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Order Parameters and Side-Chain Conformation in Ethylcellulose/Chloroform Liquid Crystal Phases

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ABSTRACT: Deuterium magnetic resonance spectra of chiral nematic phases formed by deuterated ethylcellulose dissolved in chloroform show three overlapping powder patterns, which can be attributed to three nonequivalent (CD_3CH_2) substituents at the 2, 3, and 6 positions of the 1,4-linked anhydroglucose units. The qudrupolar splittings were measured as functions of temperature and concentration. The results were analyzed in terms of side-chain conformations and the order parameters of the anhydroglucose unit.

Introduction

Liquid crystal polymers are of considerable theoretical and practical interest because they offer a unique combination of desirable properties. Of special concern to this study are cellulose-based liquid crystalline mesophases. Many cellulose derivatives form lyotropic or thermotropic chiral nematic (cholesteric) liquid crystals under suitable conditions.[1] For lyotropic systems, both the mesophase formation and the handedness of the chiral nematic depend on the type of the side-chain substituents and the nature of the solvent,[2] indicating the importance of the side-chain–solvent interactions. Furthermore, in mesophases formed by ethylcellulose, the degree of substitution has been found to have a profound effect on the twist sense and temperature dependence of the pitch, with a reversal of chiral nematic handedness occurring in some solvents.[3] The molecular factors responsible for these macroscopic observations are not well understood. A probe of side-chain conformation and dynamics is required.

Deuterium NMR techniques have been shown to yield valuable information on molecular orientational order and anisotropic motions in mesophases,[4–6] including twisted nematic phases.[7–9] In this work, the behavior of an ethylcellulose/chloroform mesophase is examined by using the ^{2}H resonance of deuterated side-chain substituents.

The ^{2}H NMR spectra are almost exclusively governed by the coupling between the nuclear quadrupole moment of the deuteron and the local electric field gradient tensor. Since the field gradient originates mainly from the electrons in the carbon–deuterium bond, the technique can be used to monitor the orientation and mobility of individual bonds. In the ^{2}H NMR spectrum of a randomly oriented uniaxial liquid crystal sample, each motionally nonequivalent C–D bond generates a Pake powder pattern. With the assumption that the average field gradient is cylindrically symmetric about the bond, the doublet splitting $\delta\nu$ (the splitting between the two strongest peaks in the spectrum) is directly proportional to the order parameter of the C–D bond, $S_{\text{C-D}}$

$$\delta\nu = (3/4)(e^2qQ/h)|S_{\text{C-D}}| \qquad (1)$$

where (e^2qQ/h) is the quadrupolar coupling constant and for an aliphatic C–D bond it is usually taken to be 170 kHz. The order parameter $S_{\text{C-D}}$ is given by

$$S_{\text{C-D}} = \langle (1/2)(3\cos^2\Theta - 1)\rangle \qquad (2)$$

where Θ is the angle between the C–D bond and director of the nematic layer and the angular brackets indicate an average over all intramolecular and reorientational motions.

For the ethylcellulose system studied, the observed quadrupole splitting can also be related to the orientation order of the anhydroglucose unit in the polymer chain (Figure 1)

$$\delta\nu = (3/4)(e^2qQ/h)[S_{zz}\langle (1/2)(3\cos^2\alpha - 1)\rangle + (1/2)(S_{xx} - S_{yy})\langle \sin^2\alpha\cos 2\beta\rangle] \qquad (3)$$

where x, y, and z are principal axes of ordering matrix fixed in the anhydroglucose unit and α and β are polar angles specifying the orientation of a C–D bond in the x,y,z frame. The angular brackets denote an average over all possible conformation states. In eq 3, it is assumed that the orientation potential for a subunit in the polymer chain can be treated as independent of the side-chain conformations, so that a single ordering matrix can be used to describe the orientation of the subunit and its side-chain substituent.[10,11]

For elongated molecules, it is usually assumed that the term involving $(S_{xx} - S_{yy})$ is negligibly small, and thus the orientation can be described by a single ordering parameter S_{zz}. As a consequence, all observed $\delta\nu$ values arising from nonequivalent deuterons should be proportional to a single

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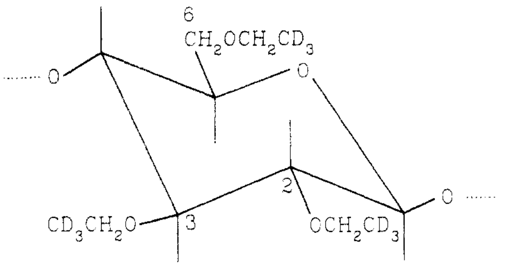

Figure 1. Anhydroglucose unit with deuterated ethyl groups at C2, C3, and C6 positions.

order parameter, and if the conformation average $\langle(1/2)(3\cos^2\alpha - 1)\rangle$ in eq 3 does not vary with temperature, the ratios of the $\delta\nu$ values should be independent of temperature.

