crystal perfection have been identified. During crystallization the high-melting crystals grow first and seem to reorganize from an intermediate crystal population. The low-melting crystals grow later. On heating for analysis the low- to high-melting ratio changes due to annealing.

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Structure and Crystallization of *n*-$C_{21}H_{44}$, *n*-$C_{36}H_{74}$, and Low Molecular Weight Polyethylene Glasses

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ABSTRACT: Glassy films of *n*-$C_{21}H_{44}$, *n*-$C_{36}H_{74}$, and low molecular weight polyethylene were prepared by vacuum sublimation onto a CsI window held at 7 K and were studied by infrared spectroscopy. The conformational disorder achieved for the glass was comparable to that of the liquid near the sublimation temperature. The chain-organizing processes were monitored for C_{21} and polyethylene as the sample was warmed to 300 K. A number of separate steps are involved. Each step occurs over a more or less broad temperature region, and sometimes the steps overlap. In the case of C_{21}, the first step involves a conformational ordering of the chains to their extended all-trans form. The extended chains initially pack in a monoclinic subcell, but they are not in longitudinal register; that is, the end methyl groups do not lie in parallel planes. At a higher temperature, the monoclinic subcell is converted to an orthorhombic subcell, but the chains are still not in register. In the last annealing step, which occurs over a narrow temperature range, the chains come into register so that the C_{21} finally assumes its stable orthorhombic crystal structure. The annealing of the polyethylene glass proceeds in exactly the same way except that there is no chain-registering step. In general, the transition temperatures are higher and the temperature range over which the transitions occur is broader for the polyethylene sample.

I. Introduction

There has accumulated over the years enormous literature on the polymethylene chain and its derivatives. There is good reason for this since this chain is an important and ubiquitous component of many natural substances and is a prototype synthetic polymer. Moreover, the polymethylene chain plays a unique role in model systems against which are tested new experimental and theoretical developments aimed at understanding the structure and dynamics of chain–molecule assemblies. It is then perhaps surprising to find that the glassy state of polymethylene systems has been studied so little. This is

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largely due to the difficulty in preparing suitable samples. Consequently, there are many interesting and fundamental questions about glassy polymethylene to be answered concerning the nature of its conformational organization and the nature of the processes that occur as the glass is warmed and transformed into a highly ordered system.

These questions are addressed in the present paper, which reports an infrared spectroscopic study of glassy films of n-$C_{21}H_{44}$, n-$C_{36}H_{74}$, and a low molecular weight polyethylene. The films were prepared by vacuum sublimation, a process in which vapors are condensed onto an infrared window maintained at 7 K. The infrared spectra of these films provide detailed information on both chain conformation and chain packing. The present work represents a continuation of our recent efforts to study and to develop vibrational spectroscopic methods for the study of simple disordered chain–molecule systems.[1]

To our knowledge, the only other vibrational study of a linear-polyethylene glass is that carried out by Hendra and co-workers,[2,3] who prepared samples by rapid quenching near liquid nitrogen temperatures of a thin film of a high molelcular weight polyethylene in the molten state. The stated purpose of their work was to establish a value for the glass-transition temperature, and in carrying it out they achieved the first successful preparation of polyethylene in the glassy state. Subsequently Geil and co-workers[4] prepared very thin films (100–1000 Å) of glassy polyethylene in a similar way for electron diffraction studies. We note that much earlier Lampe[5] reported an infrared study of n-$C_{23}H_{48}$ and polyethylene films prepared by sublimation onto a window held at 80 K. In this study, only the intense 720-cm^{-1} band was monitored. It was shown that the PE and C_{23} deposited films were, respectively, noncrystalline and partially crystalline. However, conformational structure has not been a subject of these earlier papers.

II. Experimental and Interpretive Methods

A. Film Preparation and Infrared Measurements. The samples of n-$C_{21}H_{44}$ and n-$C_{36}H_{74}$ were of high purity, 99.6–99.9 mol %.[6] The low molecular weight polyethylene sample we used was Polywax-2000 ($\bar{M}_n$ = 1790 and $\bar{M}_w/\bar{M}_n$ = 1.1). In the text, this sample is often referred to simply as "polyethylene" or "PE".

All spectra were measured with an evacuatable Nicolet Model 8000 FTIR spectrometer with an instrumental resolution of 1 cm^{-1}. The samples were cooled with a CTI Model 21 closed cycle helium cryocooler equipped with a heater and temperature controller that allowed us to vary the temperature from 7 to 300 K.

The samples were heated and sublimed onto a cold window inside the sample compartment of the cryocooler. Also inside the sample compartment was the furnace used to sublime the samples. This consisted of a small copper tube, closed on the bottom and wrapped with heating wire. The temperature was monitored with a chromel-alumel thermocouple which was soldered to the copper tube. The aperture of the copper tube (1–4-mm i.d.) was directed toward the cooled CsI window from a position 1–2 cm away from and at the level of the bottom of the window. Prior to the deposition, the system was outgassed for 2–8 h under a vacuum higher than 10^{-5} mm.

We note that the spectra shown in the figures were measured with the furnace heater turned off and with the sample held by the cryocooler at the indicated temperature, which was usually also the annealing temperature.

B. Infrared Bands Used for Structural Identification and Measurement. Table I lists the frequencies and assignments of the bands we have used to identify the various structures that constitute the deposited films and to estimate their concentrations. The assignments of these bands are well established.[7-10]

Table I
Infrared Bands Used to Identify Conformational and Chain Packing Structure

conformational bands	band freq., cm^{-1}	mode[a]	designation	ref
disordered chains	1469	δ		*b*
	1366	W	*gtg′* (kink)	7, 8
	1353	W	*gg* (double gauche)	
	1341	W	*gtt* (end gauche)	
	1300	W	*gtg*, *gtg′*	
	724	P		*b*
all-trans-n- $C_{21}H_{44}$	1326	W_9		9
	1288	W_7		
	1254	W_5		
	1222	W_3		
chain-packing bands for all-trans chains				
monoclinic subcell[c]	1475	δ_1		20
	718	P_1		19, 20
orthorhombic subcell[c]	1474	$\delta_1(a)$		10
	1462	$\delta_1(b)$		
	733	$P_1(a)$		
	721	$P_1(b)$		
orthorhombic cell C_{21}, in-register	807	$P_{11}(a + b)$		9
	765	$P_9(a)$		
	751	$P_9(b)$		
	743	$P_7(b)$		
methyl-group bands	1465	HCH asym. bending		9
	1375	HCH umbrella		

[a] δ, W, and P refer respectively to methylene scissoring, wagging, and rocking modes. If there is a subscript, this refers to a specific assignment for n-$C_{21}H_{44}$ given in ref 9. In addition, (a) and (b) refer to the a and b axis components of factor-group split bands (see ref 9). [b] Measured in this study. [c] For chains that are not in register or are in register.

