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Spectroscopic Characterization of the Microstructures in Disklike Liquid Crystalline Molecules: Model Compound for Polymers

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ABSTRACT: Vibrational spectroscopy has been used to analyze the microstructures of disklike crystalline macromolecules. These analyses suggest that the structure of the polymethylene sequences are correlated to the phase behavior of the three molecules studied. Spectroscopic analysis also suggests that two distinct conformations are associated with the ester groups attached to the "core" rings. The relative intensities of the two components correlate well with the phase transitions observed.

Introduction

Even though disklike liquid crystalline macromolecules have been recognized for only a relatively short time,[1] a considerable amount of interest exists in better characterizing their mesophases and associated properties.[1-6] The main purpose of our study is to analyze the microstructures in several of the phases found and to define those structural units necessary to achieve the liquid crystalline state.

The structures of these disklike or platelike molecules are fairly unique. In the present study, the compounds we are studying are benzenehexa-*n*-alkanoates, as shown schematically in Figure 1, although samples with considerably different cores have also been prepared. The "branches" attached to the benzene rings may vary in length and seem to influence their phase behavior.[1] Three homologues with $n = 6$–8, where n is the number of carbons in the branch, (denoted as BH6, BH7, and BH8, respectively) are the main subjects of our study. Several transitions associated with these macromolecules have been determined by thermal studies and optical microscopy.[1] Primarily on the basis of X-ray diffraction studies,[2] structures associated with some of the various phases have been proposed. The most interesting finding is that the homologue with $n = 6$ does not exhibit the intermediate liquid crystalline phase between the crystalline and isotropic phases found at extreme temperatures. For homologues with $n = 7$ or 8, these molecules do possess an intermediate state. The proposed structure for this intermediate state contains lamellar order with hexagonal symmetry in two dimensions and liquid like disorder in the third.[2] In fact, this intermediate phase is referred to as discotic or columnar, with the disks stacked on top of each other, forming columns. However, the spacing along the column axis is irregular. There is some uncertainty associated with the interpretation of the phase transitions found for the $n = 6$ molecule. In the initial study, it was proposed that this molecule also contained this intermediate phase, a conclusion that was subsequently modified.[2] Instead, a solid-solid transition was proposed.

Even though the existence of various phases and their transition temperatures have been previously established, experimental evidence suitable for microstructural analysis is rare. Most of the studies, including thermal measurements or optical microscopy, are not actually directed at

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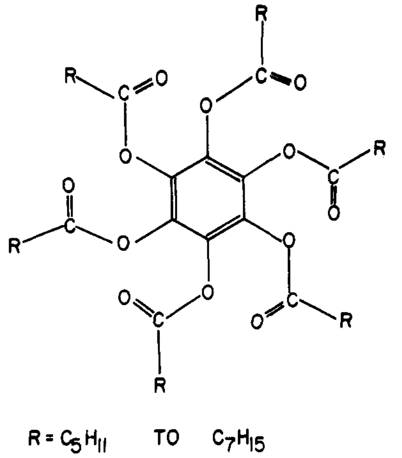

Figure 1. Schematic structure of benzenehexa-*n*-alkanoates.

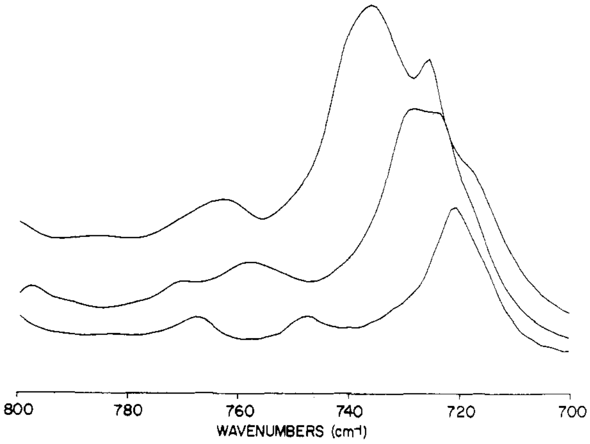

Figure 2. Infrared spectra of the CH_2 rocking region of benzenehexa-*n*-alkanoates obtained at room temperature, band resolution 2 cm^{-1}, 1000 scans. Top, BH6; middle, BH7; bottom, BH8.

