Macromolecules 1989, 22, 3600–3606

Quantitative Infrared Methods for the Measurement of Crystallinity and Its Temperature Dependence: Polyethylene

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Received October 25, 1988;
Revised Manuscript Received January 30, 1989

ABSTRACT: Vibrational spectroscopic methods are widely used to characterize semicrystalline polymers in terms of crystallinity. The temperature coefficient of crystallinity, an important and fundamental quantity, is seldom determined for lack of a sensitive method. In this paper, we describe an infrared approach to the measurement of the temperature coefficient of crystallinity. We start from the well-known observation that the integrated intensities of the bands in the spectrum of a semicrystalline polymer change with temperature. It is also known, though less appreciated, that only part of the change is due to changes in crystallinity, the remaining part being due to changes in the intrinsic intensity of the bands. We outline a method for separating these overlapping effects. The method has been applied to a variety of semicrystalline polyethylene samples. The temperature coefficients are found to be highly dependent both on the temperature and on the morphology of the sample. In addition we report crystallinity measurements on a solution crystallized low molecular weight ($\bar{M}_w$ = 13 600) sample, discuss the origin of an apparent anomalous temperature dependence of band intensity cited in the literature, and offer quantitative evidence that the temperature dependence of specific volume is, at temperatures above 0 °C, largely determined by partial melting.

I. Introduction

Infrared and Raman spectra are sensitive to the conformation and packing of chain molecules, and this sensitivity has been widely exploited to characterize semicrystalline polymers in terms of their crystallinity. An important related quantity that is rarely measured is the temperature coefficient of crystallinity. Vibrational spectroscopy has not been widely used for this measurement because of the difficulties in interpreting the temperature changes that are observed. In the infrared, it is known that a change in the temperature of a liquid or solid sample affects the shape and the intensities of the bands and that the magnitudes of the effects are dependent on the temperature as well as on the physical state of the system. For the polymethylene chain in condensed phases, we have shown quantitatively that these effects are very large in the infrared, even at ambient temperatures.[1] To measure the temperature dependence of crystallinity in chain-molecule systems, it is therefore necessary to separate the effect on the spectrum of temperature per se from the effect of structural change.

The high sensitivity of infrared spectroscopy, relative to other techniques, provides an incentive to develop methods for such measurements. In some ways, vibrational spectroscopy is uniquely suited for this. Characteristic bands can be associated with the ordered fraction and with the disordered fraction, and these bands normally have comparable intrinsic intensities. The bands remain clearly distinguishable over a wide range of temperatures and for different phases of the sample.

In this paper, we discuss the determination of crystallinity and its temperature dependence for semicrystalline polymers by means of infrared spectroscopy. The procedures are illustrated for a number of polyethylene (PE) samples that differ in crystallinity. The measurements reported here do not represent a comprehensive study of all the structural and morphological variations that can be attained in polyethylene but demonstrate what is possible, the procedures involved, and the sensitivities that may be achieved. On the other hand, some of the preliminary results are interesting in their own right.

II. Approaches

From the experimental point of view, the infrared intensity, I, of a band is defined as

$$I = \frac{1}{b\rho}\int_{\text{band}} A_\nu \, d\nu \qquad (1)$$

where b is the path length, ρ is the density of the sample, and A_ν is the absorbance at frequency ν (in wavenumbers). In our discussion, the term "intensity", unless otherwise indicated, will refer to integrated intensity as defined in eq 1.

Nearly all our measurements have been made on polymer films sandwiched between KBr or CsBr windows. In that case, a change of temperature leaves the product $b\rho$, which appears in eq 1, unchanged since, in the absence of lateral movement of the film, the number of molecules in the infrared beam remains constant. Therefore, the product $b\rho$ need not be known in determining the temperature coefficient of intensity.

If temperature is to be a variable, integrated infrared intensities are to be preferred to peak heights for quantitive measurements because they are less subject to temperature effects. The problem with peak heights is that they depend on band shapes, and band shapes are markedly affected by dynamic factors that affect vibrational relaxation[2] as well as by local inhomogeneities in the microstructure of the system. Therefore, for our purposes, peak height is an unsatisfactory measure of band intensity.

Although integrated intensities are less dependent on temperature than the peak heights, they are by no means temperature independent. The reasons for the dependence are not obvious. Elementary considerations indicate that, for harmonic vibrational modes in the absence of significant intermolecular interaction, integrated intensities should be essentially independent of temperature and phase.[1] This problem of the temperature dependence of

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0024-9297/89/2222-3600$01.50/0

intensities for the condensed state has received very little attention. Some measurements on small molecules in the liquid phase have been reported, and these show that intrinsic intensities generally decrease somewhat as temperature increases.[3]

Earlier, we reported on the temperature dependence of the infrared intensities of the polymethylene chain from 7 to 370 K.[1] This work appears to stand alone as the sole attempt to determine the temperature dependence of the intrinsic intensities of a simple system in the solid state over a wide temperature region.

