may bear on this latter possibility.

From the chiral optical measurements of the planar texture of the liquid crystal[22−24] the cholesteric sense was determined to be right-handed for PHIC lyotropic solutions doped with HIC/(R)-NIC of $x = 1$, 2.3, 15, as well as 100 (i.e., PNIC homopolymer). The CD spectra are displayed in Figure 6, and the corresponding optical rotations are reported in Table 3. All the polyisocyanates dopants noted above and (R)-PNIC itself have been studied in dilute isotropic solution and uniformly exhibit a negative CD band at near to 257 nm for the highest wavelength chromophore of the helical chromophore.[19] The absolute sense of the helix in these macromolecules has been assigned to be left-handed on the basis of forced field calculations.[28] In the current work we have extended the measurements made on the planar textures formed from the lyotropic phases of PHIC doped with the polyisocyanates to remeasure the

(28) Lifson, S.; Felder, C. E.; Green, M. M. *Macromolecules* **1992**, *25*, 4142.

(29) Similar nonlinear relations between dilute solution optical activities and q_c have also been observed for PHIC liquid crystal solutions doped with a series of copolymers composed of the HIC and (R)-1-deuterio-*n*-hexyl isocyanate with the effect considerably larger at w equals 0.40 compared to w equals 0.30. Doctoral thesis of Gu-Hong, Osaka University, Japan, 1997, pp 132−133. For discussion of the deuterated polyisocyanates and leading references see ref 19 above. Unpublished work on the copolymers of (R)-1-deuterio-*n*-hexyl isocyanate and *n*-hexyl isocyanate may be found in the doctoral thesis of C. Andreola, Polytechnic University, 1991.

(30) Okamoto, N.; Mukaida, F.; Gu, H.; Nakamura, Y.; Sato, T.; Teramoto, A.; Green, M. M.; Andreola, C., Peterson, N. C.; Lifson, S. *Macromolecules* **1996**, *29*, 2878.

(31) Guenet, J.-M.; Jeon, H. S.; Khatri, C. A.; Jha, S. K. Balsara, N. P.; Green, M. M.; Brulet, A.; Thierry, A. *Macromolecules* **1997**, *30*, 4590.

(32) Khokhlov, A. R.; Semenov, A. N. *Macromolcules* **1984**, *17*, 2678.

(33) Gupta, A. M.; Edwards, S. F. *Polymer*, **1993**, *34*, 3112.

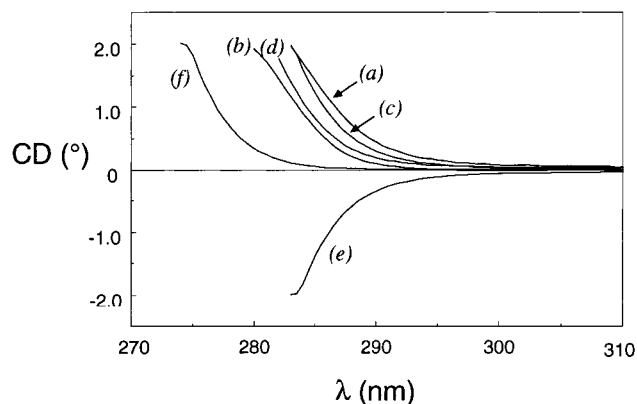(34) Baumgarten, J. L. *Macromol. Rapid Commun.* **1994**, *15*, 175 and subsequent papers by this author.

Figure 6. CD spectra (elipticity vs λ) of 10 μm planar samples of PHIC doped with copolymers HIC/(R)-NIC [99/1 (a), 97.7/2.3 (b), and 85/15 (c)], with pure (R)-PNIC (d), and with HIC/(S)-NIC (85/15) (e). The optical rotations of these samples are reported in Table 3. The CD spectrum of an approximately planar sample of pure (R)-PNIC (f) is also reported.

