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Polyisocyanates and the Interplay of Experiment and Theory in the Formation of Lyotropic Cholesteric States

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ABSTRACT: We have made the first observations of the lyotropic cholesteric liquid crystal state of polyisocyanates, in which a synthetically controlled range of the dynamic excesses of one helical sense offer new opportunities for study in the area. In poly((*R*)-2,6-dimethylheptyl isocyanate) we have generated the cholesteric lyotropic state and studied the pitch as a function of solvent, temperature, and concentration. These data were broken down into entropic, S_q, and enthalpic, H_q, terms and were compared to theoretical predictions. The data for the polyisocyanate were compared to those already known for poly(γ-benzyl L-glutamate) and schizophyllan. For all three helical polymers, the sign of S_q agrees with Straley's screw model, allowing an absolute assignment of macromolecular helical sense from liquid crystal properties. The nematic phase of the dynamically racemic poly(*n*-hexyl isocyanate) was doped with a derivative of a steroid and of menthol, and the resulting cholesteric pitch was studied as a function of temperature and dope concentration. The failure to fit these data to theoretical expectations applicable to intrinsically chiral polymers may be due to a sensitivity of the helix sense ratio of the macromolecule to the chiral characteristics of the cholesteric phase.

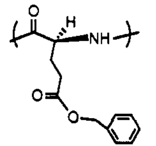
Introduction

Friedel understood that the first observed liquid crystal, the cholesteric phase,[1-3] was a variation of the nematic state with a twisting between the cholesteric molecules leading to an overall supramolecular helical arrangement. In this state, which is well described in the literature,[4,5] observation normal to the nematic layer structure of the molecules sees a continuously evolving helix with a pitch *P*. The connection though between molecular chirality and the cholesteric liquid crystal state was not made clear until many years after the first nineteenth century observations on an ester of cholesterol.[6,7] Goossens,[8] whose work was directed to the properties of small-molecule liquid crystals, i.e., thermotropic states formed from pure undissolved substances, was the first to successfully account for this connection. He ascribed this to an enthalpic chiral dispersion force.

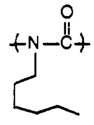
In the area of polymer liquid crystals, the theoretical development[9,10] followed different lines and focused primarily but not entirely[10] on the shape of the polymers and on the translational entropy gain associated with the formation of the liquid crystal phase. Although this theoretical work[9,10] was not directed to the source of cholesteric ordering, Straley[11] later showed that purely entropic arguments, based on the hard-core fitting of screws, could be used to explain the development of a lyotropic cholesteric phase.

Thus a theoretical dichotomy existed with enthalpic terms responsible for the formation of the thermotropic low molar mass liquid crystals[4,12] and their cholesteric twisting,[8] while entropic terms were held as the driving forces for the formation of the polymer lyotropic liquid crystal states[9,10] and their cholesteric properties.[11]

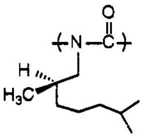
Chart I


1

poly(γ-benzyl-L-glutamate)


2

poly(n-hexyl isocyanate)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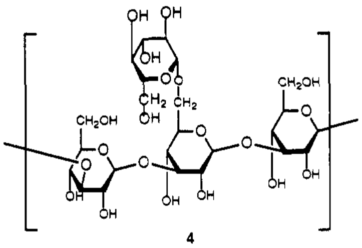
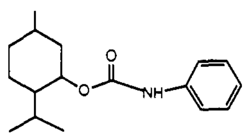
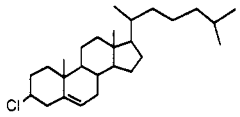
poly((R)-2,6-dimethylheptyl isocyanate)


4

single strand of triple helical schizophyllan


5

(+) menthyl phenylcarbamate


6

cholesteryl chloride

No theoretical approach was attempted to offer an explanation for the dependence of the cholesteric helix sense on solvent observed by Robinson[13] for the lyotropic liquid crystal state of poly(γ-benzyl L-glutamate) (1) (Chart I). Later, this experimental observation was connected to the dielectric properties of the solvent by Samulski and Samulski[14] using a dispersion force theory formulated in a different way from Goossens.[8] However, Kimura and his co-workers[15] later pointed out that only by combining energetic[8] and entropic terms[11] could one understand the equally mysterious inversion of helix sense with temperature observed by Uematsu and Uematsu[16] in the cho-

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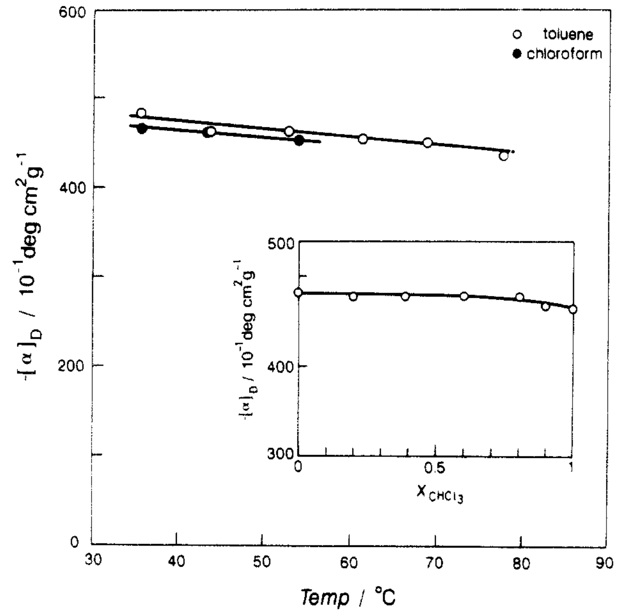

Figure 1. Specific optical rotation at the D-line vs temperature for poly((*R*)-2,6-dimethylheptyl isocyanate) (**3**) in pure toluene and chloroform and also the solvent dependence at 36 °C.

lesteric states of polyglutamates in various solvents.

Up to now experimental studies on lyotropic polymer cholesteric liquid crystals have been limited to the very few macromolecular systems which are available for such work.[16-24] Moreover, no quantitative comparisons with theory for the cholesteric liquid crystal state have been made except for poly(γ-benzyl L-glutamate) (**1**).[14,15] Since progress in this area has involved the interplay of experiment and theory, the small numbers of experimental models make it difficult to define the boundaries of understanding of the fundamental forces controlling the lyotropic cholesteric state formed by macromolecules.