Our measurements on the polymethylene chain revealed large changes in integrated intensities with temperature over a wide temperature region. It also revealed large intensity changes with changes in the physical state. As expected, we found that intensities decrease with increasing temperature. However, for the crystalline state at ambient temperatures, some of the temperature coefficients are dramatically larger than those observed at the same temperature for similar systems in the amorphous and liquid states.

The mechanisms involved in these effects are not known at present. A clue lies in our observation that, for the crystalline state, the cross-sectional area of the unit cell, that is, the area measured perpendicular to the long axis, is closely related to the observed intensity changes. As a result, for example, the intensity change due to a temperature change can be correlated with the intensity change associated with a phase change.[1] This correlation is utilized in the procedures discussed below.

A. Temperature Coefficients. The temperature dependence can be expressed by starting from Beer's law which states that the observed intensity, I_i^{obs}, of an infrared band associated with the ith component (here, the crystalline or amorphous component) of a sample is proportional to the product of the concentration, x_i, of the component and the intrinsic intensity of the band, I_i^{intr}; that is

$$I_i^{\mathrm{obs}} \propto x_i I_i^{\mathrm{intr}} \qquad (2)$$

The temperature dependence of I_i^{obs} depends on the temperature dependence of *both* x_i and I_i^{intr}. This may be expressed as

$$\partial \ln I_i^{\mathrm{obs}}/\partial T = \partial \ln x_i/\partial T + \partial \ln I_i^{\mathrm{intr}}/\partial T \qquad (3)$$

In the applications that we will discuss below, we assume that semicrystalline polyethylene consists of a crystalline fraction comprised of the orthorhombic structure and an amorphous fraction that consists of all else. The chains in the crystalline fraction are, of course, completely ordered.

The structure of the amorphous region is more complex. All the chain units in the amorphous region are to some extent conformationally disordered. The largest fraction of disordered chain units will be in the liquidlike (isotropic) regions. A smaller fraction of the units will be associated with the interfacial regions.[4-7] Because of packing constraints, these units will tend to be less disordered than those in the liquidlike region and can be considered as part of an anisotropic partially ordered region.[5,7,8]

The amorphous fraction of the sample, whose concentration is measured by the infrared bands that we will describe below, includes both the liquidlike regions and the interfacial regions. The bands used measure short-range conformational disorder (in contrast to D-LAM bands, which measure average disorder over a long section of the chain[9]). Since these bands are associated with localized vibrational modes and therefore with local disorder, their frequencies and shapes will not be highly dependent on the concentration of gauche bonds; in other words, the positions and shapes of these bands will be much the same whether the chains associated with them are in the liquidlike regions or in the interfacial regions.

Finally, we should mention that there may be some small intensity error due to the presence of chains that are highly trans but located outside the orthorhombic lattice. Trans runs of this sort should have a relatively low concentration, and in fact, there are no features in the infrared spectrum that can be identified with them. Therefore, at the level of accuracy of our measurements, their presence would not be expected to affect our results very much.

To determine the temperature dependence of the crystalline fraction, x_c, of the sample, eq 3 is written in the form

$$\partial \ln x_c/\partial T = \partial \ln I_c^{\mathrm{obs}}/\partial T - \partial \ln I_c^{\mathrm{intr}}/\partial T \qquad (4)$$

The values of the two terms on the right can be measured spectroscopically. The first term comes directly from infrared measurements on the sample. The second term may be obtained directly from infrared measurements on a sample that is entirely crystalline, although, as we will see, it is sometimes possible to evaluate the second term indirectly.

An equation analogous to eq 4 may be written for the amorphous component. Since $x_c + x_a = 1$, we have

$$x_c\, \partial \ln x_c/\partial T + x_a\, \partial \ln x_a/\partial T = 0 \qquad (5)$$

and thus, we can evaluate the temperature dependence of one component given the other, provided the concentrations of the components are known.

We will now apply these considerations to a series of PE samples that differ in their crystallinity.

B. Experimental Procedures. All infrared spectra were measured at nominal resolutions ranging from 2 to 0.5 cm^{-1} with an evacuatable Nicolet Model 8000 FTIR spectrometer equipped with a cooled MCT infrared detector.

For temperatures in the range from −28 to 100 °C, the sample was housed in a copper block assembly through which a thermostated liquid was circulated. For the 7–300 K temperature range, the sample was cooled in a Lake Shore Cryotronics CTI Model 21 closed-cycle helium refrigerator equipped with a silicon diode thermometer and a Lake Shore temperature controller.

