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Spectroscopic Analysis of Discotic Liquid-Crystalline Molecules and Polymers on External Surfaces

X. Yang,[†] S. A. Nitzsche,[†] S. L. Hsu,*[,†] D. Collard,[‡] R. Thakur,[‡] C. P. Lillya,[‡] and H. D. Stidham[‡]

Polymer Science and Engineering Department and Department of Chemistry, The University of Massachusetts at Amherst, Amherst, Massachusetts 01003.

Received September 22, 1988; Revised Manuscript Received November 30, 1988

ABSTRACT: The molecular orientation of two discotic liquid crystals, hexahydroxybenzene hexa(*n*-octanoate-6,6-d_2) (BH8-6,6-d_2) and a poly(benzene hexa-*n*-alkanolate) (PBHA-18), on external surfaces has been measured by unpolarized infrared radiation. The method allows the orientation of molecules in a cast film to be obtained as a function of temperature without tilting the sample. Discotic cores in the crystal phase of the cast film orient predominantly parallel to the external surface. The measured orientation function decreases when the temperature is raised and can be used to follow changes in molecular orientation with temperature through various phase changes and to characterize some of the accompanying structural changes. Orientation of the flexible hydrocarbon chains in the crystal phase of the oriented film is nearly parallel to the disklike cores, indicating that the gauche conformation of the C–O–C*O*–C bond is more stable than the trans one. Significant disordering of the flexible side chains occurs at the solid–solid phase transition, and the chain ends disorient much more readily than do groups near the aromatic core. Polarization characteristics of observed infrared bands are reported.

Introduction

Disklike (discotic) molecules or polymers often form thermotropic liquid-crystalline phases. The chemical structures of the molecules used in this work are well defined, and their phase transitions occur at temperatures less than 100 °C. This fact allows many experiments to be carried out to characterize the structural changes that accompany temperature and phase changes in these materials.

A number of liquid-crystalline molecules or polymers have been reported in the literature. Perhaps the most well characterized is the family of hexasubstituted benzenes, although there are other interesting candidates available.[1-4] Previous structural characterization studies of the disklike molecules used in this investigation include scattering,[5,6] thermal analysis,[7-9] nuclear magnetic resonance spectroscopy,[10] and vibrational spectroscopy.[11-13] Each of these experiments provides different structural information. Vibrational spectroscopy has provided a measure of the temperature-induced change in conformation of the side chains attached to the central core,[11] and the amount of conformational or orientational disorder in the hydrocarbon side chains has been obtained as a function of temperature by using site-specific deuterium-labeled samples prepared in these laboratories.[11,12]

Several aspects of the structures of these disklike molecules or polymers remain unclear. For example, the conformation of the C*O*–C bond orientation relative to the central plane is not understood, where C* is the carbon of the ester group. How the central cores pack relative to the principal axis of individual columns or how these parameters change as a function of temperature and at phase transitions also remain as open questions.

Highly oriented discotic systems are difficult to obtain. Under certain experimental conditions, these liquid-crystalline molecules orient significantly on external surfaces.[13] At least two different approaches have been proposed to characterize such oriented films.[14,15] These involve tilting the oriented film in the incident beam in order to obtain polarized spectra as a function of tilt angle. Since the signal intensity decreases rapidly with tilt angle, the method has been found more suited to determination of true absorbance than to orientation when dispersive infrared spectrometers are used.[15] Even with the greater light flux of Fourier transform infrared instrumentation, the method is of limited utility for orientation studies. The need to use bulky heating stages imposes an additional constraint, for the stages stop the beam incident on the sample at relatively small tilt angles.

In the current study, we have developed a useful and simple spectroscopic technique to characterize the structures of these discotic molecules. The conformations have been characterized in each phase, and changes have been followed as a function of temperature, allowing association of structural changes with the transitions observed by other techniques. These results are reported here.

Experiment

Synthesis and Characterization of Disklike Molecules and Polymer. Disklike molecules, a series of hexahydroxybenzene hexa-*n*-alkanoates (denoted BHn), have been prepared in our laboratories.[11-13] To probe local conformations of side chains, BHn's were prepared with site-specific deuterium labels. In the work reported here, BH8-6,6-d_2 is used. Each of the six side chains carries two deuterium atoms at the sixth carbon in the eight carbon chain. Mass spectrometric analysis using fast-atom bombardment with direct chemical ionization showed that the sample contains 85% d_{12} and 15% d_{11}. Discotic polymer was synthesized by

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* Author to whom correspondence should be sent.
[†] Polymer Science and Engineering Department.
[‡] Department of Chemistry.