In the work reported here we have taken advantage of our interests in the nematic properties of poly(*n*-hexyl isocyanate) (**2**)[25,26] and in the dilute solution properties of optically active polyisocyanates[27-31] to form, for the first time, the cholesteric state of polyisocyanates.

These polymers offer unique opportunities for the study of the lyotropic cholesteric liquid crystal state since the basic structure may be altered only slightly in its side-chain properties to produce variations in the helix sense excess (right- or left-handed) of these stiff helical macromolecules. In the work below we have studied the extreme situations of a polyisocyanate of a single helical sense (**3**) which forms the cholesteric state directly and as well a dynamically racemic polyisocyanate (**2**) which forms this state on doping with optically active molecules.

We have applied theoretical concepts to interpret the pitch properties of the cholesteric states of these polymers.

Experimental Results

Cholesteric State of Poly((*R*)-2,6-dimethylheptyl isocyanate) (3). Since we are reporting the temperature dependence of the pitch for poly((*R*)-2,6-dimethylheptyl isocyanate) in toluene and chloroform and in mixtures of the two, it becomes important to determine the stability of the main-chain helical conformation[31] in these solvents and over the temperature range of interest. The data in Figure 1 demonstrate that the change in optical activity at the sodium D-line is very small compared to the magnitude of the optical activity as a function of temperature and of solvent composition ($[\lambda]^{-1}$ d$[\lambda]$/dT = 0.0018 K^{-1}). Therefore, we can be assured that any temperature or solvent effects on the cholesteric property are not arising from significant conformational changes for this polymer (**3**).

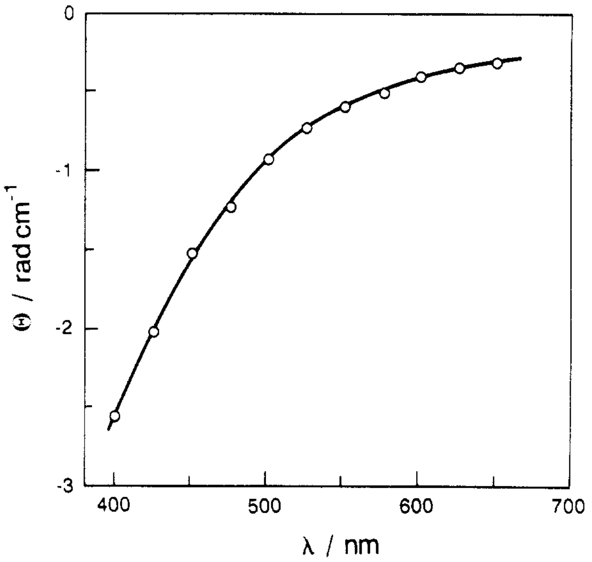

Figure 2. Optical rotatory dispersion of the approximate planar texture of poly((*R*)-2,6-dimethylheptyl isocyanate) in toluene at 36 °C (c = 0.23 g cm^{-3}).

The sense of the cholesteric helix, i.e., right- or left-handed, must be known for a full correlation to theory and for an absolute comparison among the lyotropic polymers discussed above. This information was obtained for poly((*R*)-2,6-dimethylheptyl isocyanate) (**3**) by preparing a very thin sample of the cholesteric phase in both toluene and chloroform so that the macromolecules are forced to have their long axes parallel to the cell boundary. This is known as a planar texture. In such an arrangement, the cholesteric liquid crystal has several unique optical properties. For example, it produces total reflection when circularly polarized light has the same sense and wavelength as the cholesteric helix (the Bragg reflection). On the other hand, if the light impinges normal to the cell wall of the cholesteric layer, it rotates the polarizing plane of linearly polarized light with a wavelength far shorter than $P/2$ but still longer than $P/2$ times the birefrengence of the cholesteric layer just like optically active materials. de Vries[32,33] showed that right-handed (left-handed) cholesterics produce a positive (negative) optical rotation and further that the absolute value of the optical rotation θ is in proportion to the cholesteric pitch P.

Figure 2 shows that a negative optical rotation is observed for a toluene solution of **3**. Negative optical rotations were also observed for two cholesteric solutions of **3** dissolved in chloroform and a mixture of toluene and chloroform with the mole fraction x_{CHCl_3} = 0.59. This means the cholesteric helix of **3** is left-handed in all these solvents.

In samples thicker than those necessary to observe the planar texture, an irregular texture is observed where in much of the sample the cholesteric helix axis can be parallel to the cell surface. In such an irregular texture, the pitch P of the cholesteric state can be measured either by direct observation in a polarizing microscope or by laser diffraction according to the Bragg equation.

In Figure 3 the cholesteric wavenumber, q_c ($=2\pi P$), is plotted against the inverse of absolute temperature for different concentrations c of poly((*R*)-2,6-dimethylheptyl isocyanate) (**3**) in toluene. We have assigned a negative sign to q_c in the tradition of previous work on **1**, when

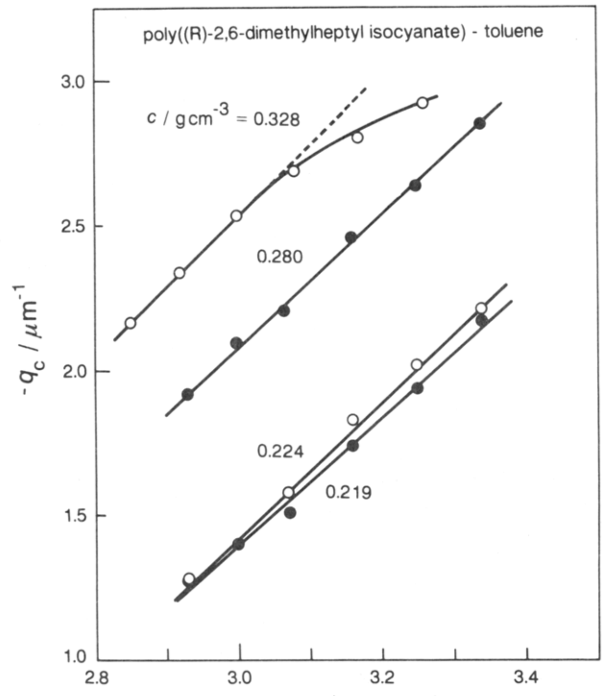

Figure 3. Cholesteric wavenumber, q_c, vs inverse temperature for poly((*R*)-2,6-dimethylheptyl isocyanate) (**3**) in toluene at various polymer concentrations shown.