For reference, an infrared spectrum of a completely amorphous sample of polyethylene was measured. The sample was prepared by an in vacuo vapor deposition of Polywax 2000 ($\bar{M}_n$ = 1790, $\bar{M}_w/\bar{M}_n$ = 1.1) onto a CsI plate at 7 K. A small furnace containing the polymer was mounted in the refrigerated cell and oriented toward the cooled CsI window. The furnace, which initially contained about 10 mg of the polymer, was heated to 300–350 °C until a sufficiently thick film (~5 μm) was deposited (see ref 10 for additional information).

Curve-fitting procedures were used to separate bands and to determine their integrated intensities. These procedures were used only in those cases where the number and peak frequencies of the bands had been previously established. The fitting was performed with the use of interactive graphic routines.

The PE samples studied are listed in Table I.

C. Infrared Band Used in the Analysis. 1. The 1400–1250-cm^{-1} Bands. Several sets of well-known infrared bands of PE were used. One set occurs in the 1400–1250-cm^{-1} region. These bands, which are associated with the amorphous fraction, have been previously assigned to specific kinds of short conformational sequences such as gtg′ and gg[11] and have been used extensively for

Table I
Semicrystalline Polyethylene Samples

sample	$(1 - \lambda)_{\Delta H}$	10^{-6}	description	crystallization conditions
A	0.75	0.1–1.0	unfractionated linear PE	annealed ~20 h at 123 °C
B	0.58	0.11	linear PE fraction, $M_w/M_n = 1.07$	quenched at −70 °C
C	0.53	1–2	unfractionated linear PE	slow cooled from melt
D	0.36	0.108	hydrogenated polybutadiene[a]	quenched at −70 °C

[a] Random ethyl branch copolymers; 2.2 mol % branch points.

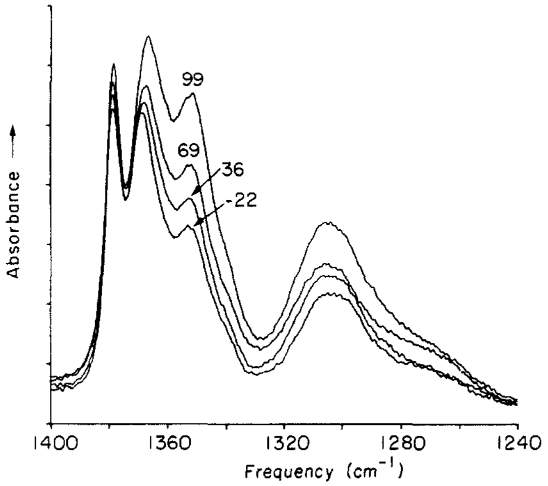

Figure 1. Temperature dependence of the infrared spectra of a low-crystallinity polyethylene (sample D of Table I) in the 1400–1220-cm^{-1} region. The temperatures of the sample, −22, 36, 69, and 99 °C, are indicated.

estimating disorder in various systems that contain polymethylene chains.

These bands are present in the infrared spectra of a PE copolymer (sample D of Table I) shown in Figure 1. Their intensity increases significantly in going from −26 to 99 °C, a temperature just below the melting point. The intensity increase is a measure of the increase in the amorphous component.

2. The 735–715-cm^{-1} Bands. Both the amorphous and crystalline fractions of PE can be monitored with the methylene rocking bands near 725 cm^{-1}. Of the three rocking mode bands in this region, two are associated with the crystalline fraction. These appear near 730 and 722 cm^{-1}, and they are significantly narrower than the third band, which represents the amorphous fraction. The latter band appears near 723 cm^{-1} and thus significantly overlaps the 722-cm^{-1} band of the crystalline fraction.

The assignment of the 730- and 722-cm^{-1} crystalline bands is well established.[12] The two bands appear in the infrared spectra of the orthorhombic n-alkanes and highly crystalline polyethylene. At room temperature, they have halfwidths (FWHH) of about 2 cm^{-1}.

When crystalline n-alkanes or PE is melted, the 730/722-cm^{-1} doublet is replaced by a broader band centered near 723 cm^{-1}. This band is characteristic of the amorphous or conformationally disordered structure.[11] The nature of this band has been clarified in our recent study of completely amorphous n-$C_{21}H_{44}$ and PE at 7 K.[10] The half-width of the 722-cm^{-1} band is about 18 cm^{-1} for liquid n-$C_{21}H_{44}$ and 20 cm^{-1} for amorphous n-$C_{21}H_{44}$ and PE at 7 K.