Local packing of the ordered (all-trans) chains is designated in terms of a unit subcell. For a particular kind of packing, the subcell may be thought of as the unit cell of the crystal that would result if the chains were infinitely long. The unit cell for such a crystal is small, containing only two methylene groups for each chain that transverses it. The subcells of interest are the monoclinic and orthorhombic, which are transversed by one and two chains, respectively. The two structures can be distinguished spectroscopically because (factor-group) band splitting occurs in the spectrum of the orthorhombic packing structure but not in the monoclinic case.[10]

Finally, we note that the most stable crystalline form of n-$C_{21}H_{44}$ has not only an orthorhombic subcell but has longitudinal ordering so that adjacent chains are "in register"; that is, the end methyl groups lie in parallel planes. We note also that longitudinal chain registering can be characterized from the splitting pattern of the higher order rocking modes.[11]

III. The *n*-Alkane *n*-$C_{21}H_{44}$

Clear films of a thickness less than 3 μm were readily obtained by sublimation of n-$C_{21}H_{44}$ onto a CsI window at 7 K. The furnace temperature was maintained at or slightly below 65 °C. Thicker films were difficult to obtain due to a tendency for spontaneous, partial crystallization

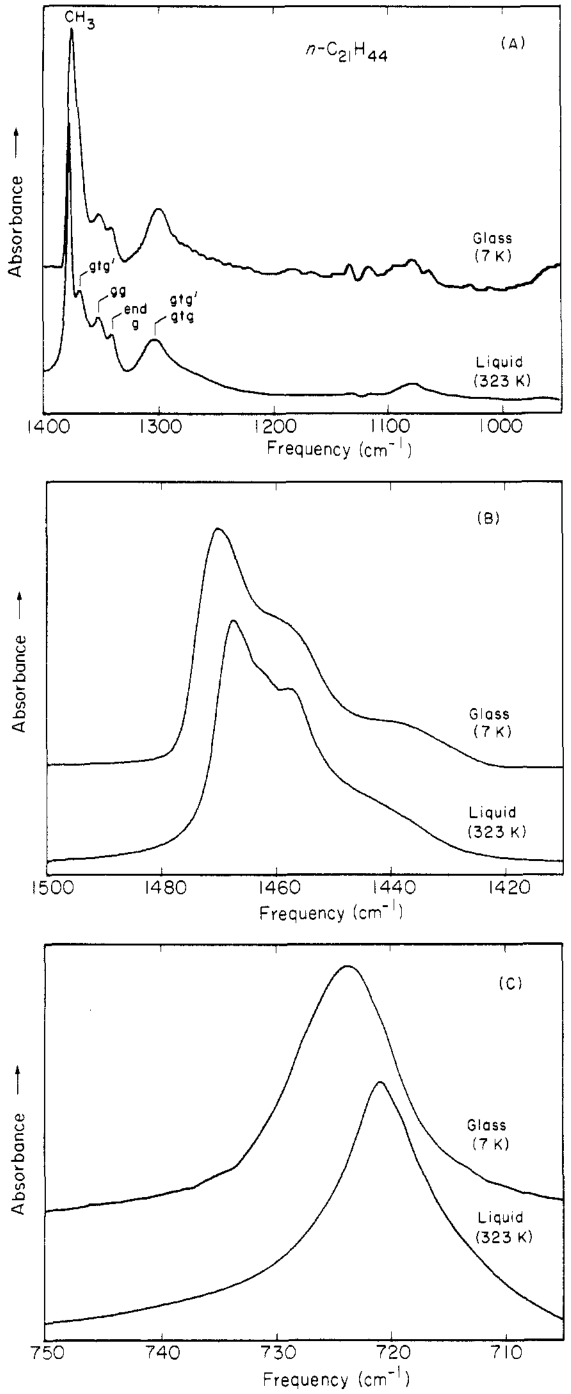

Figure 1. Infrared spectra of glassy n-$C_{21}H_{44}$ measured at 7 K and of liquid n-$C_{21}H_{44}$ at 323 K: (A) the conformationally sensitive, methylene wagging and CC-stretching mode regions (wagging bands that are known to be associated with local conformations are labeled; see Table I.); (B) the methylene scissoring mode region; (C) the methylene rocking mode regions.

during the sublimation process. In spite of experiments with a variety of differently designed furnaces and varied sublimation rates, the thickest film of amorphous C_{21} that we were able to prepare was about 8 μm.

A. Conformational Structure of the As-Deposited Glassy Film. The conformational disorder of the chains that comprise the as-deposited films of C_{21} appears to be similar to that of the liquid at ambient temperature. This may be inferred from Figure 1 which shows the infrared spectrum of the C_{21} film at 7 K along with the spectrum of liquid C_{21} at 323 K. These spectra much resemble each other but are entirely different from the spectrum of crystalline C_{21}, which is shown in ref 9.

An important question is whether or not there is a significant difference in the trans/gauche ratio between the glass and the liquid. For C_{21}, we have found this difference to be small. An estimate of the concentration of gauche bonds can be made on the basis of the asymmetry of the methylene scissors band near 1469 cm^{-1} (Figure 1B). The asymmetry of this band that is defined by the absorptivity ratio $A(1440)/A(1469)$ is an appropriate measure because absorption at 1440 cm^{-1} is entirely due to the presence of gauche bonds.[12] A comparison of the value of this absorptivity ratio for the two states shows that the concentration of gauche bonds in the glass is slightly smaller than that in the liquid. We can put the comparison on a quantitative basis by first estimating the actual concentration of gauche bonds in the liquid by using the rotational isomeric state model.[13] With E_g and $E_{gg'}$ equal to 500 and 3000 cal/mol, respectively, the gauche bond concentration is calculated to be 36.7%. Our spectroscopic measurements then give a value of 33% ± 3% for the glass.

A related question concerns whether or not there is a significant difference between the glass and the liquid in the way the trans and gauche bonds are distributed along the chains. Again our data indicate there is not. This conclusion is based on a comparison of the relative intensities of certain bands in the frequency region 1400–1280 cm^{-1} that are a measure of specific conformational sequences. (See Table I.) These bands, which represent *gtg′*, *gg*, and end-*g* sequences, are present in the spectra of both the glass and the liquid, and their relative intensities are roughly the same in the two cases (Figure 1A). (We must allow for the fact that the 1366-cm^{-1} band of the glass appears as a shoulder on the 1375-cm^{-1} methyl band.)

Finally, we will comment on the significance of the fact that there are many weak bands in the spectrum of the C_{21} glass, especially in the region 1300–1100 cm^{-1}, that appear to have no counterparts in the spectrum of liquid C_{21} (Figure 1A). We believe that these bands are not apparent in the spectrum of liquid C_{21} largely because of band broadening due to thermal motion and not because of a difference in conformational disorder between the glass and the liquid. In support of this conclusion, we note that the infrared spectra of thick films of the shorter n-alkanes in the liquid phase (seen in ref 7 for C_{10}–C_{17}) indeed do show weak bands in this region, and in fact, the pattern of these bands in the region 1150–1000 cm^{-1}, which tends to be independent of chain length for the longer liquid n-alkanes, is similar to that for the C_{21} glass. However, in going to longer chain lengths, these bands become less intense and broader for the liquid n-alkanes.