Table 3. Optical Rotations Φ (rad/cm) of 10 μm Planar Samples of PHIC Doped with Copolymers HIC/(R)-NIC [99/1 (a), 97.7/2.3 (b), and 85/15 (c)], with Pure (R)-PNIC (d), and with HIC/(S)-NIC (85/15) (e)[a]

λ (nm)	(a)	(b)	(c)	(d)	(e)
589	70.0	75.2	66.0	6.6	−71.4
577	90.0	97.7	82.0	27.8	−85.8
546	340.0	369.5	238.9	79.0	−270.6
435	360.0	518.6	289.1	122.0	−388.9

[a] The CD spectra of these samples are reported in Figure 6.

cholesteric sense of the liquid crystal formed from (R)-PNIC alone and found it also to be right-handed in toluene at room-temperature based on the absorption CD band. This is in contrast to prior work[15] which had assigned the sense of the cholesteric to be left-handed based on the ORD of the planar texture.[35]

We know from the chiral optical measurements (Figure 6, Table 3) of the planar textures of the cholesteric states formed by using the polyisocyanate dopants HIC/(R)-NIC on the lyotropic phase of PHIC (Figures 4 and 5), that the cholesteric sense is uniformly right-handed. We know similarly (see above) that the sense of the cholesteric state formed entirely from (R)-PNIC is also right-handed. If the various polyisocyanate dopants act to cause an increase of one of the helical senses of the PHIC which forms the liquid crystal phase, as would be consistent with what appears to be the mechanism in the small molecule dopants (see the discussion above and Table 1), that excess would have to be the same sense as that of the dopants themselves, left-handed.[19,28] This follows from the fact that the purely left-handed (R)-PNIC forms a right-handed cholesteric state, the same as for the doped systems. Therefore, if there is a transfer of chiral information from the polyisocyanate dopants to the PHIC in the liquid crystal it must be driven by a lower energy for homochiral over heterochiral helical interactions.[36] This conclusion is independent of the absolute assignment of helix sense to the optically active polyisocyanates or for that matter of the absolute twist sense of the cholesteric states but

depends only on the fact that (R)-PNIC and the HIC/(R)-NIC copolymers have the same helical sense, as demonstrated by the dilute solution CD spectra, and that the cholesteric senses formed by (R)-PNIC and by PHIC doped with HIC/(R)-NIC are the same. One of the prerequisites for "ferrochirality" in the polyisocyanates appears to be met.[34]

The experimental results discussed above demonstrate that the dopant copolymer chains are chirally perturbed in the cholesteric phases (Figure 5) and suggest that the helical conformation of the matrix PHIC chain, racemic in dilute solution, may be also affected by the cholesteric state to take an excess of one helical sense. If the latter is correct,[37] one has to consider interactions not only between the dopant and the PHIC chains but also between matrix PHIC chains to attempt to understand the HTP in PHIC lyotropic solutions. Although there exists experimental evidence suggesting the importance of chiral perturbations to nonracemic states of the mesogen molecules in thermotropic liquid crystals,[38] theoretical work concerned with the cholesteric state in thermotropic liquid crystals has not generally taken this into account.[20,39]

If the key role in the conversion of the lyotropic phase of PHIC to the cholesteric state arises from the properties of this polymer in allowing the formation in the liquid crystal of the nonracemic macromolecule with an excess of one helical sense we could expect that a lyotropic nematic phase formed from a polymer which does not allow the formation of nonracemic conformations could not be doped to the cholesteric state. This may be tested by forming the lyotropic nematic phase from a racemic mixture of PBLG and PBDG since here the helical senses of these polypeptides are fixed as right- and left-handed respectively by the overwhelming chiral influence of the enantiomeric amino acid units; that is, each chain is fully of a single helical sense.[9] We therefore examined three small molecule dopants (cholesteryl chloride, bridged binaphthyl-4, and menthylphenyl carbamate) added up to their solubility limits to the PBLG/PBDG nematic phase in three different solvents (chloroform, dichloroethane, and dioxane−dichloromethane mixture (1/4)) and failed to form a measurable cholesteric state (the nematic microscopic pattern was maintained). This experiment demonstrates that the chiral dipole−quadrupole dispersion interaction between polymer and dopant molecules in the Goossens theory is not strong enough to induce cholesteric ordering in this lyotropic system, as is reasonable from its distance dependence, and supports the mechanism proposed for the formation of the cholesteric state in PHIC.[40]

(35) In the current work the ORD spectrum of the planar texture was found to be too weak to separate the intrinsic optical activity of the (R)-PNIC, which is negative, from the cholesteric effect. This is the likely source of the error in the earlier cholesteric sense assignment. There had been an attempt to correlate the now known incorrect sense of the cholesteric phase of (R)-PNIC and its temperature dependence with the absolute sense of the polymer helical backbone using screw fitting arguments but without a certain conclusion.[19]

(36) The question of homochiral vs heterochiral packing of the helical states of isotactic vinyl-based polymers, e.g., polypropylene, is of great interest. For a leading reference see: Meille, S. V.; Allegra, G. *Macromolecules* **1995**, *28*, 7764. This is also related to crystallization of enantiomeric mixtures: Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, Resolutions*; Wiley: New York, 1981.