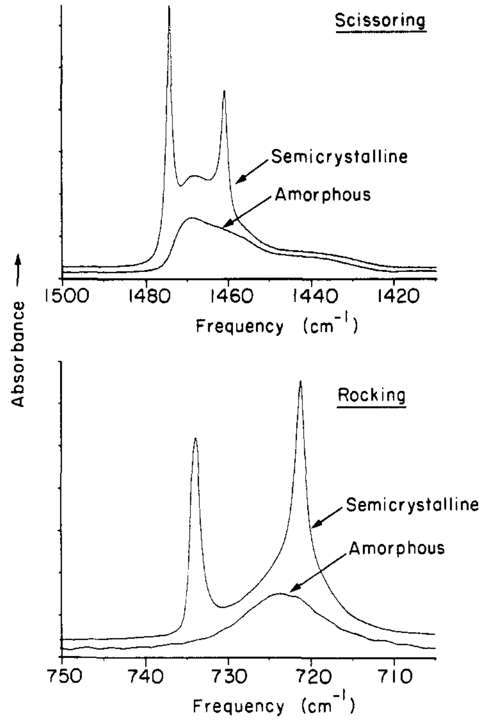

Figure 2. Infrared spectra in the methylene scissoring and rocking mode regions of a low-crystallinity PE (sample D of Table I) and an amorphous deposit of Polywax 2000 (ref 4), both at 7 K.

The lower half of Figure 2 shows the rocking mode bands for two samples at 7 K. The spectrum of the semicrystalline sample, which is a copolymer (sample D), shows two narrow bands. A third band, which is associated with the amorphous fraction, is very broad and lies hidden under the two narrow bands. Just below the spectrum of the semicrystalline sample is shown the spectrum of a totally amorphous film of Polywax 2000 deposited from the vapor and maintained at 7 K. This spectrum shows the rocking mode band associated with amorphous PE; that is, it shows the band that is hidden in the spectrum of the semicrystalline sample.

The necessity of using curve-fitting procedures to separate the bands and measure their integrated intensities is now apparent. Although the amorphous content of the semicrystalline PE sample, whose spectrum is shown in the lower half of Figure 2 and has just been described, is high, ~64%, the amorphous band near 723 cm^{-1} is, as we have emphasized, nevertheless largely obscured by the two bands from the crystalline fraction. However, because the halfwidths of the amorphous and crystalline bands are disparate, the curve-fitting technique is effective in resolving the bands.

3. The 1475–1420-cm^{-1} Bands. This complex of bands, which is due to methylene scissoring modes, is quite similar to the 735–715-cm^{-1} methylene rocking bands in the disposition and shape of the component bands and in their assignment. Again, there are three bands. Two are narrow and belong to the crystalline fraction. They appear at 1473 and 1463 cm^{-1}. The amorphous band, which is much broader, is at 1467 cm^{-1}. As is the case for the rocking modes, the assignment of the crystalline bands is well established.[12] The amorphous band is characterized in ref 10 and 11. The widths (FWHH) of the crystalline bands are found to be about 2 cm^{-1} for the n-alkanes at room temperature. The width of the amorphous band is 15 cm^{-1}, both for liquid n-$C_{21}H_{44}$ at 300 K and for a deposited amorphous film of n-$C_{21}H_{44}$ and PE at 7 K.[10]

The methylene scissoring bands are shown in the upper half of Figure 2, which shows infrared spectra of a semicrystalline PE (sample D) and of a totally amorphous film

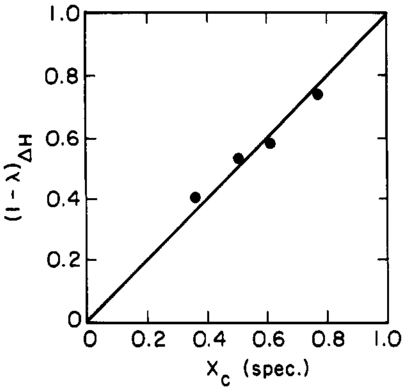

Figure 3. Crystallinity, $(1-\lambda)_{\Delta H}$, determined calorimetrically, plotted against crystallinity, x_c(spec), determined spectroscopically from the 735–715-cm^{-1} bands with the use of eq 6, for the samples listed in Table I.

of PE, both at 7 K. As in the case of the complex of bands in the 735–715-cm^{-1} region, band overlapping is a major problem. In fact, it is a bigger problem here because the amorphous band is highly asymmetric. The asymmetry makes band fitting more difficult and less accurate, and for this reason, we have preferred to use rocking mode bands in the 735–715-cm^{-1} region.

III. Measurements

A. Determination of Crystallinity. Two sets of measurements are reported on in this section. The first is to provide a check on the method that uses the 735–715-cm^{-1} bands for determining crystallinity. The second set utilizes this method to determine the amorphous content of a solution-crystallized sample of PE.