right- and left-handed cholesteric states were designated by positive and negative pitch, respectively.[20] The data points for each concentration fit a straight line except for the highest concentration at the lowest temperature, where the system may be at the solubility limit. We obtained similar linear plots in a wide variety of solvents from the cholesteric data of **1** by Uematsu and co-workers[16–20] and for the cholesteric state of schizophyllan (**4**)[23] (cf. Figure 9).

Although the temperature range allowed to us by the solvent in this study (Figure 3) did not reveal any inversion of cholesteric helix sense as encountered in various solvents for the cholesteric state of **1**,[16–20] linear extrapolation of the lines in Figure 3 point to such an inversion at higher temperatures. This conclusion also follows for mixtures of toluene and chloroform shown in Figure 4. At constant temperature q_c strongly depends on the solvent composition and takes a minimum at a mole fraction x_{CHCl_3} around 0.6.

Cholesteric State of Poly(*n*-hexyl isocyanate) Doped with Optically Active Substances. Although doping of nematic to cholesteric phases is a common procedure for low molar mass mesogens,[34] there is only one nonquantitative example in a lyotropic polymer liquid crystal.[35] In our work concentrated solutions of poly(*n*-hexyl isocyanate) (**2**) in toluene are transformed from the nematic to the cholesteric state by doping with either (+)-menthylphenyl carbamate (**5**) or cholesteryl chloride (**6**). Figure 5 shows a polarizing micrograph of the cholesteric phase produced at 25 °C with a dopant mole fraction of **5** of 0.0277 for a polymer concentration of **2** of 0.28 g cm^{-3}. The spacing of the fringes of the fingerprint pattern defines the pitch of this sample and others similarly measured (see Experimental Section). The sign of the pitch (or q_c) was determined to be negative and positive for solutions doped with **5** and **6**, respectively, from optical rotation measurements similar to those in Figure 2.

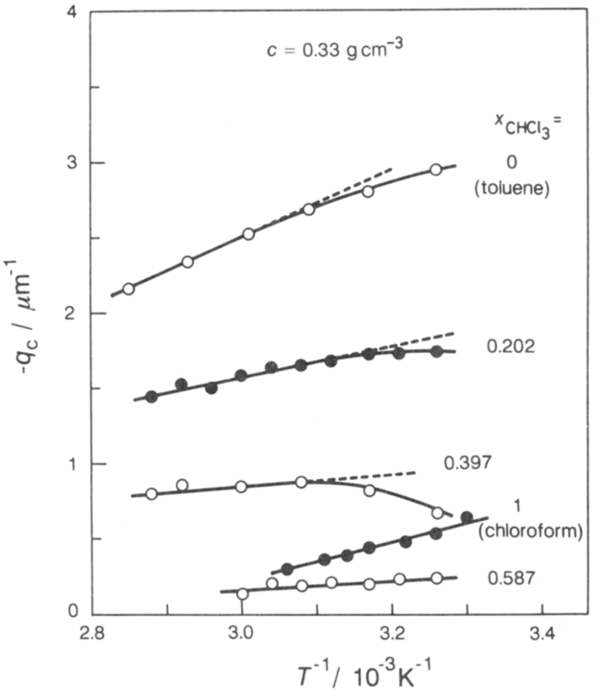

Figure 4. Temperature dependence of q_c for poly((*R*)-2,6-dimethylheptyl isocyanate) (**3**) in the mixed solvents toluene and chloroform at a fixed polymer concentration of 0.33 g cm^{-3}.

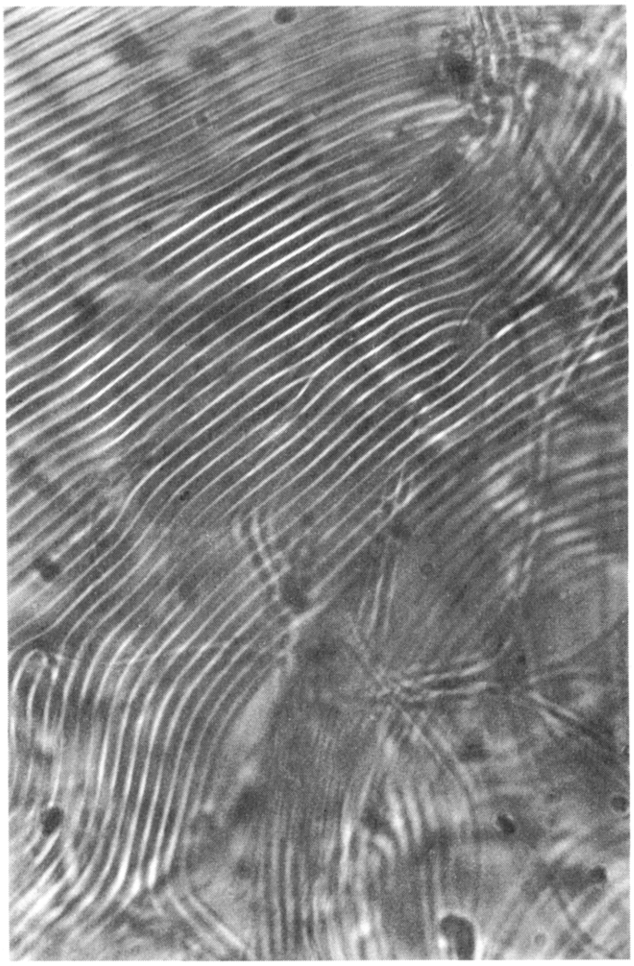

Figure 5. Polarizing micrograph of the cholesteric state of poly(*n*-hexyl isocyanate) in toluene doped with (+)-menthylphenyl carbamate at 25 °C (c = 0.28 g cm^{-3}; x_{MPC} = 0.0277).