Experimental Section

The deuterated ethyl (CD_3CH_2)cellulose (EC-d_9) was synthesized by reacting cellulose acetate with deuterated ethyl iodide in dimethyl sulfoxide as described in ref 12 (series D method). On the basis of GPC measurements, the weight-averaged molar mass of the sample was found to be 90 000. A total degree of substitution (DS) value of 2.7, including both the deuterated and nondeuterated substituents, was determined from the deuterium and proton NMR spectra of isotropic solutions. A circular reflectance spectroscopy measurement showed that the EC-d_9 sample forms a right-handed mesophase in chloroform.

For a commercial sample of ethylcellulose of molar mass 40 000, Suto[13] estimated from viscosity measurements that the critical concentration for formation of a liquid crystal phase in chloroform at 25 °C was 28.8 wt % polymer, with a biphasic region extended to 32 wt %. The critical concentration increased slightly with temperature; at 45 °C the corresponding concentrations were 31.2 and 35.5 wt % polymer, respectively. A sample of ethylcellulose of DS 2.52 and a weight-average molar mass 168 000 gave a slightly higher critical concentration, measured by optical microscopy, of 36 wt % in chloroform at room temperature.[3] Thus, samples with concentration higher than 39 wt % polymer were used in this study to ensure the formation of anisotropic solutions. Samples containing 39.9, 44.7, 47.7, and 49.2 wt % EC-d_9 were prepared by weighing appropriate amounts of EC-d_9 and chloroform into 5 mm o.d. NMR tubes and then sealing under vacuum. To aid dissolution, the tubes were kept at 40–50 °C for several days to several weeks, depending on the concentration of the sample. All four samples exhibited typical cholesteric reflection colors.

The ^2H NMR measurements were performed with a Varian XL-300 spectrometer operating at 46.1 MHz, with a 5-μs pulse, an acquisition time of 0.5 s, and spectral width of 20–40 kHz. Since the whole spectrum width in all cases is less than 7 kHz, the quadrupole echo pulse sequence was not employed. However, to assess the possible effect of molecular diffusion,[7,8] several spectra of the sample containing 44.7 wt % EC-d_9 were recorded using the quadrupole echo sequence, but no significant line shape distortion was observed when the delay times were varied between pulses. Proton decoupling was found to improve significantly the resolution of overlapping peaks; therefore, all spectra were recorded with high-power proton decoupling. To obtain an acceptable signal/noise ratio, 1000–2000 free induction decays were accumulated.

The orientating effect of the magnetic field was investigated by keeping the sample in the field and recording spectra at different time intervals. During a 10-h overnight run, there was no detectable change in the recorded powder spectra, indicating the magnetic field is not strong enough to orient the helicoidal structure of the cholesteric phase.

Results and Discussion

A typical experimental spectrum, shown in Figure 2a, consisted of three overlapping powder patterns. In addition, there was a small narrow center component, which increased with increasing temperature and decreasing concentration. For the least concentrated sample (39.9 % EC-d_9) a much large center peak was observed at 55 °C (Figure 2b), indicating that the system has entered the biphasic region. For spectra obtained at lower temperature or higher concentration, the small center peak may be caused by the presence of a small amount of isotropic phase formed from low molecular weight fractions of ethylcellulose. Fractionation of polydispersed cellulose derivatives has been observed between the isotropic and anisotropic phases with the lower molar mass chain preferring the isotropic phase.[14,15]