The first set involves measurements on the four samples of PE listed in Table I. The crystallinity is given by

$$x_c = \frac{I(722 + 730)}{I(722 + 730) + \alpha I(723)} \tag{6}$$

where I represents the observed infrared intensities for the bands indicated. The integrated intensities were obtained by band-fitting methods. The 730- and 722-cm^{-1} bands are the crystalline bands and the 723-cm^{-1} band is associated with the amorphous component. The coefficient α, which is defined as

$$\alpha = \frac{I^{\text{intr}}(722 + 730)}{I^{\text{intr}}(723)} \tag{7}$$

and which from intensity measurements has been found to have a value of about 1.2, must be included to account for the fact that the intrinsic intensities of the crystalline and amorphous bands are not exactly equal.

The results of these measurements are compared in Figure 3 with calorimetric results on the same sample. The comparison confirms the accuracy of the spectroscopic method. Since $(1-\lambda)_{\Delta H}$ measures core crystallinity,[5,13] the infrared method must also be doing the same.

The second set of measurements, which were made on solution-crystallized PE, illustrates the method for a highly crystalline sample. The sample was prepared as follows. A relatively low molecular weight linear PE (NBS standard: SMR = 1482, $\bar{M}_w$ = 13600) was dissolved in hot C_2Cl_4 (~120 °C) to make a dilute solution (~0.1%). Small quantities of the solution were poured over the horizontal surface of a KBr plate. The solution spread, and the solvent quickly evaporated. This procedure was repeated until a sufficiently thick film was obtained. The resulting polycrystalline film was particularly suitable for quantitative infrared measurements because it did not significantly scatter the incident IR radiation in the frequency region of interest below 2000 cm^{-1}.

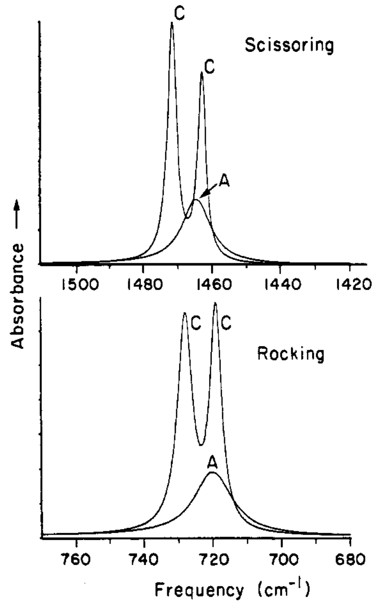

Figure 4. Crystalline (C) and amorphous (A) infrared bands obtained for a sample of solution-crystallized polyethylene. (The preparation of the sample is described in the text. These bands were resolved from the observed spectrum through band-fitting procedures.)

The infrared spectrum of this sample appears to show only the 730/722-cm^{-1} doublet. However, after the two narrow bands are removed through the use of band-fitting techniques, the presence of the 723-cm^{-1} band is revealed. Its intensity represents an amorphous content of 20%. The presence of a sizable amorphous fraction was confirmed from an analysis of the bands in the 1475–1420-cm^{-1} region. In this case, band-fitting procedures revealed the band near 1467 cm^{-1}, which is known to be associated with the amorphous fraction. Its intensity indicated that the amorphous fraction consisted of approximately 20% of the sample, in excellent agreement with the results obtained from the analysis of bands in the 735–715-cm^{-1} region. The crystalline and amorphous bands are shown in Figure 4 for both frequency regions.

The amorphous content of 20% determined from this analysis is consistent with values found earlier for crystallites formed from dilute solutions of polyethylene.[14] However, we note that the molecular weight ($\bar{M}_w$) of the present sample is 13600, much lower than that for the samples in the earlier studies, in which case the lowest molecular weight was 44000.

The measurement also has significance because it demonstrates how, for a highly crystalline sample, the amorphous fraction may be "hidden" under the crystalline bands and that a careful analysis is needed to reveal it.

B. Temperature Dependence of Crystallinity. In this section, the measurement of the dependence of crystallinity on temperature is demonstrated for the samples listed in Table I. The quantity of interest, $\partial \ln x_c/\partial T$, has been determined with the use of both crystalline and amorphous bands. In the case of a crystalline band, we used eq 4. The quantity $\partial \ln I_c^{\text{obs}}/\partial T$ was obtained from the observed temperature dependence of the band associated with the crystalline fraction. From this coefficient was subtracted the temperature coefficient of the *intrinsic* intensity of the band, $\partial \ln I_c^{\text{intr}}/\partial T$. As we have already noted, $\partial \ln x_c/\partial T$ can also be obtained from measurements on the amorphous bands through the use of eq 5.