(37) An experiment to test this was carried out without a conclusion. The CD spectrum of (R)-PNIC was taken in dilute solution followed by addition of as much PHIC as the UV extinction in the region of the 257 nm band would allow. The CD band intensity, within the limits of our detection, did not change, therefore offering no evidence, under these isotropic conditions, that the (R)-PNIC was affecting the helical sense ratio of the added PHIC.

(38) There are some indications of the deracemization of thermotropic nematogens in doped cholesteric phases. Gottarelli et al.[16] proposed a chiral twisted conformation of biphenyl-type nematogens resulting from the interaction with binaphthyl dopants. This hypothesis was supported by optical rotation measurements in isotropic solutions. See: Gottarelli, G; Osipov, M. A.; Spada, G. P. *J. Phys. Chem.* **1991**, *95*, 3879.

(39) Hanson, H.; Dekker: A. J.; van der Woude, F. *J. Chem. Phys.* **1975**, *62*, 1941; Goossens, W. J. A. *Mol. Cryst. Liq. Cryst.* **1971**, *12*, 237; Stegemeyer, H.; Finkelmann, H. *Chem. Phys. Lett.* **1973**, *23*, 227.

Conclusions

The investigation of the cholesteric pitch properties of the lyotropic liquid crystal of poly(*n*-hexyl isocyanate) (PHIC) by doping with optically active small molecules and chiral−achiral random copolyisocyanates leads to a proposed mechanism in which the chiral dopants displace slightly the otherwise equal population of the mirror helical senses of poly(*n*-hexyl isocyanate), leading to the formation of the cholesteric helical structure through chiral interactions between the matrix polyisocyanate chains. This mechanism finds parallels in the action of chiral dopants in both thermotropic and miceller lyotropic liquid crystals. In thermotropic liquid crystals experimental data suggest that high values of the HTP are often connected to the presence in the dopant of structural elements which are capable of transferring chiral information to the mesogenic molecules.[16,25,38,41,42] In aqueous miceller nematics the mechanism of cholesteric induction is likely connected to the chiral distortion of the anisometric micelle.[43] Very hydrophilic dopants display small twisting powers.

The proposed mechanism in the polyisocyanates is supported by a convincing experimental result in which polyisocyanates with unequal proportions of interconverting left and right helical senses within a single chain exhibit a nonlinear relationship between their dilute solution optical activities and their cholesteric properties, and give rise to larger cholesteric wavenumbers than polyisocyanates in which identical dilute solution ratios of the left- and right-handed helices are fixed in separate chains. In the latter the dilute solution optical activities and cholesteric properties are related in a linear manner. It could therefore be predicted that helical polymers which form lyotropic nematic phases in which the polymer structure does not allow changes in the helical ratios would yield chirally doped cholesteric phases only with very high pitch. This is supported by our inability to observe a cholesteric liquid crystal via chiral doping of lyotropic nematic solutions composed of a racemic mixture of PBLG and PBDG although the cholesteric state is classically known for liquid crystals formed from either of these enantiomers.[44]

The results of the work presented here on the polyisocyanates and the relationship of this work to the thermotropic and miceller systems is supported by theoretical work[45] which though does not exclude the contribution of chiral dispersion interactions.[20,39] Such dispersion forces though and other close contact mechanisms for transfer of chiral information where chiral conformational perturbations of the mesogen molecules are not involved are likely to be more important in thermotropic systems where the interactions among the mesogenic molecules are short range.[46]

(40) There is a report of the conversion of an aromatic polyamide of the Kevlar type which forms a lyotropic cholesteric phase in sulfuric acid on chiral doping. Our conclusion would suggest that the dopant in this case induces a chiral twisting, which is possible in the structure of this macromolecule. Panar, M.; Beste, L. F. *Macromolecules* **1977**, *10*, 1401.

(41) Gottarelli, G.; Spada, G. P.; Hansen, H. J. *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 377.