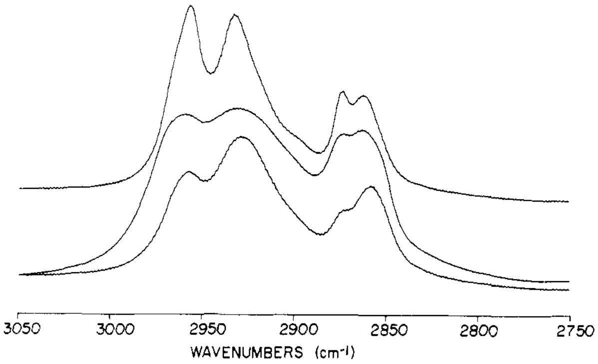

Figure 3. Infrared spectra of the CH stretching region of BH*n* at room temperature, band resolution 2 cm^{-1}. Top, BH6; middle, BH7; bottom, BH8.

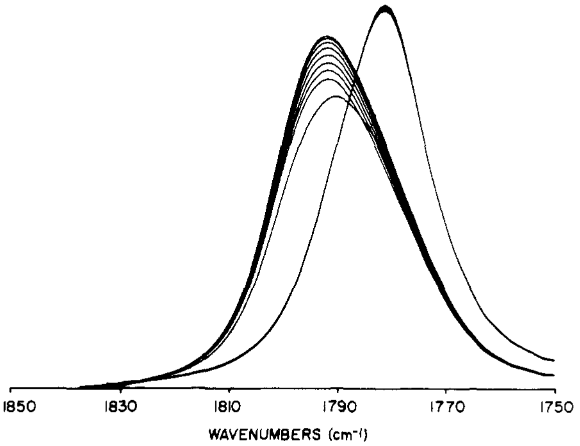

Figure 4. Infrared spectra of the C=O stretching region of BH6 at various temperatures, band resolution 2 cm^{-1}.

obtaining the details of the microstructures. X-ray diffraction results obtained from each of the phases have not been very informative and can only suggest the packing changes associated with each of the phases found.

Vibrational spectroscopy is the primary technique used in our laboratory for microstructural analysis. The specific information we seek elucidates the structural aspects of the "core", the alignment or the straightness of the polymethylene units, and their changes as a function of temperature. With vibrational spectroscopy, specific bands are also obtained that are associated with the ester groups and are characteristic of their conformation or packing. However, because of differences in the relative absorption of the aromatic units and the polymethylene units, it has usually been difficult to find bands in the vibrational spectra of thermotropic liquid crystals that can be used for structural characterization. For these discotics, which contain an exceedingly high percentage of methylene units relative to aromatic units, vibrational transitions arising from the polymethylene units have been easily assigned. On the basis of an earlier analysis of normal paraffins, the changes we observe for the methylene sequences in these discotics provide us with an opportunity to examine the "straightness" of the chains. Because of the similarity in structure between these discotics and other liquid crystalline polymers, the structural information we deduce from the spectroscopic analysis of this system can be transferred to other thermotropic liquid crystals as well. The experimental evidence showing the differences between various phases and some interpretation are reported here.

Experimental Section

The three samples used in this study were prepared in a manner similar to that used in previous studies. The hexaesters were synthesized from hexahydroxybenzene[7a] as described by Neifert and Bartow.[7b] To remove traces of fluorescent impurities, samples were recrystallized several times from absolute ethanol. Structures were confirmed by ^1H NMR spectroscopy at 300 MHz. Final samples were homogeneous on TLC and HPLC (25 cm × 4.6 mm Perkin-Elmer/Analytical C-18, 10-μM particle size, eluent 95% aqueous methanol for BH6 and BH7 and absolute methanol for BH8). Transition temperatures by optical microscopy and differential scanning calorimetry are those reported by Chrandrasekhar.[1,2] Thin films were cast on potassium bromide disks from chloroform solutions. In cases where thicker samples were needed, films were cast from the melt onto potassium bromide disks.