B. Structural Changes upon Annealing. Increasing the temperature from 7 K to 300 K converts the glassy film of C_{21} to the form of crystalline orthorhombic C_{21} that is normally observed at ambient temperatures. However, infrared spectra of the film measured at intermediate temperatures show that the solid does not pass directly from the glass to the orthorhombic crystal but rather undergoes a series of well-defined intermediate transformations. In summary, what happens is that first there is a transformation of the conformationally disordered chains to conformationally ordered (all-trans, planar) chains. As the extended chains are formed, they pack in a monoclinic subcell. At a higher temperature, the monoclinic subcell is converted to an orthorhombic subcell. The final step involves a process in which the chains undergo longitudinal ordering, that is, come into register.

All the structural changes that occur when the temperature of the sample is increased are found to be irre-

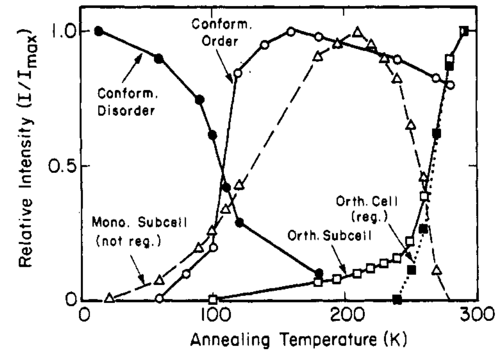

Figure 2. Structural changes with annealing temperature for n-$C_{21}H_{44}$ from 7 to 300 K as monitored by the infrared intensities of characteristic bands. The maximum intensity has been normalized to 1. The structure, the frequency of the band used to measure the structure, and the data point symbol are as follows: conformationally disordered chains, 1300 cm^{-1} (●); conformationally ordered chains (all-trans), 1254 cm^{-1} (○); monoclinic subcell packing (chains not in register), 718 cm^{-1} (△); orthorhombic subcell packing (includes both not in-register and in-register chains), 733 cm^{-1} (□); orthorhombic packing (chains in register), 765- and 761-cm^{-1} pair and 742-cm^{-1} band (see Figure 6) (■).

versible. The changes are also "instantaneous" in the sense that they appear to occur at the time the temperature is increased. Thus, an infrared spectrum, measured as quickly as possible after the warming has occurred (that is, within a time of the order of a few minutes), was found to be essentially identical with the spectrum measured several hours later.

Our study indicates that any given conformationally disordered chain becomes ordered in a single step. There is a broad temperature range over which conformationally disordered chains are transformed to ordered chains and over which the sample is comprised of order and disordered molecules.

The total number of different structural entities that we have observed is small, so that it is relatively easy to follow the changes that occur as the temperature is increased. The possible structures present consist of the following: chains that may be conformationally disordered or ordered; chain packing that may occur in monoclinic or orthorhombic subcells; chains packed in these subcells may be in register or not in register.

Figure 2 displays temperature plots of the intensities of bands that are associated with the various kinds of structure that occur during the transformation of glassy C_{21} at 7 K to orthorhombic crystalline C_{21} at 300 K. The maximum intensity of each component band has been scaled to unity. We note that the maximum value of the intensity tends to occur at a temperature where the other components have relatively low concentrations. Therefore, the relative intensities represent a crude but useful measure of concentration.

The intensities plotted in Figure 2 have not been corrected for the effects of temperature per se, that is, for the effect of temperature on band shape and on intrinsic infrared intensity. It is well-known that increased temperature tends to broaden bands. From a recent study on the polymethylene chain in the condensed state, we have found that an increase in temperature also significantly reduces the intrinsic intensity of infrared bands.[14] For C_{21} these effects are probably significant only above 200 K and only for the crystalline state. A situation where these effects are in evidence may be seen in Figure 2 for the 1254-cm^{-1} band, which measures the concentration of extended chains. Above 150 K, its intensity diminishes slightly with increasing temperature although we know that the concentration of extended chains cannot decrease. The observed decrease in intensity must be attributable to temperature per se.

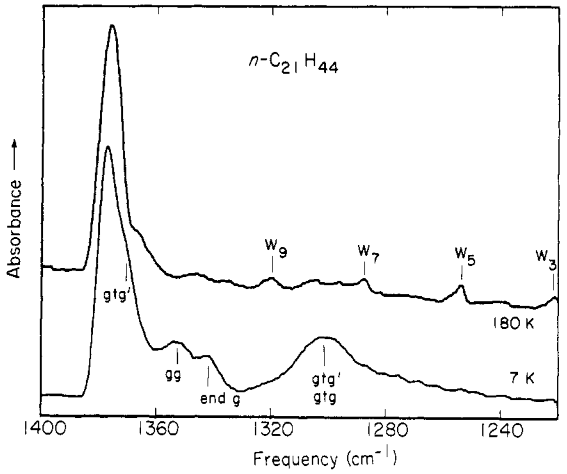

Figure 3. Infrared spectra of the as-deposited n-$C_{21}H_{44}$ glass at 7 K and of the same sample annealed at 180 K. Bands that are characteristic of the conformationally disordered and ordered chains are indicated (see Table I for meaning of labels).

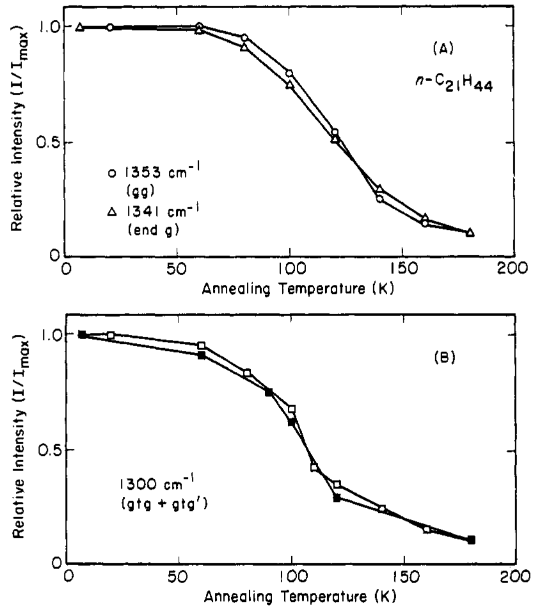

Figure 4. Infrared peak-height intensities for different bands of conformationally disordered chains plotted against annealing temperatures for n-$C_{21}H_{44}$ deposited as a glass at 7 K. The maximum intensity has been normalized to 1. (A) The 1353- and 1341-cm^{-1} bands represent *gg* and end-*g* conformations. (B) The 1300-cm^{-1} band represents *gtg'* and *gtg* conformations. The two plots for the 1300-cm^{-1} band represent two different experiments.

The various structural transitions that occur upon annealing the C_{21} film from 7 K to ambient temperatures will now be discussed in more detail.

1. Transition from Conformationally Disordered Chains to Conformationally Ordered Chains Packed in a Monoclinic Subcell. To monitor the concentration of conformationally disordered chains, we use the bands at 1300, 1341, and 1353 cm^{-1} which are listed in Table I and shown in Figure 3 for the glass at 7 K. Also shown in Figure 3 is the spectrum of the film warmed to 180 K. In this spectrum, the 1300, 1341, and 1353-cm^{-1} bands are gone, indicating that conformational disorder has all but been eliminated.

The disappearance of the disordered chains with higher annealing temperatures can be followed in Figure 4, where relative peak-height intensities are plotted against annealing temperatures. Figure 4A is based on the 1353- and

1341-cm^{-1} bands. Figure 4B is based on the 1300-cm^{-1} band and shows data from two different experiments.

