minescence[23,24] demonstrate that surprisingly little potential energy is released as vibrational energy to HX. More tentative data[26] regarding the energy partitioned to the olefin suggest that in a large fraction, perhaps approximately two-thirds, of the potential energy may be released to the product olefin. These conclusions force an alteration of our earlier description of the carbon–carbon bond of the transition state; the bond order of $\sim$1.8 must be modified to nearer 1.0. Such a change has little influence on the magnitude of computed rate constants or isotope effects. Analysis of the dependence of the activation energy difference for chloroethane-d_0, -d_3, and -d_5 upon pressure indicated that a maximum can occur at intermediate pressure which differs significantly from the equilibrium activation energy difference.

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Molecular Order in Liquid Crystalline Solutions of Poly(γ-benzyl L-glutamate) in Dichloromethane[1]

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Abstract: Poly(γ-benzyl L-glutamate) dissolved in dichloromethane forms a cholesteric liquid crystal. When allowed to come to equilibrium in a strong magnetic field, this system undergoes a slow phase transition to nematic order with polymer helix axes distributed in a narrow range about the field direction. Reorientation of polymer molecules is slow on the nmr time scale. It is shown theoretically and experimentally that this leads to a dependence of dichloromethane proton dipolar splitting on the average orientation of polymer helices with respect to the external field. This orientation can be varied by rotating the sample tube, and subsequent motion of polymer helices can be observed by following changes in the dichloromethane nmr spectrum. Dichloromethane molecules are not free to exchange rapidly between regions of sample which differ in average orientation of polymer helices.

In many lyotropic liquid crystals, long-range molecular order is produced by forces between large, nonspherical molecules dissolved in a solvent of much smaller molecules. The nature of molecular order in such systems is a topic of continuing interest, particularly in view of biological functions of lyotropic liquid crystals[2] as well as an increasing number of commercial applications of liquid crystals in general.

A number of lyotropic liquid crystals have been discovered[3,4] in which motion of the large, order-producing molecules is slow on the time scale of nuclear magnetic resonance (nmr), while the small molecules are relatively free to move about and to reorient in solution. Such systems are well suited for investigation by nmr because the small molecules exhibit more or less well-resolved dipolar splittings. Moreover, the dipolar splittings depend on the orientation of the large molecules relative to the external magnetic (or electric) field, a parameter which can be varied at will by rotating the sample tube.

We have used both the dependence of dipolar splitting on sample tube rotation and the nmr line shape to study some properties of molecular order and motion in solutions of poly(γ-benzyl L-glutamate) (PBLG) in dichloromethane. This system is particularly convenient in that the PBLG proton resonance is too wide and weak to interfere with the solvent resonance, the time scale for PBLG molecular motion varies from a few seconds to a few hours, and the line shape is not always dominated by static field inhomogeneity even for nonspinning samples.

Previous investigations[3] of dichloromethane proton resonance in PBLG solutions have demonstrated that the solution slowly undergoes a phase transition from cholesteric to nematic ordering of PBLG molecules when left in a strong magnetic field. If the sample is then rotated to some angle about an axis perpendicular to the field, its optical rotation exhibits complex behavior.[5] If a beam of polarized light is passed through the sample, it is rotated to a different extent by different regions of the sample; contorted striations are observed which move about in a complex manner for several minutes and finally disappear as the PBLG molecules become aligned along the new field direction.

In this paper we are concerned with how PBLG molecules at equilibrium in a static field produce nonzero dipolar splittings in the dichloromethane proton resonance and with the nature of molecular order and motion following a sample tube rotation.

Theory

A given dichloromethane molecule in a liquid crystal sample has at a given time t two resonance frequencies

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[1] This work was partially supported by funds from the National Institutes of Health (Grant No. USPHS TRG 2-TO1-GM-01045).

[2] J. L. Fergason and G. H. Brown, *J. Amer. Oil Chem. Soc.*, **45**, 120 (1968).

[3] (a) M. Panar and W. D. Phillips, *J. Amer. Chem. Soc.*, **90**, 3880 (1968); (b) S. Sobajima, *J. Phys. Soc. Jap.*, **23**, 1070 (1967).

[4] (a) P. J. Black, K. D. Lawson, and T. J. Flautt, *Mol. Cryst. Liq. Cryst.*, **7**, 201 (1969); (b) C. S. Yannoni, private communication.