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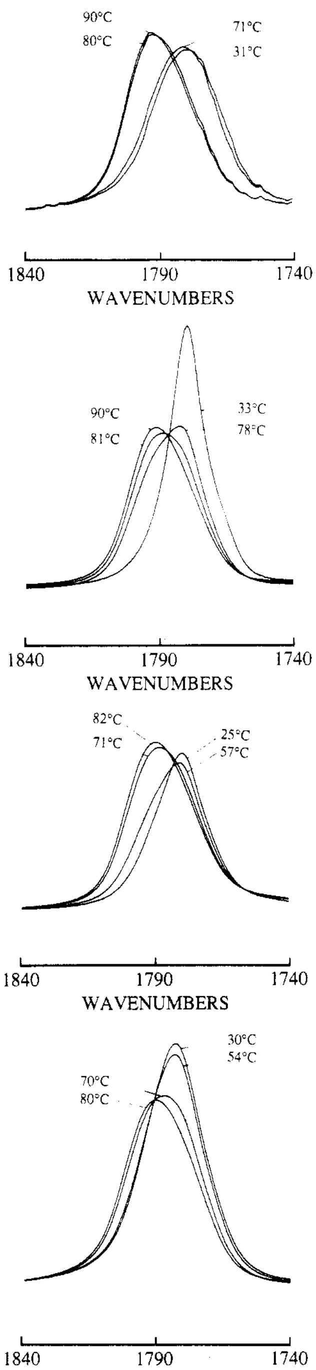

Figure 1. Infrared spectra in carbonyl stretching region. (a, top) Oriented film of BH8-6,6-d_2 at 31, 71, 80, and 90 °C. (b, bottom top middle) Unoriented KBr mull of BH8-6,6-d_2 at 33, 78, 81, and 90 °C. (c, bottom middle) Oriented film of PBHA-18 at 25, 57, 71, and 82 °C. (d, bottom) Unoriented KBr mull of PBHA-18 at 30, 54, 70, and 80 °C.

condensation of hexahydroxybenzene 1,2,4,5-tetraheptanoate ester with the acid chloride of hexadecanedioic acid in 1,1,2,2-tetrachloroethane in the presence of pyridine. The product, poly(benzene hexa-*n*-alkanolate), is designated PBHA-18 in order to conform to the BHn usage of reflecting the total of 18 carbons in the connecting chain and was precipitated by addition of a large excess of methanol. Repeated washing with methanol followed by drying in vacuo at 40 °C gave an 88% yield of a white solid. The proposed structure is in full accord with the results of C and H elemental analyses and with infrared and ^{1}H and ^{13}C NMR spectroscopies. Vapor pressure osmometry determination of the number-average molecular weight gave a value of 4600.

Phase transition temperatures for these samples observed by differential scanning calorimetry (Perkin-Elmer DSC-II) were as follows: for BH7, $T_{K,D}$ = 80 °C and $T_{D,I}$ = 86 °C; for BH8-6,6-d_2, $T_{K,D}$ = 80 °C and $T_{D,I}$ = 82 °C; and for PBHA-18, $T_{K,D}$ = 56 °C and $T_{D,I}$ = 67 °C.

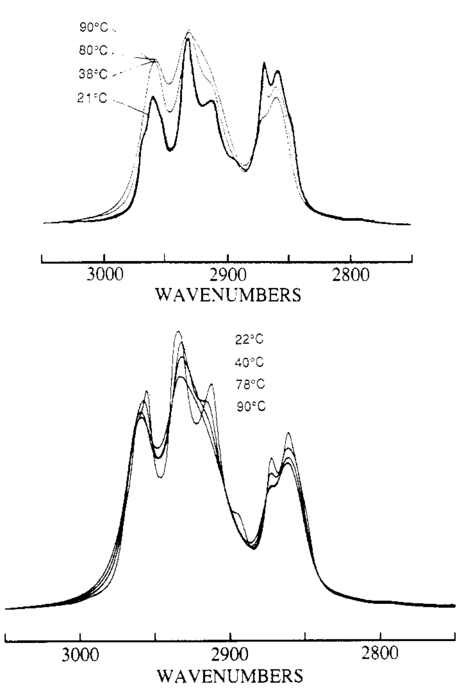

Figure 2. Infrared spectrum of BH8-6,6-d_2 in CH stretching region. (a, top) Oriented film. (b, bottom) Unoriented KBr mull.

Spectroscopic Measurements. All infrared spectra were obtained with an IBM IR32 Fourier transform infrared spectrometer. The spectra resolution was maintained at 2 cm^{-1}. At least 256 scans were signal averaged. A heating cell was constructed to hold 25-mm-diameter KBr disks. A proportional temperature controller was built which allowed control of the sample temperature to within 0.1 deg.

Oriented samples of the disklike molecules and of the polymer can be prepared by sandwiching the as-prepared powders between two KBr windows. The thermal history is extremely important to achieve significant molecular orientation on these external surfaces. All the samples were heated to 90 °C for 15 min and then cooled slowly over a period of 1.25 h to 69 and 59 °C for BH8-6,6-d_2 and PBHA-18, respectively. These samples were kept at these temperatures for an hour and were then cooled to room temperature. Samples prepared in this fashion can achieve a reasonably high degree of orientation. The nonoriented samples were prepared by mulling with KBr powder. The mulls were pressed to disks to 2–3-mm thickness.