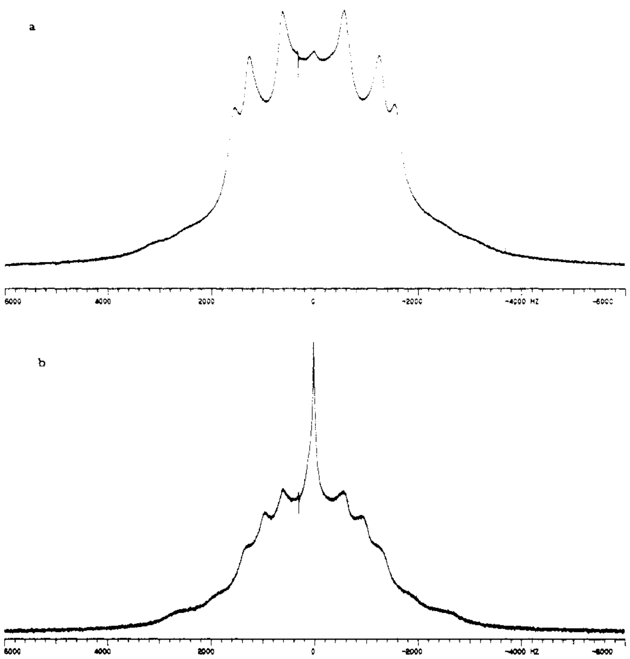

Figure 2. ^2H NMR spectra of EC-d_9: (a) 44.7 wt % in $CHCl_3$ at 302 K; (b) 39.9 wt % in $CHCl_3$ at 328 K.

The three overlapping powder patterns can be attributed to the three nonequivalent CD_3CH_2 groups at the C2, C3, and C6 positions of the 1,4-anhydroglucose unit (Figure 1). An unambiguous assignment of the powder patterns to specific substitution positions is not possible, but it can be argued that the group on C6 should show the smallest quadrupolar splitting due to the additional averaging arising from the presence of the extra C–C bond. The results of molecular mechanics calculations (MM2) for model compounds such as ethyl-substituted cellobiose and triose showed that the side chains are in a fully extended all-trans configuration, but the potential minima are broad, particularly for the C6 group. Such calculations apply to an "isolated" molecule, and the conformation in solution may be different and could be strongly affected by concentration and by the nature of solvent. The superposition of the patterns and broadening of the resonance lines cause the experimentally measured doublet positions to shift slightly from the values given by eq 1.[16] Therefore, corrections were made to the observed doublet splittings by comparing the experimental spectra with simulated spectra obtained by superposition of powder patterns of appropriate width. The temperature dependences of the corrected splittings, $\delta\nu_1$, $\delta\nu_2$, and $\delta\nu_3$, are plotted in Figure 3, parts a, b, and c, respectively, for the four different concentrations studied. The estimated error in the $\delta\nu$ values is ± 10 Hz for $\delta\nu_1$ and ± 20 Hz for $\delta\nu_2$ and $\delta\nu_3$. Taking a value of 170 kHz for the quantity (e^2qQ/h), from eq 1 we obtain