Infrared spectra were obtained with either International Business Machines Model 32 or Model 98 Fourier transform infrared spectrometers. The samples were placed in a heating cell built in our laboratory, and spectra were obtained at temperatures ranging from ~20 to 200 °C. All spectra were taken with a 2-cm^{-1} spectral resolution. Generally, 256 scans were signal-averaged to obtain a very high signal-to-noise ratio.

The CH_2 rocking regions of the three molecules are shown in Figure 2. The high-frequency CH stretching vibrations are shown in Figure 3. The C=O stretching vibration shows particular sensitivity to the phase transitions in these samples. The infrared spectra obtained as a function of temperature for the BH6 and BH7 samples are shown in Figures 4 and 5, respectively.

The Raman spectra were obtained with a Ramanor HG.2S spectrometer. This spectrometer was modified so that a microprocessor controls it in order to facilitate data collection, display, and storage. The band-pass is kept at 2 cm^{-1} at 5100 Å. The laser excitation is the 5145-Å line from an argon laser. In this case a small amount of sample can be kept and examined in a capillary tube. A Harney–Miller cell was adapted to our sample chamber

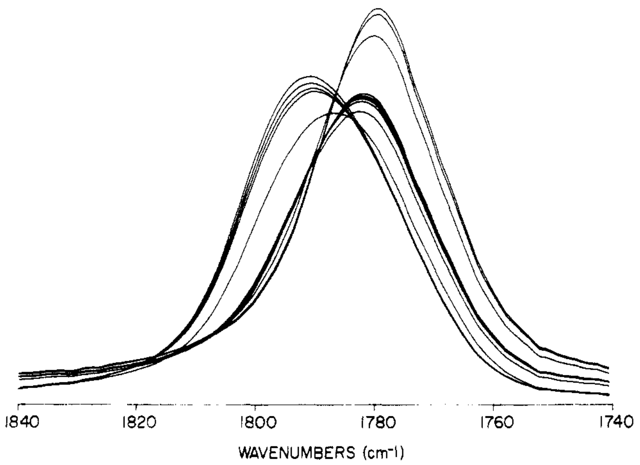

Figure 5. Infrared spectra of the C=O stretching region of BH8 at various temperatures, band resolution 2 cm^{-1}.

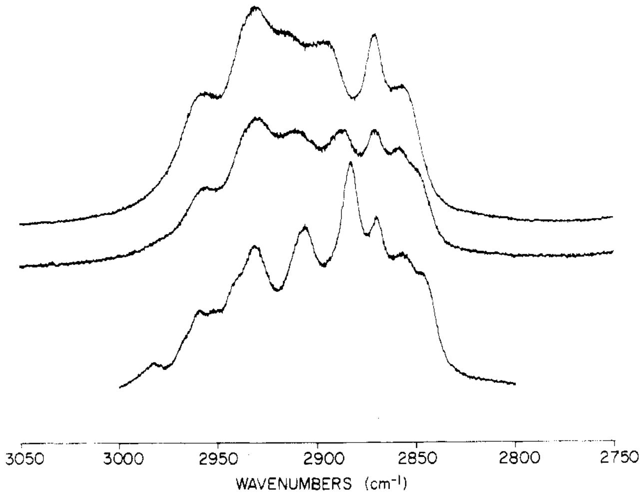

Figure 6. Raman spectra of the CH_2 stretching region of BH*n* at room temperature, 2-cm^{-1} band-pass at 5100-Å excitation. Top, BH6; middle, BH7; bottom, BH8.