Results and Discussion

Analysis of Molecular Orientation. Significant differences are found when infrared spectra obtained of films cast on a KBr plate are compared with spectra of samples mulled in KBr. These spectroscopic differences are associated in part with molecular orientation on external surfaces. As the temperature is changed, the average orientation and conformation change, and this produces changes in intensities that reflect alterations in molecular interactions, including those with the external surface. Figure 1 displays the C=O stretching vibration for a disklike molecule and a polymer in KBr mull and as a cast film as a function of temperature. Changes in both frequency and intensity are evidently different for the four different cases. Figures 2–4 show the CH or CD stretching regions. The relative intensities of these bands differ appreciably for both the disklike molecules and the polymers, depending on the sampling method used. The anisotropic cast films should display orientational, interactional, and conformational effects, while orientational effects in these spectra are expected to vanish in the isotropic KBr mulls. When the spectra of the film and mull at each temperature

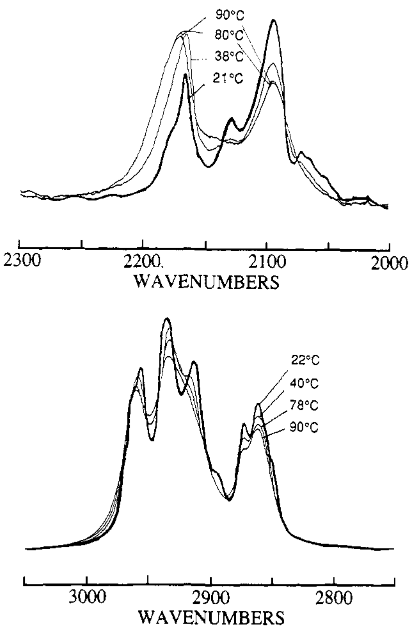

Figure 3. Infrared spectrum of BH8-6,6-d$_2$ in CD (top) and CH (bottom) stretching region.

are compared, orientational effects may be isolated, since conformational and interactional effects are expected to be common.

It is possible to obtain an experimental measure of the molecular orientation on the external surface at each temperature by comparing the integrated intensity of each isolated band of the anisotropic sample to that of the mull. The integrated band intensity, $I(T)$, can be expressed at each temperature as

$$I(T) = NkE^2M_0^2[\langle A_x(T)^2\rangle + \langle A_y(T)^2\rangle] \tag{1}$$

where k is a coefficient that depends on universal constants and absorption geometry, N is the number of molecules subtended by the incident beam, E is the incident electric field strength, M_0 is the change in dipole moment with respect to the normal coordinate, the $A_i(T)$'s are directional cosines of M_0 measured with respect to the surface normal defined as the Z direction, and the angle brackets refer to averages taken over all absorbing molecules in the beam. At normal incidence, only the X and Y components can be observed. Direct observation of the Z component requires the surface normal to be inclined to the beam propagation direction. However, since the squared directional cosines must sum to unity for any contributor to the averages, and thus for the averages, eq 1 may be written as

$$I(T) = NkE^2M_0^2[1 - \langle A_z(T)^2\rangle] \tag{2}$$

and if $NkE^2M_0^2$ can be determined, $\langle A_z(T)^2\rangle$ can be measured by measuring $I(T)$. Such a direct approach is not experimentally convenient, as the coefficients $NkE^2M_0^2$ are difficult to measure directly, and in the work that follows, a ratio method is adopted to remove them from the analysis. Let the degree of molecular orientation on the surface be represented by a function f, defined as

$$f = \langle A_x(T)^2\rangle + \langle A_y(T)^2\rangle \tag{3}$$

For a completely isotropic system, each orientation to the beam axis is equally probable, the squared directional cosine angle averages are each $^1/_3$, and f is then $^2/_3$. Any value of f that departs from $^2/_3$ would then provide a measure of molecular orientation, which can be obtained by comparing the band intensity for the cast film with that for the mull. Let $I_A(T)$ represent the measured integrated band intensity for the anisotropic film and $I_B(T)$ that for the mull. Then,

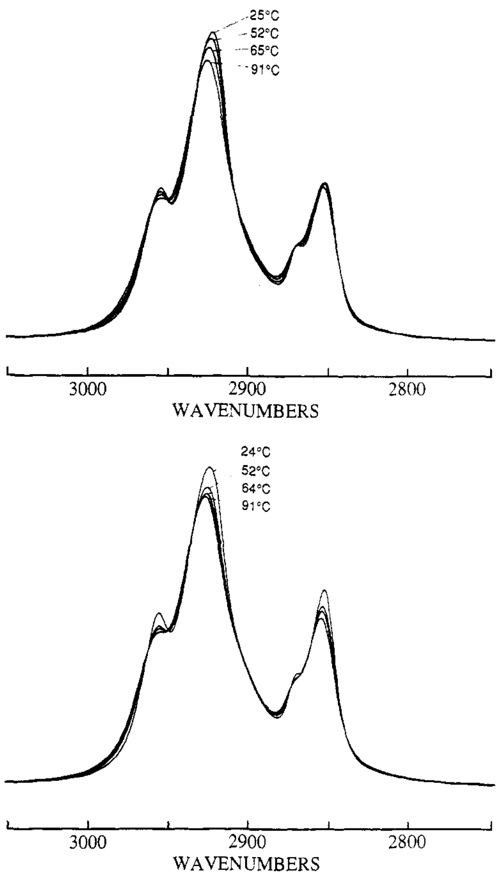

Figure 4. Infrared spectrum of PBHA-18 in CH stretching region. (a, top) Oriented film. (b, bottom) Unoriented KBr mull.