$$\delta\nu_i = 128|S_{C-D}| \text{ (kHz)} \quad (4)$$

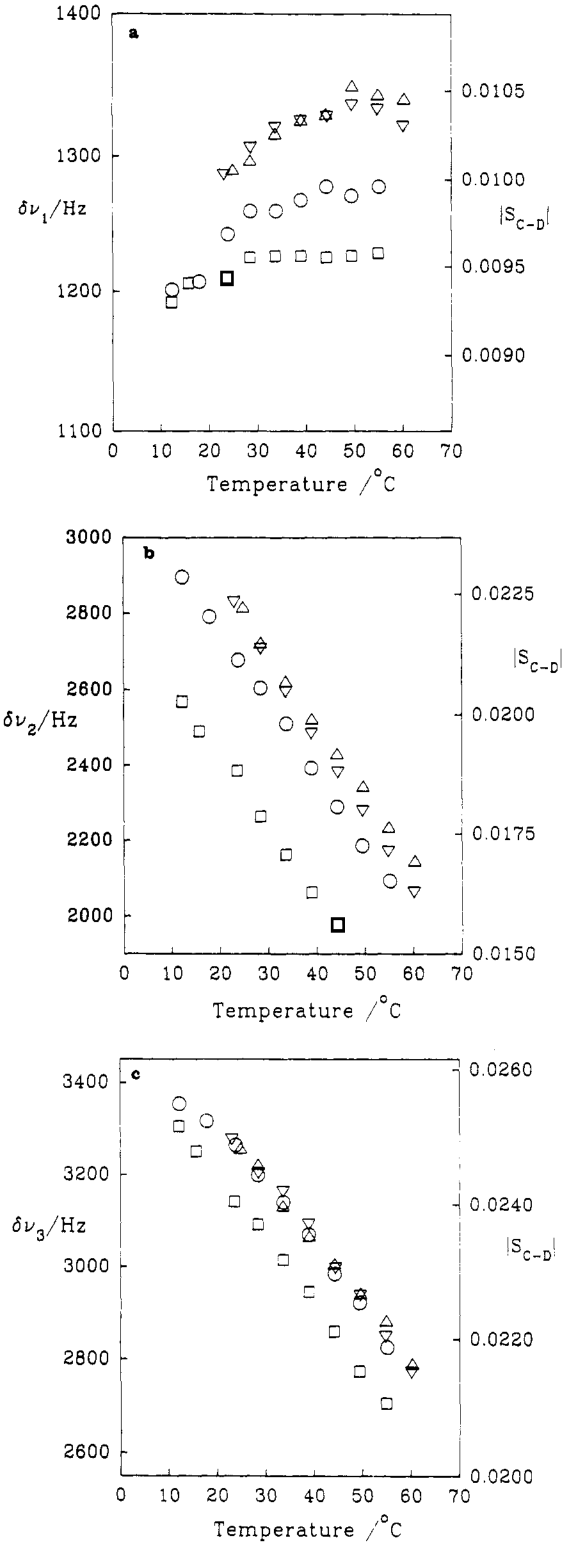

Figure 3. Variation of doublet splittings with temperature: (a) $\delta\nu_1$, (b) $\delta\nu_2$, and (c) $\delta\nu_3$. Concentrations (wt % EC-d_9 in $CHCl_3$): (□) 39.9; (○) 44.7; (▽) 47.7; (△) 49.2. Equation 4 has been used to draw the right-hand-side ordinate for showing the temperature dependence of $|S_{C-D}|$.

If the CD_3 groups are assumed to be freely rotating, then the S_{C-D} can be further related to S_{C-C}, the order parameter of the C–C bond in the ethyl group

$$S_{C-D} = (1/2)(3\cos^2\gamma - 1)S_{C-C} = (-1/3)S_{C-C} \qquad (5)$$

where γ, the angle between the C–D bond and the rotation axis, is taken to be 109.5°.

The two largest splittings decrease with increasing temperature, but the smallest splitting, $\delta\nu_1$, shows an unusual behavior by remaining almost constant. It is obvious that the ratios of quadrupolar splittings do vary with temperature, and the different temperature dependences shown by these splittings can be taken as direct evidence either that the orientation cannot be treated as axially symmetric, and therefore two order parameters, S_{zz} and $S_{xx} - S_{yy}$, are required to describe the orientation, or that the average conformations of the side-chain substituents are changing with temperature. Similar behavior has been observed in ^{2}H NMR studies of low molecular weight nematic liquid crystals.[17-19] In a detailed ^{2}H NMR study of two nematic liquid crystals, 4,4′-bis(n-heptyloxy)azoxybenzene and 4-n-octyl-4′-cyanobiphenyl, Boden et al.[20] showed that the temperature dependence of ratios of the $\delta\nu$ values along the deuterated alkyl chain cannot be attributed entirely to the changes in conformational average or solely to the biaxiality in the ordering matrix and concluded that both factors probably play important roles in determining the observed temperature dependences. Thus, the observed temperature dependence of each quadrupolar splitting reflects the variation of the two order parameters, which are the same for all three CD_3 groups, and also depends on the average conformation of the group and its variation with temperature. To compare the relative behavior of different substituent groups, we will present plots of the ratios of the quadrupolar splittings, $\delta\nu_i/\delta\nu_j$ against $\delta\nu_k/\delta\nu_j$. To simplify the discussion we will use A_i and B_i to represent the conformation-dependent terms in eq 3

$$A_i = \langle (1/2)(3\cos^2\alpha - 1)\rangle_i \qquad (6)$$

and

$$B_i = \langle \sin^2\alpha \cos 2\beta \rangle_i \qquad (7)$$

where the subscript i refers to different quadrupolar splitting $\delta\nu_i$. Since S_{zz} and $(S_{xx} - S_{yy})$ are the same for all of the CD_3 groups, it can be shown that, at a given temperature, the three observed $\delta\nu$ values are related by[18]