These data are presented in two different ways in Figures 6 and 7. Figure 6 shows a plot of q_c against the concentration of dopant **5** while Figure 7 exhibits the dependence of q_c on the inverse temperature at concentrations of two dopants, **5** and **6**. In Figure 6 we see that

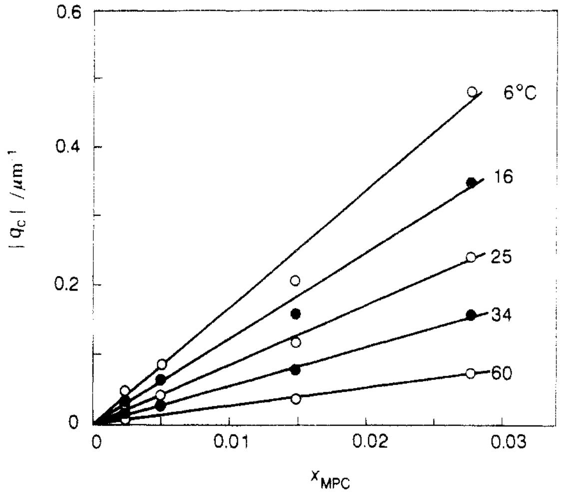

Figure 6. Dope concentration dependence of q_c at various temperatures for poly(n-hexyl isocyanate) (**2**) in toluene at a fixed polymer concentration of 0.28 g cm^{-3}.

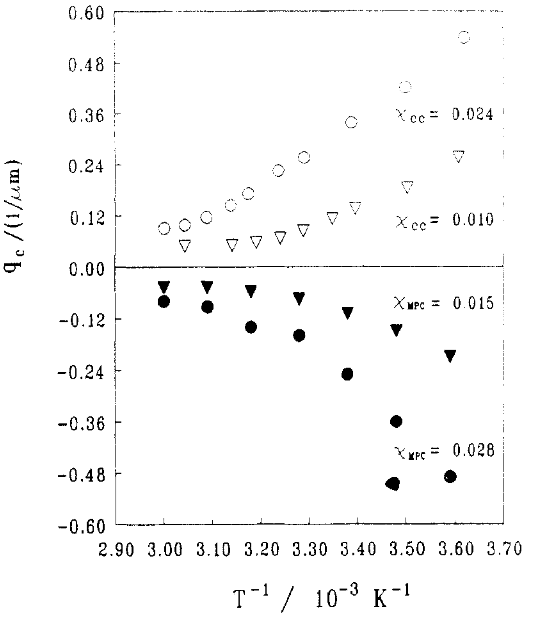

Figure 7. Temperature dependence of q_c for various dope concentrations of **5** and **6** for poly(n-hexyl isocyanate) (**2**) in toluene (c = 0.28 g cm^{-3}).

the plot is linear, in agreement with the results of many similar experiments with low molar mass liquid crystals.[34]

However, the temperature dependencies presented in Figure 7 are not linear in contrast to the results for **3** in the same solvent, toluene, shown in Figure 3. In this doped system high temperature leads asymptotically to the nematic state, i.e., $q_c = 0$.

Theoretical Results

Thermodynamic Analysis. The cholesteric liquid crystal state is specified by the cholesteric wavenumber q_c as well as the orientational order parameter. If the twist distortion of the cholesterics from the nematic state is sufficiently small, the expansion of the Gibbs free energy G in a power series of q_c can be truncated at the second-order terms, and we obtain

$$G = G_0 + (\partial G/\partial q_c)_0 q_c + (1/2)(\partial^2 G/\partial q_c^2)_0 q_c^2 \quad (1)$$

Here the free energy of the untwisted nematic state G_0 is designated by the subscript zero, which also informs us that the derivatives of G with respect to q_c are taken at $q_c = 0$. The derivative is taken at constant temperature and pressure. The first derivative $(\partial G/\partial q_c)_0$ represents the twisting force which induces the cholesteric helical structure. On the other hand, the second derivative term in eq 1 corresponds to an important property of nematic and cholesteric liquid crystals, the force which tends to restore the parallel relationship between the mesogenic molecules. The $(\partial^2 G/\partial q_c^2)_0$ term is designated the twist elastic constant usually denoted as K_{22}. An equivalent expression for G is used in the continuum theory for cholesterics.[4,5]

Since the free energy $G = H - TS$ given by eq 1 is a minimum at thermal equilibrium, q_c is given by

$$\begin{aligned} q_c &= -(\partial G/\partial q_c)_0/K_{22} \\ &= -[(\partial H/\partial q_c)_0 - (\partial S/\partial q_c)_0 T]/K_{22} \quad (2) \end{aligned}$$

From this equation, it can be said that q_c is determined from the balance between the enthalpic and entropic twisting forces and the elastic force opposing the twist distortion.

In order to discuss the temperature dependence of q_c, we have to specify the temperature dependence of the elastic constant K_{22}. In their molecular theories of lyotropic polymer liquid crystals, Straley[36] assumed that the elastic force against twist distortion in nematic and cholesteric states arises from the hard-core interaction between polymer molecules and is purely entropic. This assumption is supported by previous thermodynamic studies on solutions of poly(n-hexyl isocyanate) (**2**) in toluene and in dichloromethane,[25] or schizophyllan (**4**) in water,[23] and of **1** in dimethylformamide,[37] all of which showed that the osmotic pressure and isotropic liquid crystal phase boundary for these systems were controlled by hard-core, i.e., entropic interactions.

In the following discussion we adopt Straley's assumption,[36,38] which gives

$$K_{22} \equiv (\partial^2 G/\partial q_c^2)_0 = -(\partial^2 S/\partial q_c^2)_0 T \quad (3)$$

This and the following equations may not be applied to thermotropic liquid crystal systems where the enthalpic contribution to K_{22} cannot be neglected.[39]

Substitution of eq 3 into eq 2 yields an expression for q_c as a function of enthalpy, entropy, and T,

$$q_c = H_q/T + S_q \quad (4)$$

where H_q and S_q terms are defined as

$$H_q = (\partial H/\partial q_c)_0/(\partial^2 S/\partial q_c^2)_0 \quad (5)$$

and

$$S_q = -(\partial S/\partial q_c)_0/(\partial^2 S/\partial q_c^2)_0 \quad (6)$$

respectively. Thus it is seen that a simple thermodynamic argument for cholesterics predicts that a plot of q_c vs T^{-1}, over T ranges narrow enough so that the thermodynamic parameters are invariant, should be linear, yielding the values of S_q and H_q.