$$I_A(T)/I_B(T) = (N_A/N_B)[f/(2/3)] \tag{4}$$

where N_A and N_B are the numbers of molecules in the beam respectively in the film and mull. At temperatures above 82 °C, the samples are all in the isotropic state, and the intensity ratio measures the number ratio N_A/N_B. Experimentally, 90 °C lies well above the discotic–isotropic phase transition and was selected to measure the ratio $N_A/N_B = I_A(90)/I_B(90)$. The function, f, at different temperatures is then

$$f = (2/3)[I_B(90)/I_A(90)][I_A(T)/I_B(T)] \tag{5}$$

The dichroic ratio, R_Z, can be defined as

$$R_Z = \langle A_z(T)^2\rangle/\langle A_x(T)^2\rangle \tag{6}$$

Since the x and y axes are equivalent, $\langle A_x(T)^2\rangle$ and $\langle A_y(T)^2\rangle$ are the same and the dichroic ratio is

$$R_Z = 2\langle A_z(T)^2\rangle/[1 - \langle A_z(T)^2\rangle] \tag{7}$$

In terms of the function f, R_Z becomes

$$R_Z = 2(1 - f)/f \tag{8}$$

When the average transition moment is inclined to the surface normal, the orientational distribution function, F, is

$$F = [(R_Z - 1)/(R_Z + 2)] \tag{9}$$

F may also be written as

$$F = (3 \cos^2 \theta - 1)/2 \tag{10}$$

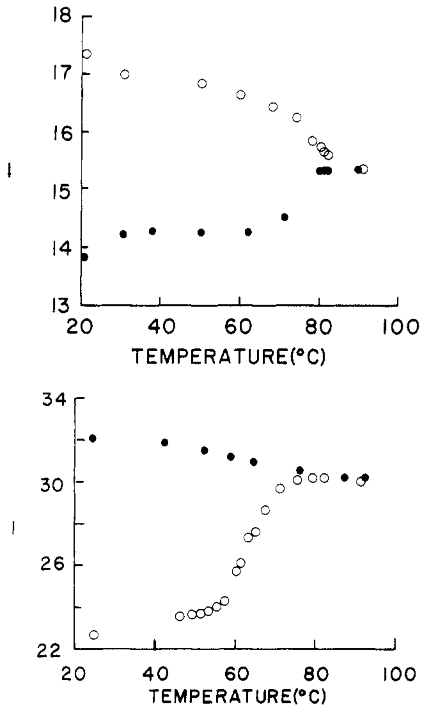

Figure 5. Intensity normalization in isotropic phase for carbonyl band. (a, top) BH8-6,6-d_2. (b, bottom) PBHA-18.

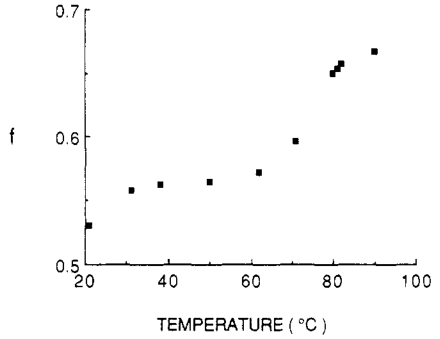

Figure 6. Measurable absorption ratio, I_A/I_B, as a function of temperature for BH8-6,6-d_2.

where θ is the angle between the average transition moment direction and the surface normal. In terms of f, the orientational distribution function, F, may be written as

$$F = (2 - 3f)/2 \qquad (11)$$

or, if N_A and N_B are the same, simply as $1 - I_A/I_B$. However, experimentally it is more convenient to use eq 5 to measure f and eq 11 to measure F.

The intensities for the C*═O* stretching vibration observed in BH8-6,6-d_2 and PBHA-18 are summarized in Figure 5. By use of the above relations, f, R_Z, and F can be calculated, and their changes as a function of temperatures are displayed in Figures 6–8. In the absence of symmetry, the analysis can be conducted for each localized vibration in order to obtain the orientation of individual chemical groups. The presence of symmetry forces linear combinations of symmetrically equivalent localized vibrations and restricts the results of the analysis to overall molecular orientation independent of the orientations of individual chemical groups.