The plots in Figure 4 have very similar shapes in spite of the the fact that they are based on bands that represent different conformational sequences. This indicates that the conformationally disordered fraction of the system remains essentially unaffected by the ordering process; i.e., the system remains made up of ordered and disordered molecules, with no significant degree of partial ordering.

Figure 4 indicates little, if any, structural change occurs at temperatures below 50 K. Changes begin to be detected near 60 K and take place most rapidly over the temperature interval 80–160 K. At a temperature near 107 K, approximately one-half the chains have been converted to the all-trans form. The transition is essentially complete at a temperature near 180 K.

Concomitantly with the disappearance of disordered C_{21} chains, fully extended, all-trans chains appear. The methylene wagging bands marked on the 180 K spectrum in Figure 3 are characteristic of the fully extended molecule. The frequencies of these bands correspond to those reported in ref 9 for all-trans C_{21} (see Table I).

The intensity of the 1253-cm^{-1} band of the all-trans or nearly all-trans conformers is used in Figure 2 to monitor the concentration of ordered chains. Within experimental error, the two plots, one showing the buildup of ordered chains and the other showing the depletion of disorder, complement each other. Both plots show an inflection point around 105 K. The peak intensity of the 1254-cm^{-1} band reaches a maximum near 170 K and then, as noted earlier, falls off gradually at higher temperatures due to the negative temperature coefficient of the peak height of the band.

As the extended chains of C_{21} are formed, they are found to pack mainly in a monoclinic subcell. The bands at 1475 and 718 cm^{-1}, marked in Figure 5, indicate this type of packing. These bands appear as the conformational ordering process begins, and their growth with higher annealing temperatures tends to parallel the growth of the conformationally ordered chains up to about 180 K as may be seen in Figure 2. At higher temperatures, the monoclinic form is depleted through a transition to the orthorhombic form as will be discussed in the next section. Also, we will show in the next section that the chains packed in the monoclinic structure are not in register.

The 718-cm^{-1} band, which was used to monitor the monoclinic structure in Figure 2, was isolated from its overlapping neighbors by curve-fitting techniques. Its half-width was found to be quite small, full-width at half-height being less than 4 cm^{-1}, which implies that the monoclinic packing is well defined.

2. Transition to Orthorhombic Subcell Packing. At an annealing temperature around 120 K, a new type of structure appears, namely chain packing in an orthorhombic subcell. This is indicated by the appearance of bands near 1462 and 733 cm^{-1} that are associated with the orthorhombic structure of crystalline polyethylene (Figure 5). It appears possible that the transition to orthorhombic packing occurs in two different ways. From Figure 2, we see that increasing the annealing temperature from 120 to 180 K results in the formation of some of the orthorhombic form. In the transformation to orthorhombic packing in this temperature region, the initial state could be the glass (i.e., chains could undergo some conformational ordering in the glass and pack immediately in the orthorhombic form) or, alternatively, the monoclinic form (i.e., the chains could undergo a monoclinic to orthorhombic transition). However, in the higher temperature region, 180–300 K, the transition to the orthorhombic form must be from the monoclinic form only since there is little left of the glass. This is in keeping with the fact that in this temperature region the growth of the orthorhombic form almost exactly compensates for the loss of the monoclinic form.

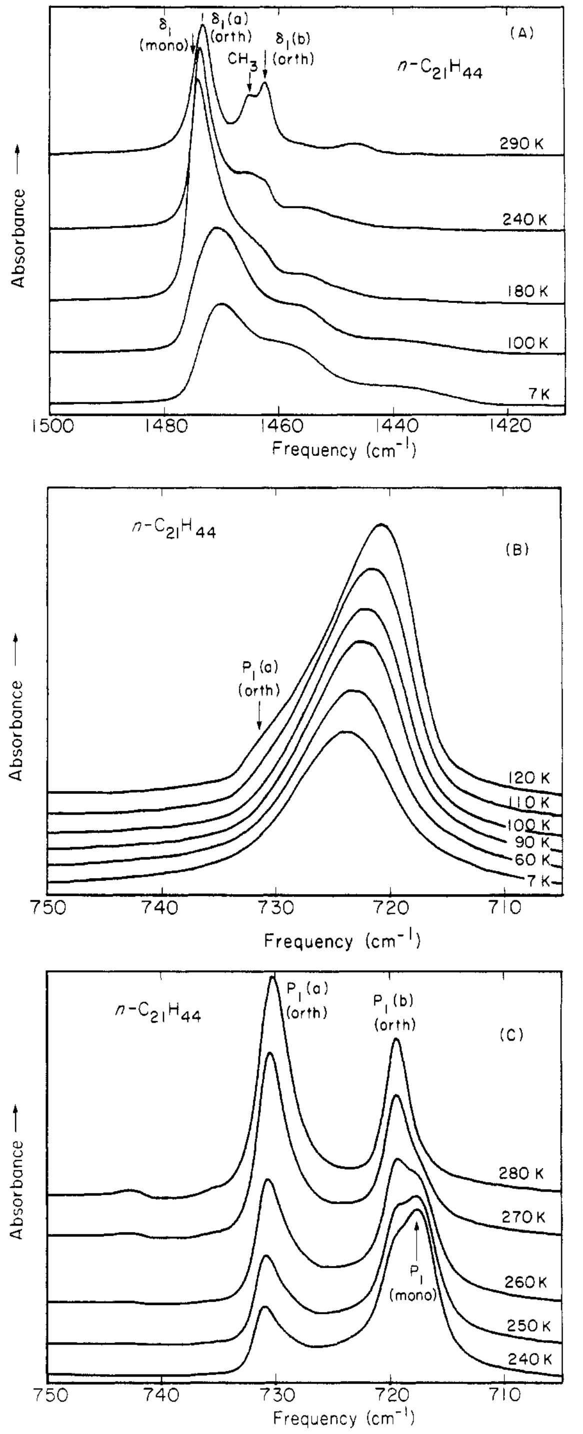

Figure 5. Infrared spectra of n-$C_{21}H_{44}$ deposited as a glass at 7 K and annealed at progressively higher temperatures. The spectra were measured at the annealing temperature. Part A is for the methylene scissoring mode region and parts B and C are for the methylene rocking mode region. (See Table I for band designations.)