Since this thermodynamic analysis is developed[4] without regard to the molecular basis of the observation, its correlation with the experimental data does not furnish, by itself, insight into the molecular structural basis of the cholesteric properties. Below we have tried to connect molecular theories for the cholesteric liquid crystal state of solutions of chiral rods to the above thermodynamic analysis.

Correlation of the Thermodynamic Analysis with Molecular Theory. Kimura and his co-workers[15] formulated the Helmholtz free energy of rodlike polymer solutions in cholesteric states by statistical thermodynamics. The free energy was derived as a function of the variables of polymer concentration, the orientational order parameter Q, and the wavenumber q_c of the twist distortion. The polymer was assumed to be a threaded rod which has length L, hard-core diameter d, and thread height Δ. Although the phase boundaries of the liquid crystal are determined overwhelmingly by entropic forces, the intermolecular interactions responsible for the cholesteric twisting are hypothesized to arise from both hard-core interactions following Straley[11,36] and chiral dispersion forces following Goossens.[8] That is, the intermolecular potential was assumed to be $u_{ij} = \infty$ (when the hard cores of two polymers i and j overlap) or $u_{ij} = B(\mathbf{r}_{ij})(\mathbf{a}_i{\cdot}\mathbf{a}_j)(\mathbf{a}_i \times \mathbf{a}_j){\cdot}\mathbf{r}_{ij}/r_{ij}$ in the absence of such overlap. $B(\mathbf{r}_{ij})$ is a (pseudoscalar) coefficient of the chiral dispersion force acting between polymers i and j whose centers of mass are distant r_{ij}, and $\mathbf{a}_i$ and $\mathbf{a}_j$ are unit vectors parallel to the axes of the polymers i and j, respectively.

The molecular theory of Kimura and co-workers uses perturbation theory[40] and Cotter's scaled particle theory.[41] The elastic constants for the bend, splay, and twist distortions are purely entropic, as we assumed in eq 3. In addition, the theory is developed for a polymer rod and does not therefore consider any flexibility of the polymer.

Assuming reasonably that the molecular parameters L, d, and Δ are independent of temperature, the final results of this theory can be written in the form[42]

$$(\partial^2 S/\partial {q_c}^2)_{0,T,V} = (L/3\pi d^2)\phi k_B T \tag{7}$$

$$(\partial U/\partial q_c)_{0,T,V} = (8/3\pi^2 d^2)\phi^2 (Ld)^{-2} \int B(\mathbf{r}_{ij}) z \, \mathrm{d}\mathbf{r}_{ij} \tag{8}$$

$$(\partial S/\partial q_c)_{0,T,V} = (8/\pi^2 d^2)\phi(\lambda\Delta/d) f(\phi) k_B T \tag{9}$$

where ϕ is the volume fraction of the polymer, V and U the volume and internal energy of the system, respectively, and z the shortest distance between the two interacting polymers i and j; λ is a proportional constant of the order of unity, and $f(\phi)$, which comes from Cotter's scaled particle theory,[41] is defined by

$$f(\phi) = (1 - \phi/3)/(1 - \phi)^2 \tag{10}$$

The terms k_B and T have their usual meanings of the Boltzmann constant and absolute temperature.

In order to compare the theory of Kimura et al. with the thermodynamic parameters S_q and H_q, the quantities at constant volume (in eqs 7–9) must be converted to those at constant pressure.[43] Allowing reasonably that

$$\begin{gathered}(\partial U/\partial q_c)_{0,T,V} \cong (\partial H/\partial q_c)_{0,T,p} \\ (\partial S/\partial q_c)_{0,T,V} \cong (\partial S/\partial q_c)_{0,T,p} \\ (\partial^2 S/\partial {q_c}^2)_{0,T,V} \cong ((\partial^2 S/\partial {q_c}^2)_{0,T,p}\end{gathered} \tag{11}$$

the two terms S_q and H_q are expressed in terms of the molecular parameters as

$$S_q = -(24/\pi)\phi f(\phi)(\lambda\Delta/d)/L \tag{12}$$

$$H_q = (8\phi/\pi k_B L^3 d^2) \int B(\mathbf{r}) z \, \mathrm{d}\mathbf{r} \tag{13}$$

Therefore, we can conclude that the H_q and S_q terms arise respectively from a chiral dispersion force between polymers, and a translational entropy gain by a twisted relationship among the polymers which allows the closest penetration of the threaded hard cores.

Regarding the threaded hard-core interaction, Figure 8 is a reproduction of a figure from Straley's theoretical treatment of the lyotropic cholesteric state.[11] In this treatment Straley[11] attempted to extend Onsager's ideas on the nematic state[9] by pointing out that two screws may approach most closely in either a clockwise or counterclockwise relationship depending on their screw sense, leading to a smaller excluded volume for the twist state allowing closest approach.

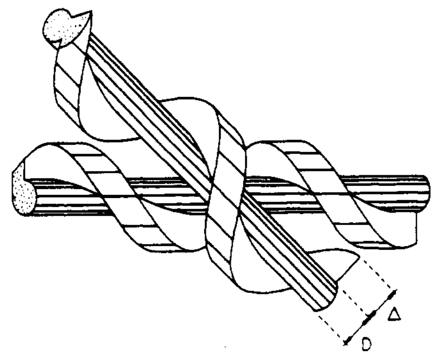

FIG. 3. Geometry of two threaded rods. The upper rod may approach the lower most closely if its principal axis is rotated clockwise with respect to the axis of the lower.

Figure 8. Figure 3 reproduced from: Straley, J. P. *Phys. Rev. A* **1976**, *14*, 1835–1841, with the kind permission of the publisher and the author.