Orientation of the Cores. The major goals of this investigation are to demonstrate that the oriented film/KBr mull technique can be used to assess molecular orientation on external surfaces, to elucidate the structures of disklike liquid-crystalline molecules in each phase, and to identify structural changes at phase transitions. The method also promises the polarization characteristics of infrared active vibrations.

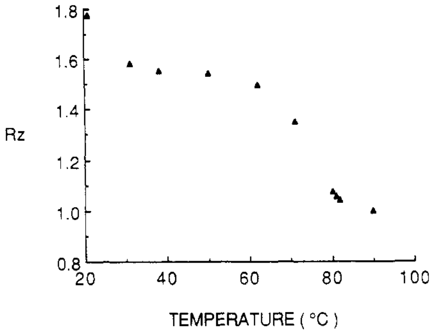

Figure 7. Dichroic ratio, R_Z, as a function of temperature for BH8-6,6-d_2.

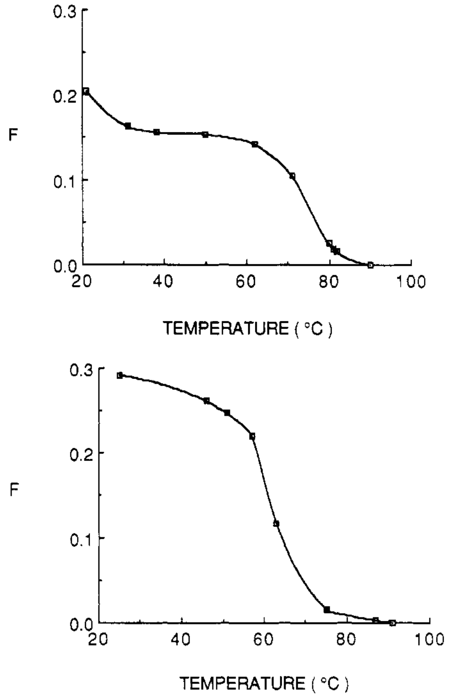

Figure 8. Orientation function, F, for (a, top) BH8-6,6-d_2 and (b, bottom) PBHA-18.

The carbonyl stretching vibration was used for the structural characterization in earlier work,[12,13] as it is highly localized. In the earlier work, it was suggested that the BHn's have molecular symmetries isomorphic with C_6 and that each of the six planes containing a O—C*═O* group makes a 57° angle with the plane of the benzene ring in the low-temperature phase. It is also possible that the BHn's may have molecular symmetries isomorphic with S_6. The work reported here cannot distinguish C_6 from S_6, since no Raman data are available. However, the interpretation of the infrared data in terms of molecular orientation does not depend on the distinction.

Due to symmetry restrictions imposed by strict C_6 symmetry, the net transition moment of the infrared active C═O stretching vibration near 1780 cm^{-1} must either lie along the C_6 axis or be perpendicular to it, independent of the angles made by these planes, for the six carbonyl stretches must transform as $A + B + E_1 + E_2$ under C_6. The A vibration has its transition moment along the molecular symmetry axis; the E_1 pair has a transition moment in a plane perpendicular to the C_6 axis; and the remaining vibrations are silent in the infrared. Raman activity is expected for the A, E_1, and E_2 vibrations. It is also possible, but unlikely, that the carbonyl group orientations alternate above and below the benzene ring, and if so, the appropriate symmetry is S_6. The infrared argument is unaltered, however, for the six carbonyl stretches must transform as $A_g + E_g + A_u + E_u$. In this case, the infrared active A_u component is polarized out of the plane of the benzene ring, while the E_u component is polarized in a plane parallel to the benzene ring; due to the presence of a center of symmetry in S_6, the A_g and E_g components are silent in the infrared but active in the Raman. Near room temperature, the infrared intensity is dominated by the A component if the symmetry is C_6 (or by the A_u component if the symmetry is S_6), and the orientation of the core on the external surface in all cases can be determined by measuring the relative intensity I_A/I_B at room temperature. After normalization (i.e., essentially setting $I_A(90)/I_B(90) = 1$), this ratio was found to be 0.795 and 0.708 for BH8-6,6-d_2 and PBHa-18, respectively. The f and R_Z values calculated from eq 5 and 8 are 0.530 and 1.774 for BH8-6,6-d_2 and 0.472 and 2.237 for PBHA-18.

Assuming that the molecules are either completely oriented or totally random in orientation, the degree of molecular orientation, F, at room temperature is then calculated from eq 9 or 11 to be 0.205 for BH8-6,6-d_2 and 0.292 for PBHA-18. The average angle made by the transition moment to the surface normal is calculated from eq 10 and is approximately 47° for BH8-6,6-d_2, while it is slightly less (about 43°) for PBHA-18. This shows that preferential packing occurs on the external surface and suggests that the orientation measured can be used to characterize structural changes associated with the phase transitions.