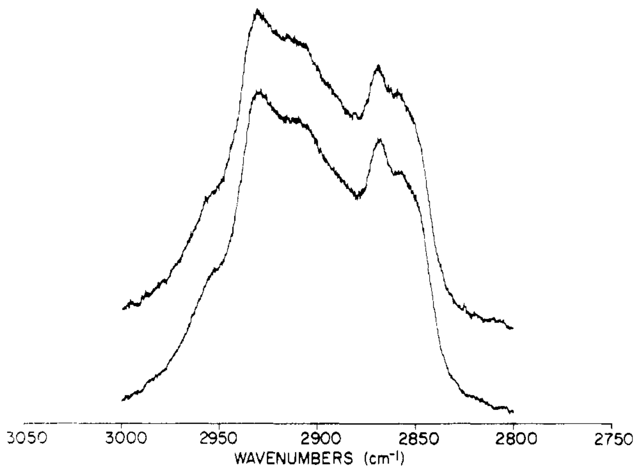

Figure 7. Raman spectra of the CH stretching region of BH7 at high temperatures, 2-cm^{-1} band-pass at 5100-Å, 5145-Å excitation. Top, 80 °C; bottom, 96 °C.

so that the temperature of the sample could be varied from approximately -160 to +200 °C. All the Raman spectra collected were sent through the serial port of the microprocessor to an International Business Machines Model 9000 computer for further analysis.

The Raman spectra in the CH stretching region are shown in Figure 6. The Raman spectra in this region obtained at high temperatures are virtually identical for all three molecules. Representative spectra obtained for the BH7 sample are shown in Figure 7.

When necessary, in order to obtain a more quantitative measure of the contributions of overlapping components, band deconvolution routines using nonlinear regression algorithms have been written for the IBM 9000 computer associated with the infrared spectrometer. In general, an observed composite band can be approximated by a Lorentzian function or a sum of Lorentzian and Gaussian functions. In the former case $f(x) = Af_1(x)$, whereas in the latter case $f(x) = A[(1 - g)f_1(x) + gf_2(x)]$. In these equations: $f_1(x) = \exp[-(\ln 2)(2(x - x_0)/\Delta x)^2$ and $f_2(x) = 1/[1 + 2((x - x_0)/\Delta x)^2]$, where x is the position along the abscissa, x_0 is the position of the peak, Δx is the bandwidth, g is the relative contribution of the Gaussian component, and A is the relative amplitude. In the band resolution, the computer programs were designed to accept three (height, position, and half-width) or four (height, position, half-width, and g) parameters for each peak, depending on whether the Gaussian or a combination of Gaussian and Lorentzian functions was used. The least-squares fitting was carried out with the observed data stored on the IBM 9000 computer associated with the Fourier transform infrared spectrometer. The original data and the fitted curve can be compared visually after each fit. In the crystalline state, one Lorentzian band gives excellent fit. However, two bands are necessary to describe the observed data in the discotic or isotropic phases. No constraint was placed on the variation of parameters used. In general, 10–50 iterations were carried out until the change χ^2 was reduced to less than 0.1% of the value calculated in the previous iteration. Convergence to local minimum in χ^2 space was avoided by a computer search of the region around the minimum.

Results and Discussion

One of the main goals of our analysis is the characterization of the structural aspects of disklike or platelike liquid crystalline macromolecules in various phases. It is generally accepted that this type of molecule forms columns similar to stacks of chips or coins.[1,2] The "cores" stack on top of each other with the "branches" extended from the core. However, it is not clear what structural differences exist between the molecules that do form the liquid crystalline phase vs. those that do not. Nor is it clear how structural disorder is introduced when the temperature is increased. Therefore, a main objective of our spectroscopic analysis is to assess the "straightness" of the polymethylene chain. This aspect of the chain structure has also been the focus of much discussion in other studies of thermotropic liquid crystalline polymers.[8-10] Much of our present study is based on the extensive analysis carried out previously for normal paraffins.[11-13]