Such an excluded volume effect is concerned with hard-core interactions, i.e., entropic forces given by eq 9, which corresponds to the S_q term in eqs 4–6.

Straley's screw model[11] implies that, for example, right-handed molecular screws with appropriate ridge and valley interactions to allow the fitting shown in Figure 8 should give rise to an S_q term driving the cholesteric state to be left-handed; i.e., S_q should be a negative term. The opposite molecular screw sense would give the opposite result.

Comparison of Theory with Experiment for the Cholesteric States of Polyisocyanates 2 and 3, PBLG (1), and Schizophyllan (4). (A) Thermodynamic Theory. As already shown in Figures 3 and 4, the linear relation between q_c and $1/T$ holds for poly((*R*)-2,6-dimethylheptyl isocyanate) in toluene (except near the solubility limit at the highest concentration at the lowest temperature) and in chloroform solutions. Similar linear plots can be obtained from the literature data for PBLG (1) in various solvents[16–20] and for schizophyllan (4) in water.[21–23] Figure 9 shows some examples of these plots of q_c vs $1/T$ for the three polymers. The signs of q_c for PBLG (1) and for schizophyllan (4) were determined by ORD measurements[17,19,22] comparable to those we reported in Figure 2. These linear relations (Figure 9) are consistent with an overwhelmingly entropic elastic force against the twist distortion (eq 3).

The values of H_q and S_q (Table I) for poly((*R*)-2,6-dimethylheptyl isocyanate) (**3**), PBLG (**1**) (in *m*-cresol and TCP), and schizophyllan (**4**) were obtained from the linear plots of q_c, against T^{-1} (Figure 9). Those for poly((*R*)-2,6-dimethylheptyl isocyanate) (**3**) in toluene at c = 0.33 g cm^{-3} were estimated from the straight lines fitting the data points at higher temperature (cf. Figures 3 and 4).

The following conclusions can be drawn:

(1) For all the systems, the values of H_q and S_qT are comparable in magnitude near to room temperature. This means that both the entropic and enthalpic terms of the twisting force are equally important in determining the cholesteric twisting.

(2) The signs of S_q for the polyisocyanate solutions are positive and opposite to the signs of S_q for the PBLG and schizophyllan solutions, irrespective of the solvent conditions. It follows from the definition of the sign of q_c

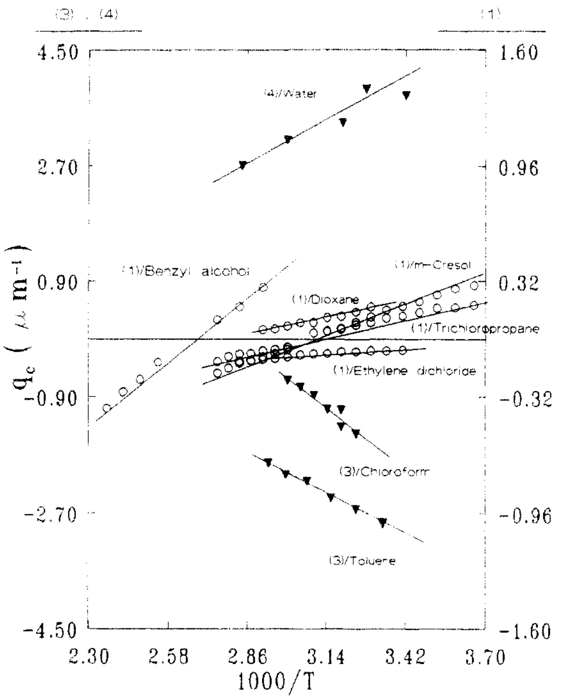

Figure 9. Plots of q_c vs $1/T$ for cholesteric liquid crystals of three optically active polymers: Schizophyllan (4), PBLG (1), poly((*R*)-2,6-dimethylheptyl isocyanate) (3).

along with eq 4 that the entropic cholesteric twisting force acting on the polyisocyanate molecules is right-handed and that those acting on the PBLG and schizophyllan molecules are left-handed.

(3) Similarly, the sign of H_q informs us that the polyisocyanate molecules interact with each other by a left-handed enthalpic twisting force which is also opposite in direction to the enthalpic twisting forces for the PBLG and schizophyllan solutions.

(4) The signs of H_q and S_q are opposite in each of the polymer lyotropic systems analyzed. The opposite direction of the enthalpic and entropic twisting forces would force a sense inversion of the cholesteric helix sense with temperature.

(B) Molecular Theory. Figure 9 and the data in Table I allow the use of Straley's theory discussed above (Figure 8) to be used in an interesting way to assign the helix sense to the three macromolecules studied here (Figure 9).

Inspection of Figure 9 shows us that in all solvents the slopes of the lines for 1 lead to a negative q_c at high temperatures with identical behavior for 4 and the opposite tendency for 3. By the extension of Straley's hypothesis portrayed in Figure 8 and discussed above, 1 and 4 would be right-handed screws and 3 left-handed. This is seen in quantitative terms in Table I with the actual signs and magnitudes of the S_q terms. As seen below, these conclusions are correct.

The absolute sense of poly(γ-benzyl L-glutamate) is known to be right-handed by comparison of its chiral optical properties with that of myoglobin for which the absolute assignment of the α-helical segments by Kendrew and his co-workers was determined crystallographically in 1960.[44,45] An X-ray analysis of schizophyllan assigns a right-handed screw sense to this triple-helical polysaccharide.[46] The polyisocyanate 3 has been assigned as a left-handed helix on the basis of a force field evaluation of side chain–main chain intramolecular interactions.[47] Thus, the assignment of helical (screw) sense from the cholesteric liquid crystal properties is consistent with independent evidence in the three polymers studied.