As expected, the orientation function for both the disklike molecules and the polymer decreases with an increase in temperature. As shown in Figures 6–8, the first decrease in the f or R_Z value occurs at the 32 °C solid–solid phase transformation. The solid structure changes from an ordered crystalline phase to a less ordered crystalline phase in this transition.[11] A decrease in molecular orientation at elevated temperatures is consistent with a loss of molecular order.[11] In a previous study, it was shown that the flexible arms exhibit a continuously increasing degree of disorder with increasing temperature.[17] The orientation of the disklike molecules is maintained at temperatures below the crystalline–discotic transition, although a decrease occurs near the 32 °C solid–solid transition. The orientational distribution function for both the disklike molecules and the polymer decreases with increasing temperature. In Figure 8, there are two breaks evident at the ordered crystal–disordered crystal (phase II–phase I) transition and in the vicinity of the discotic–isotropic transition for the disklike molecules, but there seems to be only one for the polymer. The tilt angle between the disk core and the column axis may change at the disordered crystal–discotic transition in BH8-6,6-d_2.[18]

Orientation of the Flexible Chains. The CH_2 and CH_3 stretching vibrations exhibit very significant differences for the two types of samples as shown in Figures 2–4. As shown in Figure 3, the relative intensities of the CD_2 stretching vibrations observed differ as a function of temperature. These stretching vibrations are localized with well-defined transition moment directions. Based on the orientation angle of the ring determined from the dichroic ratio of the $C^*{=}O^*$ stretching vibration, the orientation of the flexible arms attached to the core can be inferred. The conformation of these flexible arms has been found to be entirely trans in the low-temperature crystalline state by using site-specific deuterium-labeled samples.[11,12] Neither the relative orientation of these flexible arms to the central ring nor the conformation of the ester group has been determined experimentally.

In principle, the orientation of the flexible chain can be determined from the dichroism of the CH_2 or CH_3 stretching vibrations in the 2800–3000-cm^{-1} range. Expected at 2873 and 2962 cm^{-1},[20] the in-skeletal-plane symmetric and asymmetric CH stretching vibrations of the CH_3 groups in BH8-6,6-d_2 are found respectively at 2872 and 2962 cm^{-1}, as shown in Figure 2. The out-of-skeletal-plane asymmetric CH stretching vibrations of the CH_3 groups are expected near 2953 cm^{-1} but are not resolved clearly in the spectrum of BH8-6,6-d_2 at any of the temperatures used in this investigation. Both the symmetric and one of the asymmetric in-skeletal-plane CH stretching vibrations of the CH_3 groups have transition moments in the skeletal plane and are therefore expected to display very similar behavior as the temperature is changed. In fact, as shown in Figure 2, in the oriented sample the symmetric component decreases in intensity as temperature increases, while the asymmetric component displays the opposite behavior. Presumably, this apparently anomalous behavior of the 2962-cm^{-1} band is due to its composite nature, as the unresolved in-skeletal- and out-of-skeletal-plane components of the asymmetric CH stretching vibrations contribute to the absorption differently at different temperatures as the chains alter conformations. Thus, both the symmetric CH stretch and the in-skeletal-plane asymmetric stretch decrease in intensity with increasing temperature in the oriented sample, while the out-of-skeletal-plane asymmetric stretch increases in intensity. Although the transition moment associated with the in-skeletal-plane bands lies in the skeletal plane, probably nearly along the CH_2–CH_3 bond, interpretation of orientational intensity contributions may be obscured by Fermi resonance of the 2873-cm^{-1} band with the first overtone of the asymmetric CH_3 deformation. Small environmentally induced shifts in the fundamental frequencies can lead to large changes in the intensity of one component relative to the other as the resonance condition is altered.

The symmetric CH_2 stretching vibration near 2860 cm^{-1} has a transition moment in the plane containing the planar zigzag carbon skeleton.[20] The asymmetric CH_2 stretching vibration expected near 2920 cm^{-1} splites in the crystal at room temperature into two components at 2933 and 2914 cm^{-1};[20] the splitting is removed in the higher temperature phases. Since the symmetric and asymmetric CH_2 stretching vibrations have mutually perpendicular transition moments, changes in the relative intensities of the two bands can indicate chain orientation with respect to the core. However, the bands are composites of a number of nearly degenerate CH_2 stretching contributors which characterize the behavior of whole chains rather than of individual CH_2 groups. Nonetheless, Figure 2 shows that in the oriented sample of BH8-6,6-d_2 the asymmetric CH_2 stretch increases in intensity with increasing temperature, while the symmetric component decreases, relative to the unoriented sample.