(42) Gottarelli, G.; Hansen, H. J.; Spada, G. P.; Weber, R. H. *Helv. Chim. Acta* **1987**, *70*, 430. See also: Huck, N. P. M.; Jager, W. F.; de Lange, B.; Feringa, B. L. *Science* **1996**, *273*, 1686.

(43) Spada, G. P., Gottarelli, G., Samori, B., Bustamante, C. J.; Wells, K. S., Liquid Crystals, **1988**, *3*, 101; Pape, M., Hiltrop, K. *Mol. Cryst. Liq. Cryst.* **1997**, *307*, 155 and references therein.

(44) Uematsu, Y.; Uematsu, I. *Mesomorphic Order in Polymers*; ACS Symposium Series, No. 74; American Chemical Society: Washington, DC, 1978; p 136.

(45) See Sato et al. in ref 4 above.

Table 4. Molecular Weight and Optical Rotation of Optically Active Copolyisocyanates

copolymers	molecular weight/10^4	$[\alpha]^{20}_D$ in hexane
HIC/NIC (63/37)	142[a]	−527
HIC/NIC (85/15)	190[a]	−523
HIC/NIC (96/4)	66.6[a]	−434
HIC/NIC (97.7/2.3)	145[b]	−365
HIC/NIC (99/1)		−165
HIC/NIC (99.5/0.5)	110[c]	−151
HIC/NIC (99.9/0.1)		−57
mixtures of HIC/(*R*)-NIC (85/15) and HIC/(*S*)-NIC (85/15)		
60/40		−108
67/33		−162
80/20		−328
90/10		−413

[a] Determined by light scattering. [b] Determined by viscometry. [c] Data taken from ref 48.

Experimental Section

Materials. Poly(*n*-hexylisocyanate) was prepared and polymerized to the fairly narrow range of molecular weights necessary for this work using the very useful titanium-based method developed by Novak.[47] The polymerized samples were divided into several molecular weight fractions by fractional precipitation with benzene as the solvent and as the precipitant. Two of the fractionated samples were used to prepare the liquid crystal solutions. The weight average molecular weights of the two samples were determined to be 73 000 and 133 000 by gel permeation chromatography with a calibration curve constructed using standard PHIC samples of known molecular weights.

All the optically active copolyisocyanates used in this work were synthesized by M. P. Reidy as part of his doctoral thesis at the Polytechnic University.[48] Some of these materials were divided into three fractions by fractional precipitation and the middle fractions were used as dopants; the molecular weights of the samples were determined by light scattering or viscometry (cf. Table 4). The other materials were doped as they stand.

(+)-Menthylphenyl carbamate **10** was prepared by the reaction of (+)-menthol (purchased from Aldrich Chemical Co.) with phenyl isocyanate as described in the literature.[15] Cholesteryl chloride **6**, cholesterol **5**, cholestane **9**, and camphor **11** were purchased from Aldrich Chemical Co. and used as received. Cholesteryl propionate **7** and cholesteryl nonanoate **8** were purchased from Sigma and also used as received. The binaphthalene derivatives **1**−**4** were synthesized following literature procedures.[49]

Preparation of Liquid Crystal Solutions. In most doping experiments, the PHIC sample with molecular weight 73 000 was used, and the sample with molecular weight 133 000 was only used to obtain data shown in Table 1 and Figure 2. In the text, the PHIC sample with the molecular weight of 73 000 is referred to simply as PHIC without specifying the molecular weight. All the solutions used in the doping experiments were made at 30% and 40% w/w (weight of total polymer/[(weight of total polymer) + (weight of toluene)]).

Cholesteric solutions for all the small molecule doped systems were prepared by first dissolving the PHIC in toluene so as to obtain about 0.5 cm³ of solution in a 2 mL glass stoppered test tube and stirring with a magnetic stirrer. This solution was left for 1 day and the small molecule dope was then added as a solid, which dissolved within an

(46) Kuball, H.-G.; Bruning, H.; Muller, T.; Turk, O., Schonhofer, A. *J. Mater. Chem.* **1995**, *5*, 2167. Kuball, H.-G.; Muller, Th.; Bruning, H.; Schonhoffer, A. *Mol. Cryst. Liq. Cryst.* **1995**, *261*, 205. Kuball, H.-G.; Bruning, H., Chirality, **1997**, *9*, 407. Kuball, H.-G.; Weiss, B.; Beck, A. K.; Seebach, D. *Helv. Chim. Acta* **1997**, *80*, 2507.