Table II
Experimentally Measured Values[a] of $\partial \ln I^{\text{intr}}/\partial T$ and $\partial \ln I^{\text{obs}}/\partial T$ for Various Polyethylenes at 300 K

		bands,[c] cm^{-1}			
	sample[b]	1400–1330	1367	730	723
$\partial \ln I^{\text{int}}/\partial T$		0.8	0.4	−0.65	−1.2
$\partial \ln I^{\text{obs}}/\partial T$	A	2.0			
	B	2.1		−2.25	0.25
	C	2.5			
	D	2.5	2.0	−5.2	0.90

[a] In units of K^{-1} × 10^{-3}. [b] See Table I for sample description. [c] All bands except the 730-cm^{-1} band measure the amorphous component.

We will now discuss the measurement of the temperature dependence of the intrinsic intensities. Then we will proceed to the subject of principal interest, the temperature dependence of crystallinity.

1. Determination of the Temperature Dependence of Intrinsic Intensities. The bands we have used are listed in Table II where their frequencies or frequency regions, along with their observed temperature coefficients, $\partial \ln I^{\text{intr}}/\partial T$, are indicated. All the bands used except the 730-cm^{-1} band are characteristic of the amorphous phase.

The intensity–temperature coefficients of the amorphous bands were determined from infrared measurements on liquid n-$C_{16}H_{34}$ over the temperature range 25–90 °C. The spectra of the liquid were measured with the use of an infrared cell of "fixed" thickness; that is, the effect of temperature on the sample thickness was negligible. It is necessary, however, to take into consideration the change of the density, ρ, of liquid n-$C_{16}H_{34}$ with temperature. For this purpose, we have

$$\partial \ln I^{\text{intr}}/\partial T = \partial \ln I^{\text{uncor}}/\partial T - \partial \ln \rho/\partial T \qquad (8)$$

where I^{uncor} is the observed value of the intensity, uncorrected for temperature change. The quantity $\partial \ln \rho/\partial T$ has a value of about −0.9 × 10^{-3} K^{-1} over the temperature range considered.[15]

We note in Table II that, for liquid n-C_{16}, the temperature coefficients, for the bands in the 1400–1330-cm^{-1} region as well as for the 1367-cm^{-1} band, are positive rather than negative. This contrasts with the normal situation where intrinsic infrared intensities decrease with increasing temperature. In the case of the polymethylene chain in the liquid state, the increase occurs because the bands measured belong to modes associated with gauche bonds, whose concentrations, of course, increase with temperature. The intensity increase from this factor more than compensates for the loss due to a decrease in the intrinsic intensity. The temperature coefficients derived from n-$C_{16}H_{34}$ are appropriate for PE, since the concentration of gauche bonds in the amorphous fraction of the polymer and in the liquid n-alkane can be expected to increase with temperature in essentially the same way. This expectation follows from calculations based on the rotational isomeric state model, which indicates that the values of the trans/gauche ratio and its temperature coefficient for liquid n-$C_{16}H_{34}$ are very near the values for much longer chains.[16]

The temperature coefficient of the crystalline band at 730 cm^{-1} was also determined. Two methods were used, and they give comparable results. One method uses the observed relation between the temperature coefficient of the intensity of the 730-cm^{-1} band and the temperature coefficient for lateral expansion of the unit cell for orthorhombic chain packing. This relation was established earlier for PE and n-alkanes in the crystalline state.[1] At 300 K, the lateral expansion coefficient for crystalline PE has a value near 0.025 K^{-1}, and this leads to a value of −0.75 × 10^{-3} K^{-1} for the intensity temperature coefficient. The second method used to estimate the temperature coefficient of the 730-cm^{-1} band is also indirect. In this case, the observed values of the temperature coefficients of the crystalline 730-cm^{-1} band and the amorphous 723-cm^{-1} band, both measured for a PE sample of known crystallinity, are used. From these values, the intrinsic temperature coefficient of the 730-cm^{-1} band can be found from eq 3 written in the form

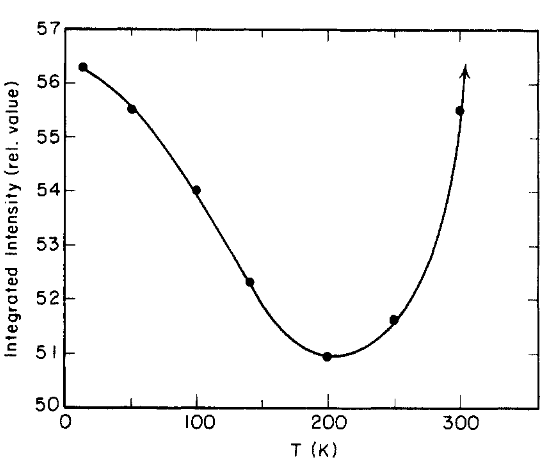

Figure 5. Infrared intensity, integrated over the frequency region 1400–1200 cm^{-1}, plotted against temperature for sample D (Table I), which is a low-crystallinity polyethylene. At temperatures higher than 300 K, the relative intensity continues to increase.