As can be seen in Figure 2, the CH_2 rocking vibrations of the three molecules differ considerably. The strong peak observed in the 700-cm^{-1} region is found at 733, 730, and 721 cm^{-1} for the BH6, BH7, and BH8 molecules, respectively. Numerous previous studies have shown that the CH_2 rocking vibration in the 700-cm^{-1} region is particularly sensitive to chain packing in polymethylenes.[12,13] The usual spectroscopic features observed include a doublet at approximately 720 and 730 cm^{-1} arising from crystal field splitting.[14-16] None of the molecules studied shows this evidence of intermolecular interaction, making it very unlikely that "branches" pack in a well-defined unit cell. The CH_2 rocking vibration has also been found to be characteristic of the localized conformation of polymethylene sequences.[17] This rocking vibration is usually found near 720 cm^{-1} only when a minimum of four consecutive trans sequences exist.[12,17] Therefore, we would interpret that the polymethylene sequences in BH6 or BH7 do not exist in the fully trans conformation. Only BH8 has a fully extended branch.

This conclusion is also consistent with observations in the relatively simple infrared active CH stretching region shown in Figure 3. The methyl stretching vibrations are found at 2873 cm^{-1} (methyl symmetric stretching vibration) and at 2956 and 2967 cm^{-1} (methyl asymmetric stretching vibration).[18] If the polymethylene chains are indeed fully trans in conformation, two bands near 2920 and 2855 cm^{-1} are to be expected.[18] They are assigned to the CH_2 asymmetric and symmetric stretching vibrations.[18] This is observed for the BH8 molecule only. These two bands for the BH6 and BH7 molecules are found at approximately 2933 and 2862 cm^{-1}. Essentially all of the characteristic bands assigned to fully trans polymethylene sequences, including CH_2 bending vibrations (not shown), are consistent with our interpretation of the conformations associated with the three molecules. It is interesting to note, however, that the characteristic bands for all three molecules are located at identical positions at high temperatures when the order of the polymethylene sequences in BH8 is destroyed. But it should be emphasized that it is difficult to assess quantitatively the degree of disorder causing the spectroscopic differences observed.

Although they are not as well understood, the Raman active bands in the CH stretching region can be extremely rich in structural information. The spectra obtained for the three molecules are dramatically different. In addition, their temperature dependence follows the phase transitions observed by thermal measurements. The spectra are shown in Figures 6 and 7. As mentioned earlier, virtually identical spectra in this region are obtained for BH7 or BH8 in the liquid crystalline or the isotropic phases and for BH6 in the melt. Several years ago, it was brought to our attention that significant spectroscopic changes in this region can be associated with conformation or packing changes for polymethylene sequences in lipid bilayers.[18] Those observations are unexpected since CH stretching vibrations are so highly localized that they should be relatively independent of chain microstructures. This belief has been supported by a long history of infrared spectroscopic data. Eventually, it was found that the unusually strong bands and their intensity distribution arise from Fermi resonance interaction between the appropriate CH stretching component and the overtones of the CH_2 vibrations.[18-20] The sensitivity of the Raman active CH stretching vibrations to changes in microstructure actually arise from the "amplification" associated with the Fermi resonance scheme and are therefore useful for structural analysis.

Undoubtedly, a number of the small peaks in the 2800–3200-cm^{-1} region of the spectra obtained for the BH7 or BH8 molecules are associated with the progression of CH_2 bending modes that have borrowed a considerable intensity from the CH_2 stretching vibration. From the coupled oscillator model,[11] the progression of CH_2 bending vibrations for the fully trans methylene sequences has been predicted. Despite a number of attempts however, the exact prediction of both the frequency and intensity of the components involved in the Fermi resonance interaction even for the normal paraffins is still beyond our present capabilities.[18-20] However, it is useful to compare the spectra we obtain from these disklike molecules to the equivalent polymethylenes (C_5H_{12}, C_6H_{14}, and C_7H_{16}). The methyl stretching vibrations seen at 2870–2871 or at 2956–2957 cm^{-1} are well assigned and can be seen in the Raman spectra at all temperatures. The CH_2 asymmetric vibration near the 2885 cm^{-1} are also quite insensitive to changes in the phase. However, the small peaks seen in the spectra associated with BH7 or BH8 can vary significantly in intensity as a function of temperature and disappear completely at the crystalline–liquid crystalline transition. Their frequencies are virtually identical with the components observed for the equivalent normal paraffins in the solid state, particularly for the BH8 molecule.