[5] W. D. Phillips, private communication.

ω_+ and ω_- given by

$$\omega_\pm = \omega_0 \pm (3\gamma^2\hbar/4r^3)(3\cos^2\theta(t) - 1) \qquad (1)$$

where $\theta(t)$ is the instantaneous angle between the interproton vector (of length r) and the external field. ω_0 is the proton Zeeman resonance frequency. The observable resonance frequencies are obtained by multiplying eq 1 by a distribution function $P(\theta)$ and integrating over θ. ω_+ will then differ from ω_- if $P(\theta)$ is not uniform. Use of this procedure for thermotropic liquid crystals is well established.[6,7]

For PBLG–dichloromethane solutions where the long, rigid PBLG helices are all more or less parallel and move much more slowly than dichloromethane molecules, it is appropriate to average motions of dichloromethane relative to PBLG independently from motions of PBLG relative to the external field. Figure 1 shows the relevant geometry. We find

$$\begin{aligned}3\cos^2\theta - 1 = {} & (3\cos^2\alpha - 1)(3\cos^2\gamma - 1)/2 + \\ & (^3/_2)\sin 2\gamma \sin 2\alpha \cos(\phi - \phi') + \\ & (^3/_2)\sin^2\gamma \sin^2\alpha \cos 2(\phi - \phi') \qquad (2)\end{aligned}$$

In averaging the last two terms of eq 2, it is reasonable to assume that the values of $(\phi - \phi')$ are equally probable because of the nearly cylindrical symmetry of the PBLG helices. In this case these terms average to zero, and we have

$$\langle 3\cos^2\theta - 1\rangle = C_\gamma(3\cos^2\alpha - 1) \qquad (3)$$

where the angular brackets denote an average over γ and ϕ, and C_γ stands for $\langle 3\cos^2\gamma - 1\rangle/2$. C_γ is nonzero in liquid-crystal solutions because dichloromethane molecules are not free to reorient at random. Whether all dichloromethane molecules are oriented to the same extent or some are highly oriented and in rapid exchange with unoriented molecules does not affect the calculation leading to eq 3.

The average over α, describing orientations of PBLG molecules relative to the external field, is more complicated than that over γ. Denoting this average by a bar, we obtain the average dipolar splitting

$$S = \overline{|\omega_+ - \omega_-|} = \left|(3\gamma^2\hbar C_\gamma/2r^3)\int_0^\pi P(\alpha)(3\cos^2\alpha - 1)\sin\alpha\, d\alpha\right| \qquad (4)$$

where $P(\alpha)$ is the probability that a PBLG molecule will have angle α between its long axis and the external field. Only those PBLG molecules which interact with the given dichloromethane are included in this distribution. In the next section we demonstrate that this may selectively exclude some values of α. However, in the limiting case that all PBLG molecules included in eq 4 are parallel and make angle α_0 relative to the external field, $P(\alpha)$ becomes a δ function, and we find

$$S = S_0|3\cos^2\alpha_0 - 1| \qquad (5)$$

where S_0 is the collection of constants in eq 4.

It is clear that the measured dipolar splitting S depends on the angle α_0 between PBLG molecules and the external field. S has period π, and a given value of S corresponds to any of four angles, $\pm\alpha_0$ or $\pi \pm \alpha_0$. Since the ends of a PBLG helix are for our purpose indistinguishable, angles α_0 and $\pi + \alpha_0$ define identical orientations of PBLG, denoted henceforth by α_0 alone. Thus a measured value of S corresponds to either of two orientations $\pm\alpha_0$ of PBLG helices relative to the external field.

The actual value of α_0 can be determined uniquely in spite of the double-valued nature of S. If a given orientation of the sample has a splitting S_1, we can associate a value of either $\pm\alpha_1$ with it. If the sample is now rotated by α_{12} deg, the new angle α_2 has a value of either $|\alpha_1| - \alpha_{12}$ or $-|\alpha_1| - \alpha_{12}$. Since these two values are unequal in general, the value of α_1 is known uniquely. Because of the measurement of the dipolar splitting at two angles, this type of determination is referred to as a double angle experiment.