3. Longitudinal Registering of the Orthorhombic Structure and Evidence for Epitaxial Growth. Films of the C_{21} glass annealed at a temperature just below about 250 K consist of extended chains packed in monoclinic and orthorhombic subcells in a ratio of approximately 1:2. Our spectra indicate that at this temperature the chains in the

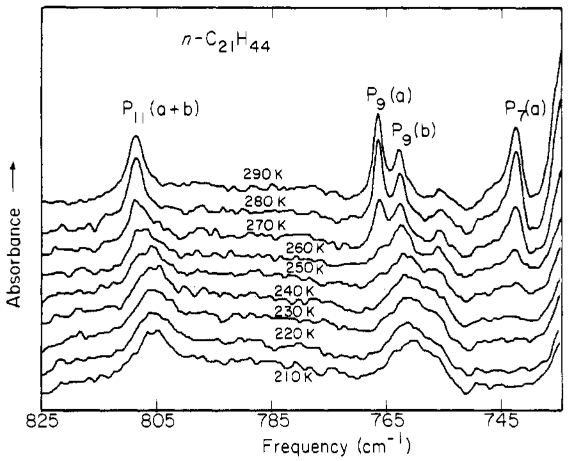

Figure 6. Infrared spectra of n-C$_{21}$ originally deposited as a glass at 7 K. These spectra, which cover the rocking mode progression region, are used to monitor the transition from the out-of-register to the in-register form of the orthorhombic packing. Chain registering is indicated by the growth of the P$_9$ doublet near 765 cm^{-1} and the P$_{11}$(a + b) and P$_7$(a) bands near 807 and 743 cm^{-1}.

orthorhombic structure are not in register. However, annealing at temperatures above 250 K initiates a new kind of transition in which the chains come into register. The temperature range of the transition is narrow since the transition is completed at about 280 K, as may be seen in Figure 2. Presumably this transition begins at a temperature that corresponds to the onset of longitudinal mobility for the extended chains.

The method used to monitor this transition will now be discussed. For reasons given elsewhere,[11] the appearance of the 733/721-cm^{-1} doublet (Figure 5C), which is associated with the first member (P$_1$) of the rocking mode progression, indicates orthorhombic subcell packing but does not indicate whether or not the chains are in register. However, the higher member bands of the progression do yield this information since their splitting pattern is determined by the relative longitudinal position of adjacent chains. Most importantly, there can be no splitting at all for these higher members unless the chains are in register.[16] The rocking mode band P$_9$ near 767 cm^{-1} (shown in Figure 6) is a single, broad band at annealing temperatures below about 250 K. Between 250 and 280 K, this band splits, and this indicates a transition from the not-in-register structure to the in-register structure. The pronounced sharpening of the P$_{11}$(a + b) and P$_7$(a) bands shown in Figure 6 also relfects the in-register transition.

Our spectra show that the orthorhombic crystals of C$_{21}$ in the fully annealed film are preferentially oriented with respect to the surface of the CsI window. This is indicated by the observed intensity ratio of the 733- and 721-cm^{-1} components of the rocking mode fundamental (Figure 5C). For random orientation, the value of the ratio I_{733}/I_{721} is a little less than 1.0.[10] However, for the annealed film near room temperature, it is observed to be about 2.0. Orientation was confirmed by polarization measurements, although the exact nature of the alignment could not be determined unambiguously. Similar epitaxial crystallization has been reported for films of n-alkanes and PE prepared by vapor deposition on a KCl surface at 25 °C.[15]

IV. Low Molecular Weight Polyethylene

Films were prepared in the manner described for C$_{21}$ except, of course, much higher sublimation temperatures were necessary. The polyethylene sample, as noted in section II, was Polywax-2000, for which $\bar{M}_w$ = 1790 and $\bar{M}_w/\bar{M}_n$ = 1.1. Furnace temperatures up to 350 °C were used, and amorphous films were obtained with thicknesses that were between 3.5 and 10 μm. Thermal decomposition occurred starting at a temperature near 320 °C, as was evident from the appearance of infrared bands at 910 and 990 cm^{-1} that are associated with terminal vinyl groups. From the intensities reported for these bands,[16] we found that the vinyl concentration was about 1 mol %. Assuming one scission per chain, we estimate that the average chain in the deposit consists of about 100 carbon atoms.

A. Conformational Structure of the As-Deposited Film. A comparison of the infrared spectra of the as-deposited films of polyethylene and C$_{21}$ indicates that the chains are similar in their conformational disorder. The CH$_2$ scissors and rocking mode regions are shown in Figure 7A,B for polyethylene and in Figure 1B,C for C$_{21}$. The shapes of these bands for the two samples at 7 K are very similar. However, the value of the peak intensity ratio $A(1440)/A(1469)$ indicates a higher concentration of gauche bonds for the PE glass than for the C$_{21}$ glass. This is apparently a result of the higher sublimation temperature used for PE (about 620 K as compared with 338 K for C$_{21}$) and indicates, as we found earlier for C$_{21}$, that the trans/gauche ratio for the chains in the glass at 7 K is near that for the chains in the gaseous state at the sublimation temperature.

B. Structural Changes upon Annealing. The structural changes that the polyethylene glass undergoes upon annealing parallel those observed for C$_{21}$, except for longitudinal registering which, of course, is unique to C$_{21}$. The similarities between the transformations of PE and C$_{21}$ may be seen by comparing how their spectra evolve with increasing temperature. The similarity is most apparent in the methylene scissors region around 1469 cm^{-1} (cf., Figures 7A and 5A) and in the methylene rocking region around 724 cm^{-1} (cf., Figures 7B,C with Figure 5B,C). (We note one trivial difference between PE and C$_{21}$. In going to higher annealing temperatures, there appears in the spectrum of C$_{21}$ (Figure 5A) a band near 1465 cm^{-1} that is associated with a HCH bending mode of the methyl group.)

One difference in the annealing behavior of PE and C$_{21}$ is in the transition temperatures. The conformational ordering process for the polymer occurs over a higher and broader temperature region, as may be seen by comparing the intensity vs annealing temperature curves for PE (Figure 8) and C$_{21}$ (Figure 4A). For PE, conformational ordering begins around 100 ± 10 K and is half completed around 169 K. At 290 K, the highest temperature of our measurements, a significant fraction of the chains in the PE film have not yet converted to the all-trans form. This is clear from the 290 K spectrum in Figure 7A, which shows a tail on the low-frequency side of the 1462-cm^{-1} band that is associated with conformationally disordered chains. We estimate the fraction of disordered chains that remain at 290 K to be of the order of 10%.

As in the case of C$_{21}$, the extended chains of PE pack together in a monoclinic structure that changes to orthorhombic at a higher temperature. However, for PE, the temperature regions for conformational ordering and for conversion from monoclinic to orthorhombic packing tend to overlap, and this makes it difficult to assign a temperature range that is characteristic of the packing transition. It appears that this temperature range is similar to that for C$_{21}$ except that it extends to higher temperature, partly at least as a consequence of the fact that the process of conformational ordering itself continues on at temperatures well above 300 K. The annealed orthorhombic PE film shows preferential orientation with respect to the