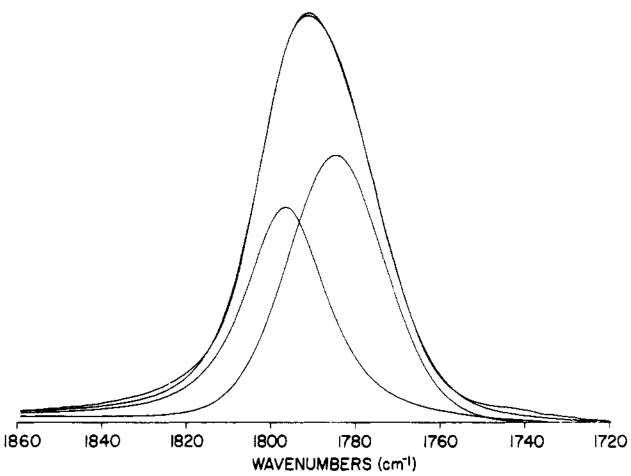

Figure 8. Results of a two-component fit to the data.

Since normal paraffins have a fully trans conformation in the solid state, therefore, by analogy, we interpret the polymethylene sequences in BH7 or BH8 to be extended in the crystalline state. However, these sequences disorder rapidly when the temperature is raised. In fact, we would interpret that the "branches" contain a considerable amount of conformational disorder even in the liquid crystalline or discotic phase. The Raman spectra shown in Figure 7 are quite similar to the Raman spectra associated with the molten state of normal paraffins.[18] Only strong bands at 2850, 2906, and 2928 cm^{-1} in addition to methyl stretchings remain at temperatures above the crystalline–discotic transition. This spectroscopic evidence would suggest that the differences between the conformational distributions are rather small for these molecules between the discotic phase and the isotropic phase. In both states, the polymethylene sequences are rather disordered. It should be noted that, although we found rather good agreement between the frequencies observed for the BH7 and BH8 disklike molecules and those for normal paraffins, we cannot predict the broad contours under these relatively sharp bands. It has been well established that intermolecular Fermi resonance interactions contribute significantly to the broad bands observed in the CH stretching regions.[18-20]

Even though the polymethylene bands do not exhibit any differences between the discotic and isotropic phases, we found that the vibrational bands associated with the ester group are extremely sensitive indicators of the phase transitions observed by thermal measurements. For example, the changes observed for the C═O stretching vibration in the 1700-cm^{-1} region are shown in Figures 4 and 5. It is clear that the frequencies stay relatively constant at 1781 cm^{-1} for BH6 in the crystalline state and then abruptly shift to 1792 cm^{-1} at melting. However, for the BH8 molecule the band observed at 1780 cm^{-1} in the crystalline phase gradually shifts to 1781 cm^{-1} in the discotic phase and then shifts to 1790 cm^{-1} in the isotropic phase.

In the band deconvolution procedure two bands gave the best fit for the series of data obtained as a function of temperature. These two components are found at 1781 and 1793 cm^{-1}. Examples of the fit are shown in Figure 8. The frequencies obtained from the fitting procedure stay relatively constant, as shown in Figure 9. This result gives us additional confidence that only two components are associated with the C═O stretching vibration of these disklike molecules.

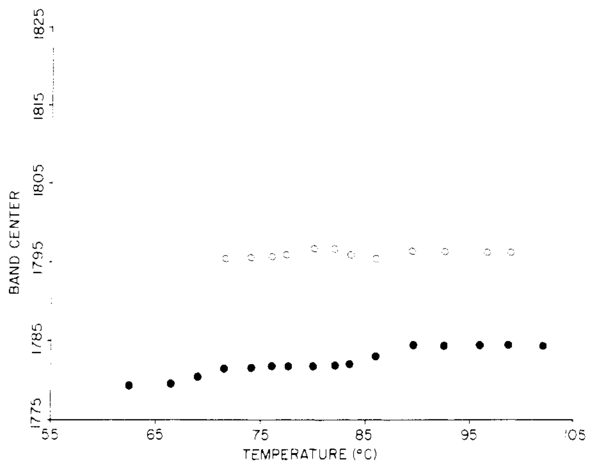

Figure 9. The frequency of the two components as a function of temperature.