The two stretching modes of the CD_2 group in BH8-6,6-d_2 provide dependable orientation information. The transition moment of the symmetric CD_2 stretching vibration lies in the plane of the carbon atoms, while that of the asymmetric CD_2 stretching vibration is orthogonal to it. Figure 3 shows that in the oriented sample of BH8-6,6-d_2 the higher frequency asymmetric component of the CD_2 stretching vibration intensifies with increasing temperature, while the intensity of the symmetric component decreases. These changes indicate that, at the 6 position, the planar zigzag chain is roughly parallel to the

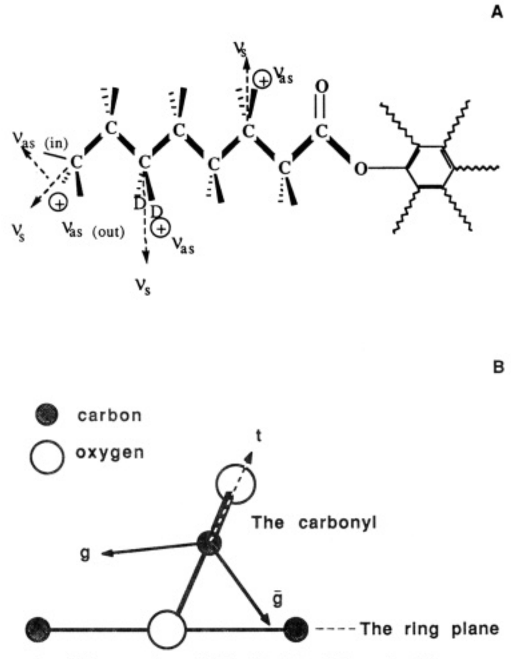

Figure 9. Orientation of the C*O*–C bond with respect to the core.[15]

external surface and thus to the benzene ring at room temperature. The chain disorders with increasing temperature to allow increasingly larger numbers of CD_2 groups to rotate and bring the asymmetric CD_2 stretching transition moment roughly parallel to the external surface. Since the symmetric CD_2 stretching transition moment is perpendicular to that for the asymmetric CD_2 stretch, the opposite behavior is found for it.

All these spectroscopic changes indicate that at low temperatures the plane containing the zigzag chain is nearly parallel to the benzene ring. These results are consistent with the rotational isomeric model for the C–C*O* bond in ester molecules proposed by Abe.[19] In that model, the lowest energy state is the gauche conformer. The schematic drawing shown in Figure 9 indicates that the trans conformation will lead to the plane of the zigzag carbon chain being approximately perpendicular to the central core. Only the g or g′ conformations can yield the dichroism observed for the CH_2, CH_3, and CD_2 stretching vibrations and be consistent with the Abe model.[19] Thus, the gauche conformer of the C–C*O* bond is the lower energy state, and in this state, the zigzag carbon chain lies in a plane nearly parallel to that of the benzene ring.

Disorder of the Flexible Chains. The studies conducted in earlier work using specifically labeled deuterium-substituted molecules provided a measure of conformational order as a function of temperature.[11] In the current study, changes in the characteristics of polarized infrared spectra are consistent with the expected disruption of conformational order as temperature increases. Because of extensive band overlap in the CH stretching region, estimates of structural order can only be given with band heights rather than band areas. For each temperature, the absorbance difference measured for the unoriented and oriented samples, $P(T)$, defined as

$$P(T) = 100[I_B(T) - I_A(T)]/[I_B(25) - I_A(25)] \quad (12)$$

is a function of molecular orientation. This difference is a maximum at room temperature, decreases as temperature increases, and finally vanishes when both samples attain the isotropic phase. This difference is plotted as a function of temperature in Figure 10, which shows, first, that the major change in the structural order occurs at the solid–solid transition and, second, that the CH_3 vibrations change much more than do the CH_2 vibrations. These facts suggest that the chain ends may disorient much more readily than do the groups near the core. This suggestion has been confirmed by using a series of specifically deuterium-labeled molecules. Details will be reported in a separate publication.

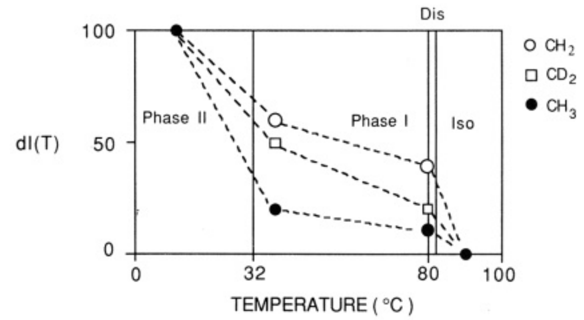

Figure 10. Phases and $P(T)$ for CH_2, CH_3, and CD_2 stretching vibrations of BH8-6,6-d_2.

Analysis of the bands due to the C=O stretching vibration suggests that the degree of core orientation on the external surface may be higher for the polymer than for the molecule. Intensity changes for the CH_2 stretching vibrations of the polymer are much smaller than are those for the small molecules. This indicates that despite the slightly greater tendency of the central cores to orient, the polymer contains a considerable amount of conformational disorder in the flexible chains even at room temperature. Thermotropic liquid-crystalline polymers are known to contain only polymethylene chains that lie in a narrow range of lengths. For the disklike polymers, if the chain has insufficient flexibility, the columnar phase may be difficult to form; if the chain is too flexible, the conformational entropy may overwhelm the orientational entropy contribution to the free energy, and the columnar phase may again be difficult to form. Based on Chandrasekhar's diffraction data for BH7,[5] a connecting chain that contains 18 carbon atoms, such as that used in synthesis of PBHA-18, would have to contain several gauche bonds to make the polymer fit the discotic lattice formed by the monomer. While there is no evidence in the work reported here that the organization of the polymer is columnar or that if columnar it has lattice dimensions similar to those of the monomer, it is entirely possible that the polymethylene chain connecting the disks in the polymer may be long enough to allow columnar structures to form. If so, the chain cannot be fully trans in conformation and simultaneously satisfy spatial requirements imposed by monomer column spacing. Furthermore, the number of gauche conformers along the chain could not change much with temperature if the columnar phase were maintained with monomer column spacing, consistent with the striking near temperature independence of the CH_2 stretching bands of PBHA-18.