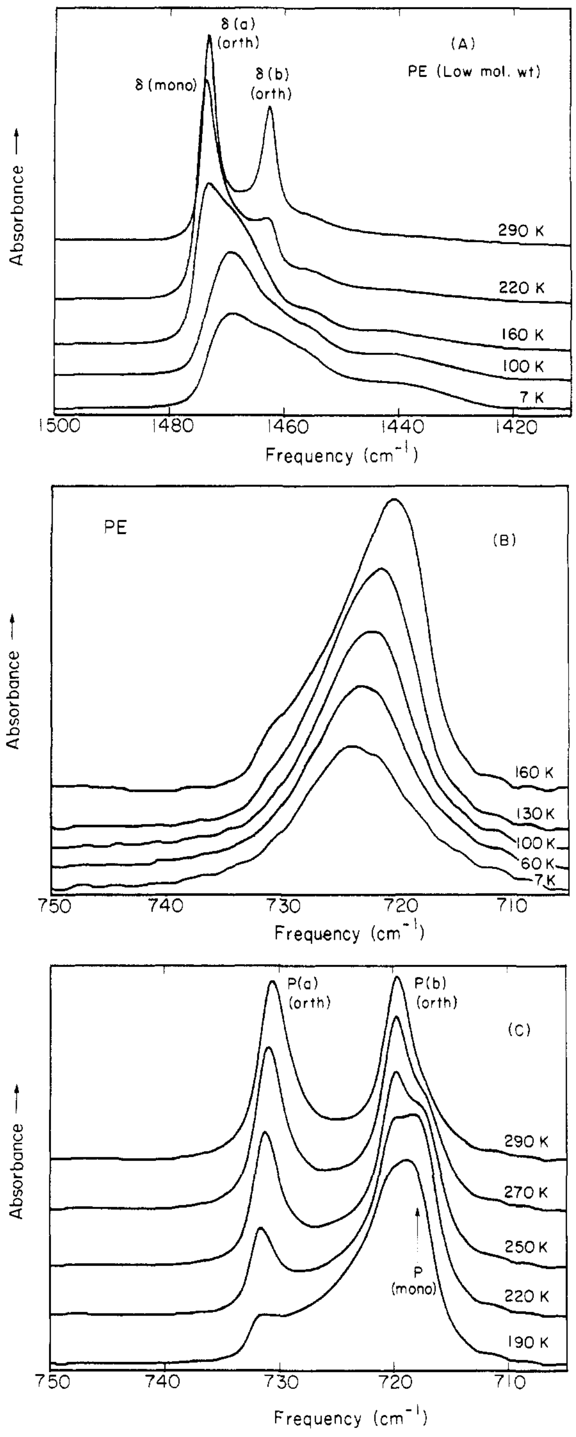

Figure 7. Infrared spectra of a low molecular weight polyethylene deposited as a glass at 7 K and annealed at progressively higher temperatures. The spectra were measured at the annealing temperature. Part A is for the scissoring mode region and parts B and C are for the rocking mode region. (See Table I for band designations.)

surface of the CsI window. It appears that nature of the orientation is very similiar to that for C_{21}.

V. Some Other Observations

A. n-$C_{36}H_{74}$ Glass and Its Annealing Behavior. A study, similar to that on C_{21} but much more limited, was made on C_{36}. Glassy films were prepared in the same manner as for C_{21} and PE. The furnace temperature was near 125 °C, and the thickest films obtained were in the range 2–3 μm.

The structure of the glass and the changes in the structure that were observed upon annealing paralleled those found for C_{21} except that the transitions occurred at higher temperatures. However, the films of C_{36} were too thin to reveal small differences in the structure or temperature behavior between C_{21} and C_{36}. Also, the transition temperatures for C_{36} were not accurately determined because spectra were measured at large temperature intervals. Although we could not determine directly the temperature at which conversion to the all-trans form commenced, a value of 82 ± 10 K was estimated by interpolation of the C_{21} and PE data. (The method may be inferred from Figure 12 and will be discussed below in section V-D.) The temperature at which half the chains had been transformed to the all-trans conformation was estimated from our spectra to be 140 ± 10 K.

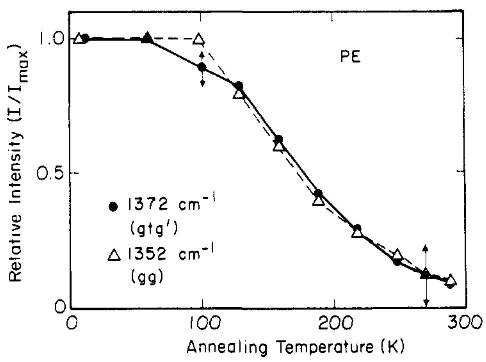

Figure 8. Infrared peak-height intensities for two bands of conformationally disordered chains plotted against annealing temperatures for a low molecular weight polyethylene deposited as a glass at 7 K. The maximum peak height has been normalized to 1. The 1372- and 1352-cm^{-1} bands represent the *gtg′* and *gg* conformations, respectively. (See Table I.)

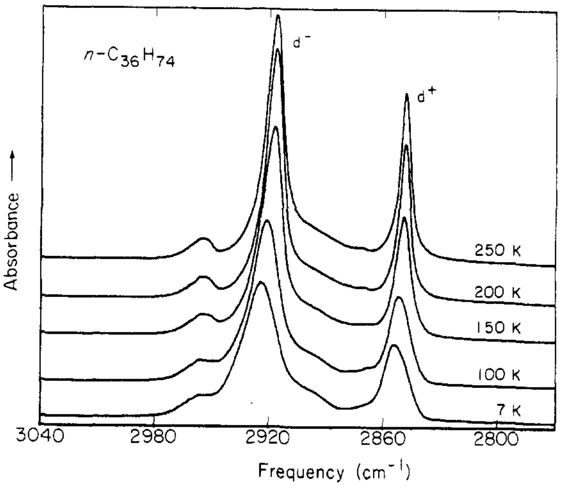

Figure 9. Infrared spectrum in the C–H stretching region for n-$C_{36}H_{74}$ deposited as a glass at 7 K and annealed at progressively higher temperatures. The two dominant bands are associated with methylene antisymmetric (d^-) and symmetric (d^+) C–H stretching.

The C–H stretching region plays an important role in the analysis of hydrocarbon chain structure by vibrational spectroscopy, and therefore we will discuss the principal changes that occur in this region upon annealing glassy C_{36}. The changes are similar to those observed when a liquid n-alkane crystallizes.[17] The spectra in Figure 9 show the prominent methylene antisymmetric (d^-) and symmetric (d^+) C–H stretching bands. The frequencies of these bands for the as-deposited film at 7 K are 2925.1 and 2854.9 cm^{-1}, respectively. However, when this film is annealed at 250 K so that the chains are in the all-trans form, these bands move to 2917.0 and 2849.4 cm^{-1}. The resulting frequency shifts (8 and 5.5 cm^{-1}) are nearly identical with the shifts

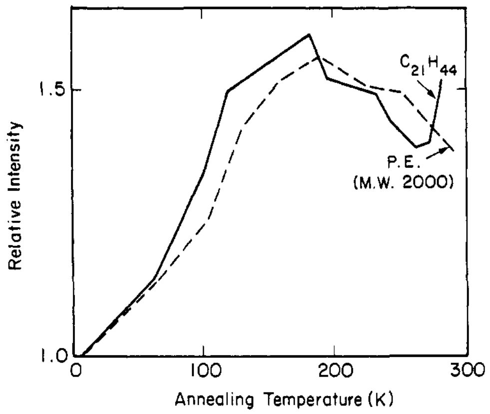

Figure 10. Temperature dependence of the relative value of the integrated intensity of the rocking mode band (750–700 cm^{-1}) of C_{21} and low molecular weight polyethylene deposited as glasses at 7 K and annealed at progressively higher temperatures.

observed when *n*-alkane transform from the liquid to the crystalline state.[17] The other principal change in the annealing process is a significant reduction in bandwidths. The half-widths (FWHH) of d$^-$ and d$^+$ go from respective values of 23 and 15 cm^{-1} to values of 11 and 7 cm^{-1}, a reduction that is similar to that which occurs when the liquid is crystallized. These changes are largely attributable to conformational ordering.