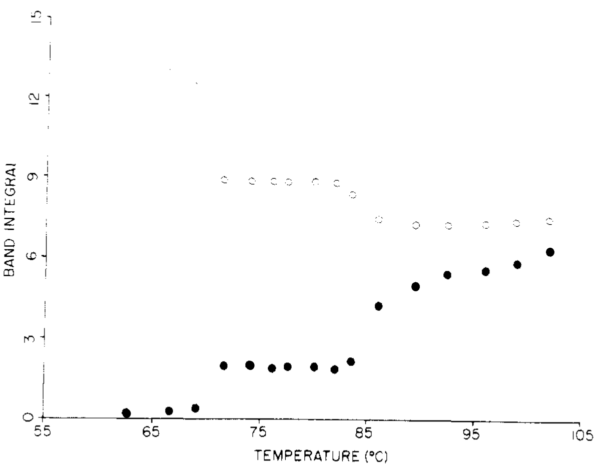

Figure 10. The relative intensity of two fitted components for BH8 as a function of temperature: (O) 1781-cm^{-1} component; (●) 1795-cm^{-1} component.

The gradual shift of the band position as a function of temperature really cannot be correlated with the structural changes of these molecules. Therefore, instead of measuring the frequency of the overall band as a function of temperature, we have plotted the integrated intensities obtained from the fitting procedure of the two components as a function of temperature in Figure 10. As can be seen in this figure, the relative intensities change abruptly at temperatures associated with the crystalline–discotic and discotic–isotropic phases. For the BH6 molecule, only one transition was found, at the crystalline–isotropic transition.

Our analysis of the C=O stretching vibration would suggest that two possible conformations exist for the ester groups of these disklike molecules. One exists primarily in the crystalline state, while the other exists primarily in the isotropic and discotic phases. The relative population can vary significantly as a function of temperature. Conformational calculations have been carried out for these disklike molecules.[21] Several conformations can exist with the C=O bond at different angles with respect to the benzene ring. Because of the sterically crowded nature of these molecules, these conformations will be sensitive to changes in nonbonded intermolecular interactions. The most favorable packing suggested by the theoretical analysis is that the disklike molecules form pairs with the C=O bonds pointing at an angle in the opposite directions. It is extremely unlikely that this angle between the C=O bond and the plane containing the benzene ring can decrease. Therefore, we would suggest that this angle may actually increase, changing the distance between the disks. To our knowledge, no other experimental evidence showing this structural change is available at this moment. However, we have carried out a normal vibrational analysis of a disklike molecule with the ester group in various geometries. We found that the calculated results suggest that the C=O stretching vibration will vary in frequency corresponding to changes in this angle. However, the magnitude of change cannot be reproduced accurately. That analysis will be published in the near future.[22]

Conclusion

Unlike those of most thermotropic liquid crystals, the vibrational spectra obtained for the samples in this study are quite informative in regard to the microstructures of the flexible units. When taken in its entirety, our spectroscopic analysis suggests that the polymethylene sequences of the BH6 molecule, which does not form the liquid crystalline state, are quite disordered. This is in contrast to the two other molecules studied, BH7 and BH8. In those cases, the polymethylene chains seem to be observed, particularly for the latter sample. The spectra obtained for BH8 are quite similar to those obtained for normal paraffins. However, the spectroscopic features associated with the polymethylene sequences disorder rapidly when the temperature is raised. Our spectra indicate that the degree of disorder in the intermediate discotic state is similar to that in the isotropic state. The ester group, attached directly to the core benzene ring, shows quite a different behavior. We found two components, representing two conformations. The relative amount of these two components seems to change at the temperatures at which phase transitions occur. The possibility that the core stack column may expand at higher temperatures has been suggested. It is difficult to understand why the main difference found between the two types of disklike liquid crystalline polymers is not related to the polymethylene sequences but to the ester group. However, the effective polarizability of the polymethylene sequences is extremely important in structural stability, and the fully trans sequences found in some of the molecules would be the most important structural parameter.