(47) Patten, T. E.; Novak, B. M. *Macromolecules* **1993**, *26*, 436 and references therein to earlier work.

(48) Synthesis of all the copolyisocyanates used is described in the doctoral thesis of M. P. Reidy, Polytechnic University, 1991. See also ref 18 above.

(49) Simpson, J. E.; Daub, G. H.; Hayes, F. N. *J. Org. Chem.* **1973**, *38*, 1771. van Es, J. J. G. S.; Biemans, H. A. M.; Meijer, E. W. *Tetrahedron: Asymmetry* **1997**, *8*, 1825.

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hour at most, and the solution stirred for one more day to obtain a viscous, clear, and homogeneous solution.

Cholesteric solutions for the copolymer doped systems were prepared by first making a mixture of the polymer (PHIC) with 2% of the chiral HIC/NIC copolymer or in the case of Figure 5 with 2% of the mixture of copolymers (weight of copolymer/weight of PHIC) in benzene. After the elimination of the benzene by freeze-drying, all the mixtures were dissolved in toluene (30% and 40% w/w) and stirred in a 2 mL stoppered glass test tube for 2 days. In a typical procedure, 4 mg of the copolymer and 200 mg of PHIC were weighed into two 20 mL vials, and then 5.0−6.0 mL of benzene was added to each vial to dissolve the polymers. After the polymers were completely dissolved, accurately weighed benzene solutions were mixed to give a relative weight ratio of the copolymer to PHIC of exactly 2%. The mixture was stirred vigorously to dissolve completely the added PHIC polymer. The resulting solution was then subjected to freeze-drying for at least 3 days to obtain a mixture of copolymer−PHIC with 2% of copolymer. The appropriate amount of the sample prepared by this method was weighed into a 2 mL stoppered glass test tube, and an exact amount of toluene was added to obtain a solution of a certain concentration (30% or 40%). This glass test tube was fixed onto the plate of a magnetic stirrer, and stirred for a couple of days until the polymer was entirely dissolved; the resulting solution is clear and in a homogeneous state.

Optical rotation measurements on dilute solutions of the copolymers and of the mixtures of the 85/15 copolymers (for Figure 5) were carried out in hexane at 20 °C. The values of $[\alpha]_D$ obtained are shown in Table 4 below.

Cholesteric Pitch Measurements. Each of the prepared solutions mentioned above was transferred into a measuring cell with a 2.0 mL microsyringe, and the neck of the cell was flame sealed. The measuring cell was 1−2 mm in thickness with a neck to accept the sample as previously described.[15] The cells were kept at room temperature until a good fingerprint pattern was obtained (usually 1 day). The 40% solutions with the mixture of 85/15 copolymers were heated at 40 °C for a few hours before the pitch was measured.

Fingerprint patterns showing the classic retardation lines for the doped PHIC solutions in toluene were observed using a NIKON OPTIPHOT2-POL polarizing microscope, at different temperatures using a homemade copper jacket with circulating water as described elsewhere.[15] The microscopic images were saved by using a CCD color video camera and a camera adapter connected to a Power Macintosh 7500/100 computer. The measurements of the fingerprint spacing, which is equal to half of the cholesteric pitch, were made with NIH Image 1.6 version software.

Optical Rotation and CD Measurements. The optical rotation measurements for dilute PHIC solutions doped with small molecule dopants were made on a JASCO DIP-370 or a Perkin−Elmer 141 polarimeter. The corresponding CD experiments were made on a JASCO J 710 dichrograph with a 0.01 cm quartz cell. The test solutions were prepared by dissolving PHIC in hexane (2.5 mg/mL) and adding a certain amount of the small dopant (50 mg/mL for compounds **6**−**8** and **11**, and 150 mg/mL for compound **9**).

The measurements for the planar texture cholesteric solutions were made with the JASCO J710 dichrograph for recording the CD spectra, and with a JASCO DIP-370 polarimeter for measuring the optical rotation at different wavelengths. Sandwich quartz cells with a 0.001 cm path length, sealed with wax, were used for both measurements. Observation through a polarizing microscope revealed almost no anisotropy; i.e., the object between crossed polars was dark for almost the entire contents of the cell. We measured the optical activity of the planar texture of dopants at different wavelengths and the CD spectra continuously.

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