B. Temperature Dependence of the Integrated Intensiy of the 720-cm^{-1} Band. This dependence, which is shown in Figure 10 for both C_{21} and PE, is notable in that the intensity of the 720-cm^{-1} methylene rocking band increases dramatically with increased temperature up to about 190 K and then decreases. This dependence is of interest because it illustrates a formidable but not widely appreciated problem that may be encountered in using infrared spectroscopy for quantitative studies of the structure of solids. The intensity behavior shown in Figure 10 is the result of two temperature factors that have effects of opposite sign. The initial increase is associated with the conversion of the sample from the glass to the crystalline phase and is a result of the fact that the intrinsic intensity of the 720-cm^{-1} band is significantly greater for the polymethylene chain in the crystal than in the glass.[18] However, above 190 K, at which temperature the conversion to the crystal is largely complete, the second factor begins to dominate. This has to do with the fact that the intrinsic intensity of infrared bands undergo a significant decrease with increasing temperature. This effect is much larger for the crystal than for the glass, and its magnitude increases with increasing temperature.[14,18] Finally, we note that the temperature behavior of the intensity of the 1465-cm^{-1} scissoring band is similar to that of the 720-cm^{-1} band.

C. 1/*T* Plots Associated with the Transitions. From the plots in Figure 2, we can derive temperature coefficients that are associated with the transformation of structure A into structure B. There are some temperature regions, especially around the inflection points of the S-shaped curves, where the relation between concentration and temperature appears to be approximately linear. For some of these regions, we have plotted the mole fraction ratio x_B/x_A against $1/T$ and from the plot have obtained an energy which we have designated E^*.

The values of E^* that we obtained are such as to suggest that they are related, albeit in a complex way, to activation energies associated with the transition of A to B.[21] Figure 11, for example, is a plot of the 1300-cm^{-1} band intensity against $1/T$ and represents the transition from conformational disorder to conformational order. Plots are shown for both C_{21} and low molecular weight polyethylene. These plots lead to values for E^* of 1.1_5 and 1.4_2 kcal/mol for C_{21} and PE, respectively. The difference between the values is probably significant and may reflect the fact that the transition is not as clean-cut for the PE as for C_{21}; i.e., the conformational ordering and the formation of the orthorhombic cell may occur together in the case of PE. In any event, the two values are of the same magnitude as the energies associated with barriers involved in conformational rearrangement.

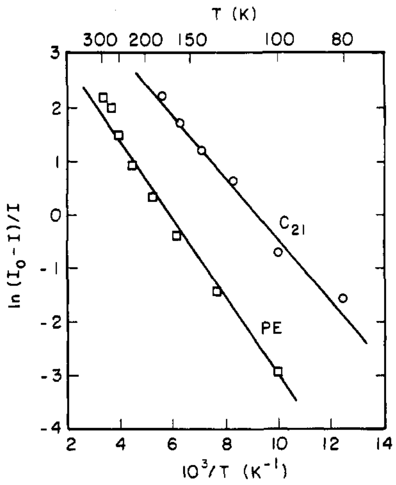

Figure 11. Plots of the peak-height intensity of the 1300-cm^{-1} (conformationally disordered chains) band against $1/T$ where T is both the annealing temperature and the temperature at which the infrared spectra were measured. The plots are for C_{21} and low molecular weight polyethylene.

In the temperature region 120–180 K, the 733-cm^{-1} band of C_{21} is used as a monitor of orthorhombic packing in which the chains are not in register (Figure 2). As we have noted earlier, there are two possible processes involved. In one of these, the conversion is either from the out-of-register monoclinic extended chain or else from conformationally disordered chains in the glass to extended chains packed not in register, in an orthorhombic subcell. In either case, the relatively low value, 0.9 kcal/mol, found for E^* is appropriate: a relatively low barrier is to be expected for a process involving partial rotation of the chain unaccompanied by significant longitudinal displacement and for a process involving localized conformational ordering.

However, a much larger value of E^* is obtained for the final annealing step of C_{21}, in which the extended chains go from an out-of-register (nematic like) orthorhombic structure to the in-register orthorhombic structure. This process, which occurs at temperatures between 240 and 280 K, can be followed either with the 733-cm^{-1} band or with any band in the complex of bands near 760 cm^{-1}. (See section III-B-3.) For this transition, a value for E^* is found in the range 9–16 kcal/mol. This large value would appear to reflect the large barrier expected for the longitudinal transport of chains in an orthorhombic structure below room temperature.

D. T_{beg} and $T_{1/2}$ for Conformational Ordering in a Very High Molecular Weight Polyethylene Glass. It is of interest to estimate the lowest temperature, T_{beg}, at which conformational ordering begins in the case of a high molecular weight PE glass. This can be done by plotting the values of T_{beg} for C_{21} and for our low molecular weight PE against the reciprocal of the numer of carbons in these chains and then extrapolating this plot to infinite molecular weight. This plot is shown in Figure 12 and along with it is a similar plot for $T_{1/2}$, the temperature at

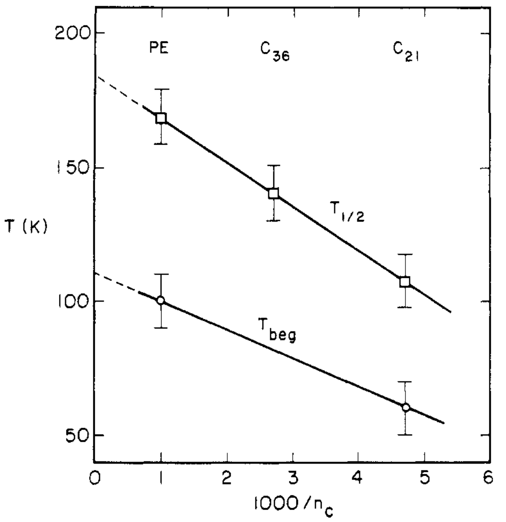

Figure 12. Plots of $T_{\rm beg}$ (the threshold temperature at which conformational organization begins in the glass) and $T_{1/2}$ (the temperature at which one-half the chains have been coverted to the all-trans form) against $1/n_c$ where n_c is the (average) number of carbons in the chains of C_{21}, C_{36}, and low molecular weight polyethylene.

which one-half the disordered chains have become ordered. The $T_{1/2}$ plot includes a data point for C_{36}, which falls nicely on the line defined by C_{21} and PE.

Extrapolation in Figure 12 gives respective values of 111 and 185 K for $K_{\rm beg}$ and $T_{1/2}$ for PE of infinite molecular weight. These values, which have errors estimated to be ±10 K, are consistent with values that we have estimated from the spectra of Hendra and co-workers,[2,3] who studied high molecular weight PE glasses obtained by a sudden quenching to near liquid nitrogen temperature of a thin film of molten PE.