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Registry No. BH6, 65201-69-6; BH7, 65201-70-9; BH8, 65201-71-0.

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Observation of a Conformationally Liquidlike Component in Crystalline Polyethylene by Raman Spectroscopy

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ABSTRACT: A low-frequency band, the D-LAM band, which is characteristic of long-range conformational disorder in the chain, has been identified in the Raman spectrum of semicrystalline polyethylene. The position and shape that is observed for this band, when compared with the completely molten polymer, indicates that the noncrystalline component in bulk crystallized polyethylene is conformationally liquidlike for crystallinities up to at least 90%.

Introduction

Vibrational spectroscopy is an effective technique for determining the conformation of chain molecules. In applications to disordered systems, however, the information that can be derived about the disordered component is in a large part limited to the conformation of short segments consisting of one or two bonds in chains that are otherwise ordered. An example is the determination of the concentration and distribution of localized conformational defects in solid *n*-alkanes.[1] Such studies capitalize on the existence of highly localized, conformationally sensitive modes that occur naturally or can be induced through deuterium substitution.[2]

Methods for determining long-range conformational disorder, the subject of the present study, have remained elusive. Some progress has been made, however, on a related problem, that of determining long-range order. Estimates of order are usually based on intensity measurements on bands that are associated with delocalized, skeletal-backbone modes of the chain. Some of these bands appear strongly in Raman spectra. These include CC stretching vibrations, which are used to measure trans-gauche ratios in the hydrocarbon chains of lipid bilayer systems,[3] and skeletal bending vibrations, especially the LAM-1 mode, which is used to detect and measure the long, ordered segments of the polymer chains that comprise lamellae in crystalline polymers.[4-8]

Well-characterized bands that measure long-range *disorder* in highly disordered systems have been unknown, however. Recently, a band in the low-frequency Raman spectra of the liquid *n*-alkanes and in molten polyethylene that seems well suited for the study of long-range disorder has been identified.[9] We will refer to this band as the D-LAM band, the "D" denoting disorder, and "LAM" because this band is related, as we will see, to the LAM-1 band of the ordered chain. From previous studies on the normal hydrocarbons C_9–C_{20} and molten linear polyethylene, it has been found that the frequency and shape of D-LAM are dependent on conformation and on the number of carbon atoms in the chains. The dependency can be accounted for in terms of a simple vibrational model.[9] We note that D-LAM bands are predicted for all disordered chain systems and have in fact been recently observed for a variety of simple noncrystalline polymers.[10]

The structure of semicrystalline polymers has been a matter of intense study since it reflects directly on macroscopic properties.[1] Of particular importance is the chain conformation, or chain disposition, within such structures. Although the nature of the ordered portions has been well established, it had been argued that liquidlike regions did not exist. In this view, deviations in properties from that expected for a perfect crystal were attributed to internal defects and interfacial contributions.[12-14] However, the evidence has become compelling that in partially crystalline polymers, in addition to an important interfacial zone,[11,15-17] chain units also exist in highly disordered conformations. The relative amount of the three major regions that are formed depends on the molecular weight and crystallization conditions.[11,17,18] The basic question arises as to the similarity between the chain conformations in the disordered regions and that of the pure melt, a question that is addressed in the present work.

Since the D-LAM band is a measure of long-range conformational disorder in the *n*-alkanes and in molten polyethylene, it is a matter of interest to see if the D-LAM band could be detected in the Raman spectrum of *solid* polyethylene, i.e., in semicrystalline polyethylene at ambient temperature, and, if found, to compare the characteristics of this band with that for the corresponding pure liquid. To carry out this objective, we have prepared a

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