Table I. Values of the Enthalpic and Entropic Cholesteric Twisting Terms, H_q and S_q, for the cholesteric States of Poly((*R*)-2,6-dimethylheptyl isocyanate) (3), PBLG (1), and Schizophyllan (4) in Various Pure Solvents

solvent	c/g cm^{-3}	H_q/μm^{-1} K	S_q/μm^{-1}
(1) Poly((*R*)-2,6-dimethylheptyl isocyanate) (MW = 8.9 × 10^4; L = 91 nm; N = 1.2[b])[a]			
toluene	0.328	-2460	4.8
	0.280	-2310	4.9
	0.224	-2360	5.7
	0.219	-2220	5.3
chloroform	0.330	-1280	3.6
(2) PBLG[18,19] (MW = 24.6 × 10^4; L = 168 nm; N = 0.562)[a]			
m-cresol[18]	0.390	1140	-3.3
	0.325	990	-2.9
	0.293	900	-2.7
	0.260	730	-2.2
	0.228	600	-1.8
	0.195	520	-1.6
	0.163	350	-1.1
TCP[c,19]	0.325	1210	-3.4
	0.293	1080	-3.1
	0.260	750	-2.3
	0.228	650	-1.9
	0.195	380	-1.2
(3) Schizophyllan[23] (MW = 47.8 × 10^4; L = 222 nm; N = 0.556)[a]			
water	0.454	1890	-2.5
	0.340	1330	-1.7
	0.277	1200	-2.0
	0.234	850	-1.4
	0.194	580	-0.85
	0.176	530	-0.88
	0.141	390	-0.76

[a] The contour length L and the number of the Kuhn statistical segments N of each sample were calculated from the molecular weight (MW) along with the following molecular weight per unit contour length M_L and persistence length q: M_L = 980 nm^{-1} and q = 37 nm[b] for poly((*R*)-2,6-dimethylheptyl isocyanate) (3); M_L = 1460 nm^{-1} and q = 150 nm for PBLG (1);[57] M_L = 2150 nm^{-1} and q = 200 nm for schizophyllan (4).[58] [Poly((*R*)-2,6-dimethylheptyl isocyanate) (3) was assumed to have a contour length per monomer and q the same as poly(*n*-hexyl isocyanate) (2).[60]] [b] The value in 25 °C toluene. [c] 1,2,3-Trichloropropane.

It should be emphasized regarding these correlations of helix sense in 1, 3, and 4 to their lyotropic cholesteric properties that they are absolute and independent of each other. There is no empirical argument involved. Prior to this work, equivalent information would necessitate an X-ray crystal diagram with atomic resolution.[45] Such an experiment is not possible in synthetic polymers where single crystals of sufficient size for crystallographic analysis cannot be obtained.

Although the correspondence between theory and experiment here is impressive in crossing the boundaries of widely varying polymer structures and solvents, including in 1 where the single-temperature value of q_c can vary in sign, further testing is essential since one can geometrically demonstrate that screw models with very small pitch compared to diameter would produce a closest fit for the opposite sense, as in Figure 8. This though would not detract from Straley's theory[11] on the hard-core source of the cholesteric ordering, which has no investment in which cholesteric sense is produced by the hard-core fitting.

The dependence of the sign of H_q on the molecular helix sense is less well understood. Although Samulski and Samulski[14] and more recently Osipov[48] have formulated a chiral dispersion energy proportional to $B(\mathbf{r}_{ij})$ (eq 8) in terms of the polarization tensor and the gyration tensor of the chiral rod, there is no basis in this work[14,48] to assign a handedness to this term.

Equations 10, 12, and 13 could in principle be used to correlate the experimentally derived values of S_q and H_q to the theoretical parameters controlling the formation of the cholesteric properties in the three polymers discussed above.[49] This work in progress will be the focus of subsequent reports as will related efforts to correlate the experimental data for 1 and 3 to theoretical predictions[48] of the effect of solvent on the cholesteric properties.

Comparison of Theory with Experiment for the Cholesteric State of Poly(*n*-hexyl isocyanate) (2) Formed by Doping. There are two theoretical treatments concerned with the cholesteric ordering induced in a nematic phase on addition of a nonracemic chiral dopant. de Gennes, on the basis of continuum theory,[4] calculated a twist distortion of a nematic director field while Osipov,[48] with a molecular theory focused on polymer lyotropic states, calculated the dispersion forced between achiral rods in a nonracemic chiral solvent. Both efforts[4,48] predict a linear relationship between q_c and dope concentration which agrees with the results presented in Figure 7 for 2 in toluene doped with 5.

The contrast between the nonlinear $1/T$ dependence of q_c (Figure 7) and the linear dependence found for the intrinsically chiral nonracemic polymer (Figure 9) could possibly be understood by considering the sensitivity of the conformational properties of 2 to chiral influences.[27-31] In an achiral or racemic environment 2 consists of a helical backbone with long stretches of right- or left-handed helical sections separated by infrequent and easily mobile helix reversals. This structure sets up cooperative interactions which cause an extreme sensitivity of the helix sense ratio to chiral influences. In one extreme studied, even an optically active solvent acts to induce a helix sense excess.[50]

This sensitivity[27-30,50] suggests the possibility that either an association of the optically active dope with 2 or even the macroscopic chiral influence of the cholesteric phase could displace 2 from the otherwise equivalence of its left- and right-handed segments. Such a situation would be strongly temperature dependent since the number of helix reversal states are related exponentially to temperature.[27-30] This introduction of a second temperature dependence could then act to displace the relationship between q_c and $1/T$ from linearity. The hypothesis that 2 is no longer acting as a racemic substance is reinforced by the fact that the pitch of the doped systems (both 5 and 6) is as small as the pitch for 3 in some of the mixed solvent systems, e.g., Figure 4.

The most intriguing source of the hypothesized helix sense excess in 2 would be the effect of the macroscopic chirality of the cholesteric phase. In a cholesteric phase though with a pitch of 50 μm, the range we are studying here, the mesogen director rotates only 0.72° for a displacement along the cholesteric helical axis of 1000 Å. This is the approximate contour length of 2. It is therefore difficult to understand how this "hardly chiral"[51] geometric arrangement of a cholesteric phase could generate a force capable of displacing the right- and left-handed helical segments of 2 from their mirror image equivalency. Nevertheless, the hypothesis of the cholesteric chirality breaking this equivalency is reinforced by recent results on the effect of dissolved 2 on reducing the pitch of cholesteric thermotropic states. This has also been interpreted as arising from an interplay of the macromolecular helical states of 2 with the supramolecular cholesteric helix,[52] in line with the similar idea discussed here. Moreover, the sensitivity of oligophenyl chiral twist conformations to thermotropic cholesteric forces[53] and parallel results on oligophenyls dissolved in lyotropic cholesteric states[54] lend further weight to the hypothesis of an interplay between the macromolecular helical senses of 2 and the supramolecular arrangement of the cholesteric phase.