The lowest temperature infrared spectrum of quenched PE that is shown by Hendra et al. is for 120 K (Figure 1, ref 2). In this spectrum, the 720-cm^{-1} band has a contour that is slightly more complicated than the totally featureless one that characterizes the glass formed by deposition (Figure 1C). This indicates that at 120 K a small amount of conformational ordering has already occurred in the quenched high molecular weight sample. That some ordering has occurred is consistent with the fact that the temperature (120 K) of Hendra's sample was about 10 K higher than our estimated value of $T_{\rm beg}$. An estimate of $T_{1/2}$ for Hendra's sample is more difficult. However, the infrared spectra (Figure 1, ref 2) and Raman spectra (Figure 1, ref 3) indicate that about one-half the conformationally disordered sample has disappeared around 200 and 180 K, respectively. These temperatures are reasonably close to our estimate of 185 K for $T_{1/2}$.

VI. Summary

Glassy films of n-$C_{21}H_{44}$, n-$C_{36}H_{74}$, and low molecular weight polyethylene ($\bar{M}_n$ = 1790 and $\bar{M}_w/\bar{M}_n$ = 1.1) were prepared by the vacuum sublimation onto a CsI window maintained at 7 K. The infrared spectra of these films were measured at 7 K and at higher temperatures. The following is a summary of our findings about the structure of the glass and the transformations the film undergoes upon annealing.

1. The conformational disorder of the chains comprising the glass was found to be approximately the same as that associated with chains at the sublimation temperature. Thus, with allowances made for differences in the effects of thermal broadening on band shape, the infrared spectrum of the glassy film of C_{21} at 7 K formed by sublimation near 338 K very much resembles the spectrum of liquid C_{21} at 323 K. Similarly the spectrum of the PE film at 7 K resembles that of molten PE near 420 K, except that for the glass the gauche bond concentration estimated from the spectrum is that appropriate for molten polyethylene at a temperature near 620 K, the sublimation temperature used in preparing the glass.

2. As the glassy films formed at 7 K are warmed, the chains reorganize through a series of processes that are of two basic types, one involving conformational ordering and a second involving interchain ordering by means of rotation about and translation along the long axis of the ordered extended chains. The transformations occur over a more or less broad temperature range and are irreversible. The structural changes appear to occur concomitantly with increases in temperatures. A spectrum measured as long as 2 h after the sample had reached the annealing temperature was found to be indistinguishable from one measured immediately after.

3. A detailed picture of the changes that occur at the molecular level during the annealing of the glassy C_{21} film has emerged form an analysis of the infrared spectra. In warming the as-deposited glass of C_{21} from 7 K, there is no evidence of rearrangement until a temperature near 60 K is reached. Then a transformation begins in which conformationally disordered chains are converted in one step to the ordered all-trans form. This conversion is essentially complete at about 180 K. The ordered, extended chains initially pack predominately in a monoclinic subcell (that is, the local packing is monoclinic). Beginning at a temperature around 180 K, the monoclinic subcell is rapidly converted, presumably by rotation about the long axis of the chains, to an orthorhombic subcell. The chains in the monoclinic and orthorhombic subcell structures are found not to be in register; i.e., the methyl end groups do not lie in parallel planes. The final step of the annealing process involves a registering of the chains in the orthorhombic structure. This occurs over a narrow temperature region between 250 and 290 K. At the completion of this step, the film has the orthorhombic structure normally associated with crystalline C_{21} at room temperature.

4. An analogous series of transformations is found to occur for a glassy film of low molecular weight PE, except, of course, the chain-registering step does not occur. The transition temperatures for PE are significantly higher, and the transition temperature regions are broader than for C_{21}.

5. The structure of a film of glassy C_{36} and the temperature dependence of the structure were studied but in considerably less detail than in the case of C_{21}. In general, the structure and behavior of the glass on annealing were similar to that of C_{21}. The transition temperatures were found to be intermediate between those of C_{21} and PE.

6. The temperature at which conformational ordering begins, $T_{\rm beg}$, and at which the ordering has occurred for one-half the sample, $T_{1/2}$, has been estimated for the case of an infinitely high molelcular weight PE. Values of 111 ± 10 and 185 ± 10 K for $T_{\rm beg}$ and $T_{1/2}$, respectively, were obtained by extrapolation from plots of $1/n_c$ vs $T_{\rm beg}$ and $T_{1/2}$ for C_{21}, C_{36}, and low molecular weight PE, where n_c is the (average) number of carbons per chain.

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Registry No. $C_{21}H_{44}$, 629-94-7; $C_{36}H_{74}$, 630-06-8; polyethylene, 9002-88-4.

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Surface-Selective Introduction of Specific Functionalities onto Poly(tetrafluoroethylene)[1]

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ABSTRACT: Exposure of poly(tetrafluoroethylene) film samples to Me_2SO solutions of the potassium salt of benzoin dianion renders metallic gold-colored, air-sensitive film samples. The color and property changes of the film are due to a carbonaceous reduction product, the thickness of which can be controlled by the duration of the exposure to benzoin dianion. Reduced layers of ca. 150–20 000 Å have been prepared. The chemical structure of the carbonaceous product is complex: it is a cross-linked polymeric carbon containing carbon–carbon single, double, and triple bonds, fluorine and hydrogen bound to sp^2 and perhaps sp^3 carbon, and a small amount of oxygen. Reduced film samples react with a range of reagents which are reactive toward unsaturation. Strong oxidants completely remove the reduced layer. Chlorine and bromine react readily, turning gold-colored films white and pale yellow, respectively. The reduced layer can be used as a reactive "handle" to incorporate hydroxyl, amino, and carboxylic acid functionalities on the surface of poly(tetrafluoroethylene): Hydroboration followed by oxidation introduces hydroxyl groups. Maleic anhydride adds radically and can be hydrolyzed to carboxylic acids. Substitution reactions of brominated films introduce amino groups.

Introduction

Modification of the chemical composition of polymer surfaces is important to a range of materials applications.[3] We are concerned with modified polymer surfaces at the functional group level and wish to answer the questions: how does the location of polymer surface functional groups at the polymer–reactive environment interface affect functional group reactivity? Can interface conditions (solvent in contact, temperature) be manipulated to control functional group chemistry? Can we use standard functional group manipulations to regulate surface properties of the polymer, in particular adsorption (of other polymers from solution), wetting, and adhesion (to metals or standard adhesives)? To address these questions we have been developing methods for introducing polar organic functionalities onto the surfaces of chemically resistant polymers.[4,5] Because these polymers are resistant to most reagents, a range of reactions can be directed at the surface functionality, not further modifying the bulk of the polymer. This paper reports two-step and multistep reactions for modifying the surface of poly(tetrafluoroethylene) (PTFE). The first step in each modification is the benzoin dianion reduction/cross-linking[1] of the PTFE surface. Throughout this manuscript this material is abbreviated PTFE-C. Subsequent reactions of this intermediate are devised to render cross-linked PTFE surfaces containing covalently attached chlorine, bromine, hydroxyl, amino, and carboxylic acid functionalities.

The work reported in this manuscript had four objectives: (1) to study the reaction of benzoin dianion with PTFE, particularly with regard to controlling the depth of reaction; (2) to characterize the chemical composition of the reduced layer (PTFE-C) to govern choices of subsequent reactions; (3) to introduce functionalities by using

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