Experimental Methods

PBLG of molecular weight 310,000 was obtained from Pilot Chemicals, Inc., and Eastman spectrograde dichloromethane was used. Neither reagent was further purified. The samples were sealed without degassing in standard 5-mm nmr tubes; all concentrations were determined by weight to an accuracy of ±0.05 wt %. Homogeneity of viscous samples was ensured by numerous inversions of the sample tube prior to placement in the magnetic field.

Nmr spectra were obtained with a Varian HR-60 spectrometer at ambient temperature (24°). After trimming the field for maximum homogeneity, the liquid-crystal sample was placed in the field and allowed to attain equilibrium nematic orientation. Although this procedure required several hours, the field homogeneity did not drastically decrease. A nonspinning sample of neat dichloromethane was found to maintain a line width of 2.3 ± 0.2 Hz for at least a day. We assume this line width as the contribution of static-field inhomogeneity to the liquid-crystal spectra.

Samples at equilibrium were run with the slowest sweep rate consistent with accurate frequency measurement (the side-band method was used). However, significant changes in the nmr spectrum were found to occur a few seconds after a sample tube rotation, and the sweep rate had to be increased to accurately follow these changes. This feature is the major limitation on the accuracy of our measurements; sweep rates as high as 6 Hz/sec had to be used. The line width in such cases for liquid-crystal samples was then, as expected, about 6 Hz.

Sample tube rotation angles were measured with a calibrated disk placed on the spinner assembly of the probe, and are accurate to ±2°. Unless otherwise stated, the sample concentration was 17.5 wt % PBLG in dichloromethane. This concentration yields the most convenient values of $CHCl_2$ line widths and rates of motion of the PBLG molecules.

Results and Discussion

When a sample of PBLG in dichloromethane is placed in a magnetic field, the anisotropy of the diamagnetic susceptibility of the PBLG molecules results in forces which align the PBLG molecules parallel to the magnetic field. Any orientation other than parallel is a nonequilibrium situation; equilibrium is attained by a rotation of less than or equal to 90°.

Figure 2 shows the measured dipolar splittings as a function of time after placement in the magnetic field for several concentrations[8] of PBLG. In agreement with Sobajima,[3b] we found that the spectrum at time zero resembled a Pake doublet,[9] due to averaging of intramolecular dipolar splittings over random orientations of dichloromethane interproton vectors characteristic of the cholesteric liquid crystal. As the PBLG molecules approached a state of equilibrium nematic

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(6) (a) W. Maier and A. Saupe, *Z. Naturforsch. A*, 14, 882 (1959); (b) A. Saupe and W. Maier, *ibid.*, *A*, 16, 816 (1961).

(7) T. M. Connor, *Mol. Phys.*, 19, 253 (1970).

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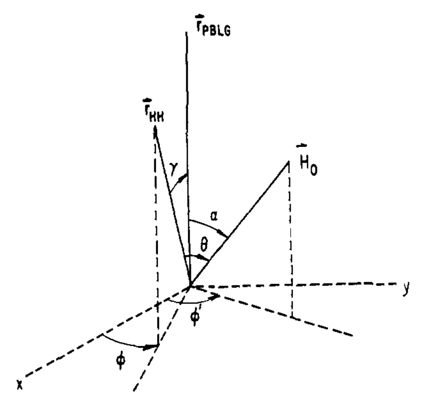

Figure 1. The relationships between the interproton vector of a dichloromethane (r_{HH}), the external magnetic field (H_0), and the long axis of a PBLG α helix (r_{PBLG}).

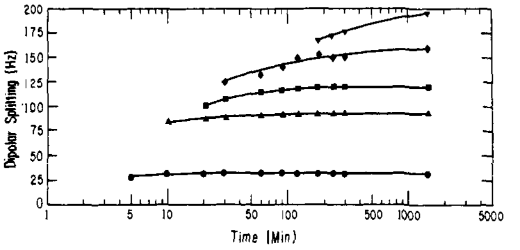

Figure 2. The dipolar splitting as a function of residence time in the magnetic field. The concentrations in wt % PBLG are: 10, ●; 20, ▲; 25, ■; 30, ◆; and 35, ▼.