$$\frac{\partial \ln I_{730}{}^{\text{intr}}}{\partial T} = \frac{\partial \ln I_{730}{}^{\text{obs}}}{\partial T} + \frac{1 - x_c}{x_c}\,\frac{\partial \ln I_{723}{}^{\text{obs}}}{\partial T} - \frac{\partial \ln I_{723}{}^{\text{intr}}}{\partial T} \qquad (9)$$

From measurements on a sample for which $x_c = 0.82$, we found $\partial \ln I_{730}{}^{\text{obs}}/\partial T$ and $\partial \ln I_{723}{}^{\text{obs}}/\partial T$ to be −1.7 × 10^{-3} and 3.8 × 10^{-3} K^{-1}, respectively. This leads to a value of 0.58 × 10^{-3} K^{-1} for the temperature coefficient of the 730-cm^{-1} band, in reasonably good agreement with the value 0.75 × 10^{-3} K^{-1} found by the first method. The average of these values has been used in Table II.

2. Partial Melting at Low Temperatures. We consider the interesting, seemingly anomalous temperature behavior of the peak intensities of some infrared bands associated with the amorphous phase. This behavior was first reported by Dahme and Dechant[17] for semicrystalline polyethylene. They observed that, as the temperature of a sample increased from 120 to 430 K, the peak intensity of the 1300-cm^{-1} band at first decreased and then at a higher temperature increased. The intensity minimum was found to occur at a temperature between 220 and 300 K. Less crystalline samples tended to be associated with a lower temperature minimum. They observed similar behavior for other amorphous bands.

We have also observed the same phenomenon. However, our measurements differ from those of Dahme and Dechant in that we used integrated intensities instead of peak heights. An intensity versus temperature plot is shown in Figure 5 for the PE copolymer (sample D) over the temperature range 7–300 K. To minimize errors arising from band overlap, we used the sum of the intensities of all the bands in the region 1400–1200 cm^{-1}. At temperatures above 300 K (not shown in Figure 5), intensities continue to increase. For our sample, the intensity minimum occurs around 200 K. The low value of the temperature at the intensity minimum is in keeping with the low values that Dahme and Dechant found for PE samples

Table III
Experimentally Determined Values[a] of $\partial \ln x_c/\partial T$ and $\partial \ln x_a/\partial T$ for Various Polyethylenes at 300 °C

	sample[b]	bands,[c] cm^{-1} 1400–1330	1367	730	723	av
$\partial \ln x_c/\partial T$	A	(–0.40)				–0.4
	B	(–0.94		–1.6	(–1.05)	–1.2
	C	(–1.51)				–1.5
	D	(–3.03)	(–2.8)	–4.8	(–3.73)	–3.6
$\partial \ln x_a/\partial T$	A	1.2				1.2
	B	1.3		(2.2)	1.45	1.65
	C	1.7				1.7
	D	1.7	1.6	(2.7)	2.1	2.0

[a] In units of K^{-1} × 10^{-3}. [b] See Table I for sample description. [c] All bands except the 730-cm^{-1} band measure the amorphous component. Values in parentheses have been calculated from eq 5.

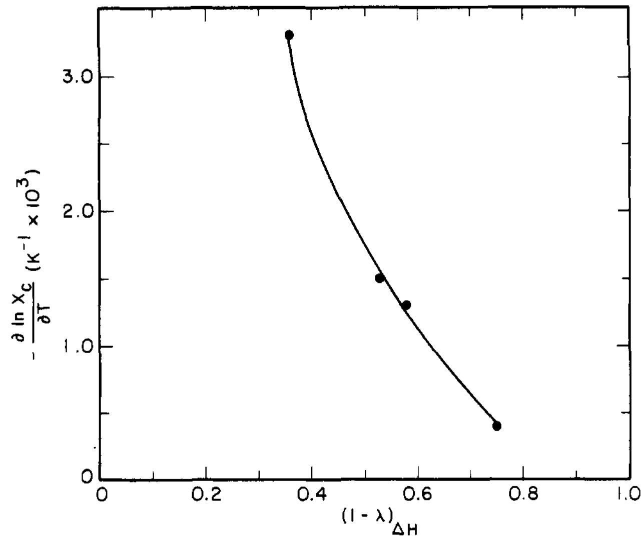

Figure 6. Temperature coefficient for crystallinity plotted against crystallinity, $(1-\lambda)_{\Delta H}$, for the polyethylene samples listed in Table I. The temperature of the samples is approximately 25 °C. (Estimated error in $\partial \ln x_c/\partial T$ is ±0.0002.)