Summary and Conclusions

A new lyotropic cholesteric state has been produced from poly(alkyl isocyanates). This polymer offers new opportunities for study in this field since it may be obtained with varying excess of one helical state. In this work a polyisocyanate of a single helical sense (3) and one which is a 50:50 mixture of left- and right-handed segments (2) were studied for their pitch as a function of temperature and solvent. The former polymer (3) formed the cholesteric state directly while the latter (2) required the use of a rare technique in polymer lyotropes, i.e., chiral doping.

Thermodynamic theory was manipulated to derive the entropic (S_q) and enthalpic (H_q) terms controlling the cholesteric pitch, and the predictions of this theory were met by the polyisocyanate (3) and by rearranged data from the literature on poly(γ-benzyl L-glutamate) (1) and schizophyllan (4). The resulting values for S_q and H_q were determined.

In the case of S_q a correlation was found which allowed a correct and absolute assignment of helix sense to the three polymers studied (1, 3, and 4).

In the case of 2 in which the cholesteric state was formed by doping with two different chiral nonracemic molecules the temperature dependence of the pitch disagreed with the theory applicable to nonracemic chiral polymers. This could arise by conversion of 2 to a nonracemic state which could be due to an interaction between the macromolecular structure and the dope or to the effect of the supramolecular chirality of the liquid crystal.

Experimental Section

(*R*)-2,6-Dimethylheptyl isocyanate was prepared and polymerized following the literature.[28] The polymerized sample was divided into four molecular weight fractions by fractional precipitation with carbon tetrachloride as the solvent and methanol as the precipitant.[55] One of the middle fractions, about 30% of the total weight, was used for the cholesteric pitch measurements. Gel permeation chromatography analysis of this fraction showed a reasonably narrow polydispersity. Its intrinsic viscosity in toluene was 1.62 dL/g at 25 °C. In the reasonable assumption that the intrinsic viscosity–degree of polymerization relationship for poly((*R*)-2,6-dimethylheptyl isocyanate) (3) would be identical with that for poly(*n*-hexyl isocyanate),[56] the viscosity average degree of polymerization and molecular weight of our sample were estimated to be 530 and 8.9×10^4, respectively. A sample of poly(hexyl isocyanate) (2) used for the cholesteric pitch measurement had been prepared previously and had a narrow distribution with molecular weight 7.0×10^4 and degree of polymerization 550.

(+)-Menthylphenyl carbamate (5) was prepared by the reaction of (+)-menthol (purchased from Aldrich Chemical Co.) with phenyl isocyanate. The D-line optical rotation was +72° at 25 °C in ethanol, and the melting point was 113 °C. This material was purified by crystallization from ethanol/water. Cholesteryl chloride was purchased from Aldrich Chemical Co. and used as is.

Cholesteric solutions were prepared by first dissolving the polymer so as to obtain about 0.5 cm^3 of solution in a 2-cm^3 ground glass stoppered test tube and stirring with a magnetic stirrer. This solution was left overnight, and for the doped system, the dope was then added and stirred for one more day. The contents were transferred into the measuring cell with a 2-cm^3 microstyringe. The measuring cell was 1–2 mm in thickness with a neck to accept the sample. The neck was then sealed in a flame under air. Each change of temperature for the sealed cell was followed by a wait, and a stable cholesteric pattern was judged by making measurements until a constant value of the pitch was obtained. In the various samples this time varied from hours to days.

The cholesteric pitch measurements for the doped poly(*n*-hexyl isocyanate) (**2**) in toluene were made using a Union Mec-3 polarizing microscope or a Nikon microscope at 50× and 100× magnification with the temperature controlled by inserting the sample in a glass cell into a copper jacket with circulating water[21] or for the measurements in Brooklyn with an electrically heated homemade device. The cholesteric pitch was measured by photographing the sample showing the classic retardation lines (see, e.g., Figure 5) and comparing it to a photograph of a standard microscopic ruler taken under identical microscope conditions. All pitch measurements above 20 μm were measured in this way, which included the poly((*R*)-2,6-dimethylheptyl isocyanate) (**3**) cholesteric states in the chloroform toluene mixture with $x_{\mathrm{CHCl_3}} = 0.587$.

All other pitch measurements were made by using laser diffraction.[21] This apparatus consisted of a helium–neon laser with wavelength 633 nm passing through the sample in a glass cell of approximate thickness 1–2 mm. This was the same sample cell as used for the microscope measurements. The sample was placed at varying distances from a graph paper attached to a screen. The distance was varied from about 4 to 40 cm so as to measure the distance from the center of the light beam to the first diffraction ring as a function of the distance between the sample and the screen. A plot was made of the ring radius against the sample screen distance. A straight line was obtained from which the apparent diffraction angle was calculated using the tangent to this line. After the refraction correction by Snell's law (using the solvent refractive index as an approximation) to the apparent diffraction angle, the true diffraction angle was used to obtain the cholesteric pitch using Bragg's equation.

The optical rotation measurements were made on a JASCO ORD/UV-5 spectropolarimeter. A circulating jacket was used to control the temperature. The cell for the dilute solution measurement (Figure 1) was 10 cm long. The same measurements for cholesteric solutions with a planar texture were made on the above spectropolarimeter for the toluene solution of **3** (Figure 2) and on a polarizing microscope for the other solutions of **3** as well as doped solutions of **2**. The cells used were a homemade thin glass cell with 0.13-mm thickness for the toluene solution and microslides with 0.2- and 0.3-mm thicknesses from Vitro Dynamics, Inc., NJ, for the other solutions. The cholesteric solutions were sucked into the cell with a vacuum, and the shorter edges of the cell were sealed with ceramic adhesive (Aron ceramics, Toagosei Chemical). 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. The optical rotation measurements were done at several temperatures controlled by a circulating jacket.

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