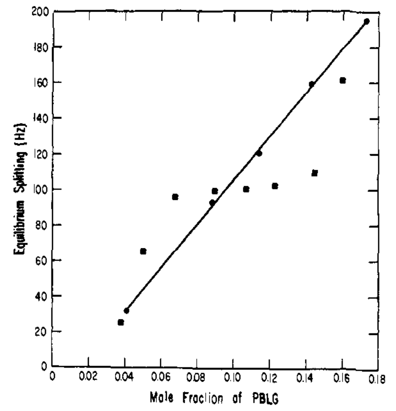

Figure 3. Effect of PBLG concentration on the dipolar splitting at equilibrium. Our measurements (●) and Sobajima's (ref 3b) measurements (■) are shown.

alignment, the doublet lines narrowed and the splitting increased. Below a PBLG mole fraction of about 0.03 no dipolar splitting was observed.

Equilibrium splittings are shown *vs.* PBLG concentration in Figure 3, together with similar results of Sobajima.[3b] Our linear relationship can be explained by assuming that C_γ in eq 3 arises from a time average over two states for the dichloromethane molecules, one being highly ordered and the other being isotropic. A linear relationship could still obtain if all dichloromethane molecules were oriented by interaction with PBLG, but to different extents. However, the former possibility is far more likely in view of the short-range nature of the interactions. The difference between our results and those of Sobajima may be due to the large difference in molecular weights of PBLG.

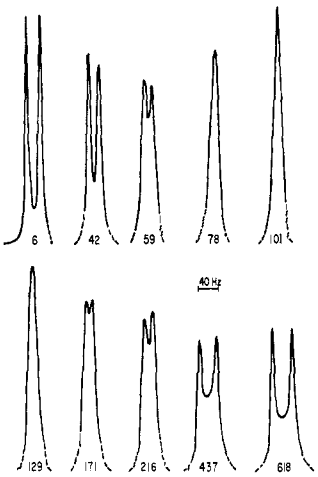

Figure 4. The nmr spectra observed after an equilibrium sample was rotated through 90°. The numbers under the spectra give the number of seconds after the rotation.

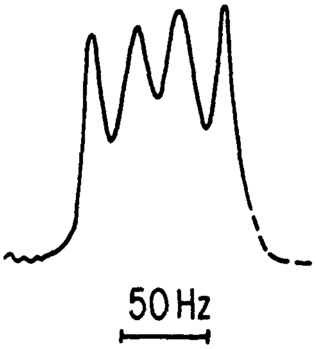

Figure 5. The nmr spectrum observed after an equilibrium sample was rotated to 90° for 12 min and then rotated −40°. Immediately before the second rotation the spectrum was a doublet as seen in Figure 4.

Immediately after an equilibrium sample was rotated through 90°, the dipolar splitting was found to be S_0,[10] in agreement with eq 5. The splitting then decreased smoothly with time through zero to an equilibrium value of $2S_0$ as partially shown in Figure 4; this corresponds to an aligned sample rotating from an orientation perpendicular to the magnetic field to one parallel to it. This observation rules out a complete randomization of PBLG axes following the rotation; if that were the case, a Pake doublet would have been observed similar to the spectrum of a new sample just placed in the magnetic field. The line widths were found to increase to about 15 Hz during recovery to equilibrium, narrowing again on a time scale similar to Figure 2. This indicates that *partial* randomization of PBLG axes does occur; however, significant order is maintained.

We used double-angle experiments to follow the variation of the orientation angle α_0 with time after a 90° sample tube rotation. The spectrum observed after rotating an equilibrium sample 90°, waiting 12 min, and rotating it −40° is shown in Figure 5. Two doublets are clearly visible, with roughly equal intensities. This is most likely due to the fact that immediately after the 90° rotation, half the PBLG molecules begin to rotate clockwise and half counterclockwise. From the spectrum in Figure 5, it is apparent that after 12 min

(10) For the 17.5 wt % sample, S_0 = 39 Hz.

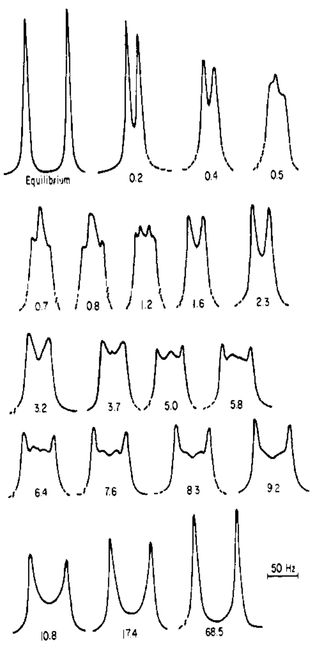

Figure 6. The nmr spectra observed after an equilibrium sample was rotated 70°. The number under each spectrum indicates the number of minutes after the rotation. The first spectrum was taken just before the rotation.

the first portion had reached −27° relative to the field while the second had reached 28°; both portions had rotated about 62° toward the 90° position.