$$\delta\nu_3 = C_1\delta\nu_1 + C_2\delta\nu_2 \qquad (8)$$

where

$$C_1 = ((A_3/A_2) - (B_3/B_2))/((A_1/A_2) - (B_1/B_2)) \qquad (9)$$

and

$$C_2 = ((A_3/A_1) - (B_3/B_1))/((A_2/A_1) - (B_2/B_1)) \qquad (10)$$

It should be noted that all of these parameters, A_i, B_i, C_1, and C_2, are expected to vary with temperature. In view of the conformation-dependent nature of C_1 and C_2, plots of the ratios of quadrupolar splittings may reveal the effect of temperature or concentration on the conformation of the substituents. For example, a plot of $\delta\nu_3/\delta\nu_1$ against $\delta\nu_2/\delta\nu_1$ for a given system is expected to yield a smooth curve if temperature variation does not cause an abrupt change in the A_i and B_i values. In Figure 4, $\delta\nu_3/\delta\nu_1$ is plotted vs $\delta\nu_2/\delta\nu_1$ for each of the ethylcellulose/chloroform systems. A straight line relationship between the two ratios of the quadrupolar splittings is apparent, indicating that the temperature effect on the conformation average terms in eq 3 is such that the resulting C_1 and C_2 values show little variation with temperature. It has been pointed out[20,21] that the observation of such linear plots cannot be taken as evidence that the conformation average terms in eq 3 have negligible temperature dependences.

It is interesting to note that, within experimental error, the ratios of the quadrupolar splittings for systems containing 39.9 and 44.7 wt % EC-d_9 fall on one line and those of 47.7 and 49.2 wt % on another (Figure 4). The results show that within a certain concentration range,

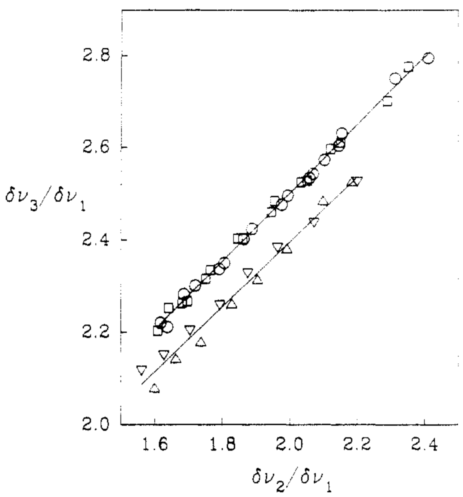

Figure 4. Plot of ratios of doublet splittings $\delta\nu_3/\delta\nu_1$ vs $\delta\nu_2/\delta\nu_1$. Concentrations (wt % EC-d_9 in $CHCl_3$): (□) 39.9; (○) 44.7; (▽) 47.7; (△) 49.2.

increasing temperature and decreasing concentration exert similar effects on the conformational averages of the three substituents and that an abrupt change in the average conformation of one or more substituents occurs between concentrations of 44.7 and 47.2 wt % EC-d_9. This change in side-chain conformation probably reflects a significant increase in the interchain interactions between these two concentrations. Figure 3 shows that the $\delta\nu_3$ values, unlike $\delta\nu_1$ and $\delta\nu_2$, remain almost unchanged as the concentration is increased from 44.7 to 47.7 wt %; thus, we conclude that the group giving rise to $\delta\nu_3$ is mainly responsible for the observed shift between two straight-line relationships exhibited in Figure 4. The data also indicate that increasing the concentration beyond 47.7 wt % EC has little effect on the measured splittings.

Obviously, without a detailed knowledge of molecular structure and conformation, it is not possible to use eq 3 to compute the order parameters of the anhydroglucose units or polymer chain. As indicated above, the conformational averages in eq 3 will change with temperature but probably less so than the strong temperature dependence usually shown by S_{zz}.[22,23] For cellulosic polymers, a strong temperature dependence of S_{zz} is also expected from the rather rapid decrease in their chain stiffness (persistence length) with temperature.[24] On the basis of this assumption we can make several comments on the order parameters and their relation to the observed values of quadrupolar splittings. Since a temperature variation will cause simultaneous and parallel changes in the values of S_{xx} and S_{yy}, the temperature dependence of $(S_{xx} - S_{yy})$ is expected to be small for elongated molecules. Results on low molecular weight nematics confirm that $(S_{xx} - S_{yy})$ shows little variation with temperature except for a slight maximum near the center of the nematic temperature range.[25-27] Therefore, the different temperature dependences observed for the three $\delta\nu$ values can be rationalized by assuming that $\delta\nu_1$ depends mainly on the term involving the biaxiality of the ordering matrix, $(S_{xx} - S_{yy})$, and that the variation in the values of $\delta\nu_2$ and $\delta\nu_3$ mainly reflect the temperature dependence of S_{zz}. Thus, our results indicate a 15–20% decrease in the value of S_{zz} over the temperature range studied.

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