Band Polarization. No detailed vibrational spectroscopic analysis appears to be available for these disklike systems. The polarization characteristics of observed infrared bands are normally expected to be useful as aids to the assignment of fundamentals. The entries in Table I include the most prominent infrared bands of an oriented film with the polarization measured as parallel or perpendicular to the surface normal at room temperature, using unpolarized incident radiation with a KBr mull standard as described above. The polarization of localized vibrations such as the CH_3 symmetric deformation mode at 1375 cm^{-1} is interesting. With the planar zigzag hy-

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Table I
Dichroism of Infrared Bands for Disklike Molecules and Polymers

BH8-6,6-d_2		PBHA-18	
cm^{-1}	dichroism	cm^{-1}	dichroism
		1780	perpendicular
1778	perpendicular		
1760	parallel		
1483	perpendicular		
1439	parallel		
1433	parallel		
		1416	perpendicular
1415	parallel		
		1379	parallel
1375	parallel		
1321	parallel		
1287	perpendicular		
		1233	parallel
		1220	parallel
1220	parallel		
		1202	parallel
1188	perpendicular		
1173	parallel		

drocarbon chain attached to the oxygen on the benzene ring in the gauche conformation, the six CH_3 deformation modes transform under C_6 symmetry as $A + B + E_1 + E_2$, or as $A_g + E_g + A_u + E_u$ under S_6 symmetry, just as do the carbonyl stretching modes. Again, the A or A_u component has its transition moment along the molecular symmetry axis and is thus parallel to the normal to the external surface when the disklike cores are oriented parallel to it, even though the transition moment of any individual CH_3 symmetric deformation may be inclined at different angles to the plane of the benzene ring and the 6-fold symmetry axis. Thus, no information concerning these angles or the orientation of the zigzag hydrocarbon chain can be secured from the polarization state in the oriented crystal. The E_1 or E_u component is required to have its transition moment in a plane perpendicular to the 6-fold axis, but there is no further directional requirement imposed by symmetry. Possibly this component does not appear in the infrared with appreciable intensity because of an indeterminacy in phase from one molecule to the next, due to small intermolecular interactional forces. Evidently, similar comments apply to the other entries in Table I.

Acknowledgment. We thank Walter Davidson, Kratos Analytical, Inc., Ramsey, NJ, for mass spectroscopic results. This research has been supported by a grant from the Materials Research Laboratory for Polymer Studies at the University of Massachusetts and a grant from the National Science Foundation, Polymers Program, Grant DMR-8407539.

Registry No. BH8-*6,6-d_2*, 111268-95-2; (hexadecanedioic acid chloride)(hexahydroxybenzene 1,2,4,5-tetraheptanoate) (copolymer), 119243-75-3; (hexadecanedioic acid chloride)(hexahydroxybenzanoate) (SRU), 119365-99-0.

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Carbon-13 NMR Investigation of Local Dynamics in Bulk Polymers at Temperatures Well above the Glass-Transition Temperature. 4. Polyisobutylene

R. Dejean de la Batie, F. Lauprêtre,* and L. Monnerie

Laboratoire de Physico-chimie Structurale et Macromoléculaire associé au C.N.R.S., 10 rue Vauquelin, 75231 Paris Cedex 05, France. *Received October 19, 1988*

ABSTRACT: Carbon-13 spin–lattice relaxation time measurements have been performed at two experimental frequencies on the considered polymer in solution and in the bulk state at temperatures well above the glass-transition temperature. The data have been analyzed by using the orientation autocorrelation functions developed for polymers and a modified function proposed for poly(vinyl methyl ether) in a previous paper.[1] As observed in the latter compound and other polymers, a fast motion of the internuclear vector must be considered. It can be assigned to librations of limited but significant extent about the rest position. Moreover, the temperature dependence of the segmental motions in bulk polyisobutylene can be understood by considering both glass-transition and secondary relaxation processes.

Detailed analysis of carbon-13 nuclear magnetic relaxation in poly(vinyl methyl ether), poly(propylene oxide), and cross-linked poly(ethylene oxides), polybutadiene, and polyisoprene, either in solution or in bulk at temperatures well above the glass–rubber transition temperature T_g, has been reported in the first papers of this series.[1–3] It has been shown that the well-known autocorrelation functions derived from models of conformational jumps in polymer

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