Immediately following a 90° rotation half of the PBLG molecules will rotate counterclockwise and half clockwise, but if the initial rotation angle is less than 90° this will not be so. In a sample at equilibrium there is doubtless some distribution of PBLG axes about the field direction, and if the sample tube is rotated less than 90°, some small fraction of PBLG helices will have their long axes forming an angle greater than 90° with the magnetic field. Torques exerted by the static field will tend to rotate such molecules back to equilibrium in an opposite sense from those rotated to less than 90°.

The spectra observed following an initial rotation of 70° are shown in Figure 6. The single doublet splits into two doublets which successively pass through zero splitting and merge into a single doublet with the equilibrium splitting. Double-angle experiments for each doublet reveal that there are indeed two counterrotating sets of PBLG molecules of unequal populations. The rotations to equilibrium after initial rotations of 70 and 90° are shown in Figure 7. Decreasing the initial rotation angle sharply decreases the intensity of one of these doublets. For initial rotation angles less than 50° only one doublet can be detected.

We have been able to approximate the spread in the distribution of the PBLG axes about the magnetic field at equilibrium. The shape of the integral of an equilibrium sample is one measure. The relative intensities of the peaks from the two counterrotating portions after various rotations from equilibrium also indicate the spread. The results in Table I clearly indicate that a significant fraction of the PBLG axes in an equilibrium sample form angles of greater than 20° with the field.

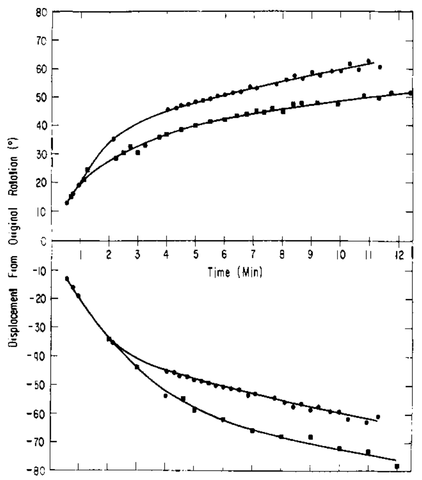

Figure 7. The motions of the PBLG molecules after an equilibrium sample was rotated to 90° (●) and 70° (■); these are clockwise rotations. The upper half corresponds to displacement in a counterclockwise direction and the lower half, a clockwise direction.

The double-angle experiments support the following picture of what happens in a liquid crystalline PBLG–dichloromethane solution after rotation of PBLG helices to a nonequilibrium orientation. The sample develops many small regions which rotate as a unit. The PBLG axes in a given region are all parallel as a result of liquid crystalline forces. Since slightly broadened line shapes are observed during reorientation, all of the regions rotating in a given direction and contributing to a given pair of peaks must rotate at very similar rates; we call these regions nematic isochromats. The fact that multiple doublets are observable in the liquid-crystal solutions demonstrates that chemical exchange of dichloromethane cannot be occurring rapidly between nematic isochromats of different orientations.

Table I

	Integral, %	Intensity, %
Within 20° of parallel	87	87
Within 40° of parallel	99	97

Conclusions

The dipolar splittings observable in dichloromethane proton resonance of liquid crystalline solutions of PBLG provide an unambiguous and sensitive measure of the orientation of PBLG molecules relative to the external field. At equilibrium, PBLG molecules line up with most of the helix axes within ±20° of the field direction. Following a sample tube rotation, this order is partially lost, but significant portions of PBLG molecules rotate back to equilibrium more or less in unison both in clockwise and counterclockwise senses. All our results demonstrate that dichloromethane is oriented highly by close association with PBLG molecules, and exchanges rapidly with other dichloromethane molecules not so ordered. However, chemical exchange of dichloromethane (ordered or not) between regions of sample in which PBLG helices are not parallel is greatly hindered.