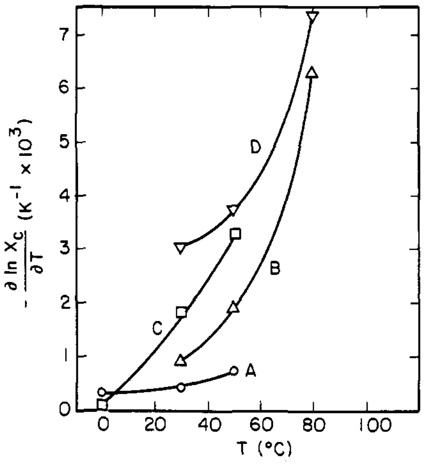

Figure 7. Temperature coefficients for crystallinity plotted against sample temperature for the samples listed in Table I. These results are based on intensities integrated over the 1400–1330-cm^{-1} region. (The systematic error in the values of $\partial \ln x_c/\partial T$ is estimated to be ±25%.)

of low crystallinity. Plots for more highly crystalline samples also show mininima. However, for these samples, the temperature dependence of intensity is less, so the observed minima are more shallow and more difficult to locate accurately.

The appearance of the minima can be explained in a simple way in terms of the relation between the temperature dependencies of the sample crystallinity and of intrinsic intensity. (Dahme and Dechant proposed a more general and qualitatively mechanistic explanation that invokes the effects on the vibrations of the chains of thermally induced motion and disorder.[17]) The temperature coefficient of the observed intensity of the amorphous band is, according to eq 3, the sum of two terms

$$\partial \ln I_a^{obs}/\partial T = \partial \ln x_a/\partial T + \partial \ln I_a^{intr}/\partial T \qquad (10)$$

whose values, in the present case, are found to have opposite signs. The value of the second term is negative and dominates the first term at low temperatures. However, the first term, whose value is positive, dominates the second term at high temperatures. Under these circumstances, $\partial \ln I_a^{obs}/\partial T$ must equal zero at some intermediate temperature and thus provide a minimum in the I_a^{obs} versus T curves. Since partial melting usually begins at lower temperatures for more highly amorphous samples, the fact that the minimum in intensity occurs at lower temperatures for less crystalline samples is accounted for. In the case of the copolymer, this minimum occurs around 200 K. Therefore, we can assume that partial melting begins to occur below this temperature.

3. Temperature Coefficients. Values of $\partial \ln x_c/\partial T$ and $\partial \ln x_a/\partial T$ were determined at 30 °C for the four samples described in Table I. The values of the temperature coefficients were obtained from the measured values of $\partial \ln I^{intr}/\partial T$ and $\partial \ln I^{obs}/\partial T$. The measured values are given in Table II.

In Table III, the value of the temperature coefficient for crystallinity is in parentheses if the band employed in the measurement is associated with the amorphous fraction. The reverse is true for the temperature coefficient of the amorphous component. For two of the four samples, more than one value of $\partial \ln x/\partial T$ was obtained for a given sample. The values, which represent independent measurements since they were obtained from different bands, are in rough agreement.

The values of the temperature coefficients for crystallinity for the four samples at about 300 K are plotted against their crystallinity in Figure 6. The coefficient is found to be very sensitive to crystallinity. Thus, we note that the value of the coefficient changes by a factor of about 8 in going from a sample of crystallinity of 75% for linear polyethylene (sample A) to 36% for the copolymer (sample D). This plot reflects the fusion process, which becomes broader with increasing molecular weight for linear chains and becomes extremely broad for copolymers.

In Figure 7 are shown the results of some limited measurements on the temperature dependence of $\partial \ln x_c/\partial T$. These results are based on intensities measured over the 1400–1330-cm^{-1} frequency region. Although there are large uncertainties in the values, it is clear, in going to higher temperatures, that the temperature coefficient increases dramatically. There are also marked differences between the samples reflecting differences in the fusion process. The coefficients appear to be very similar as the melting temperatures are approached.

Comparison of the values of the temperature coefficients obtained for polyethylene with those for other chain molecule systems is not possible for lack of data on other systems. However, recently we have measured conformational disordering of some crystalline n-alkanes in the orthorhombic phase as a function of temperature.[18] Based on the measurement of gauche-bond concentration, our preliminary results indicate that for n-$C_{60}H_{122}$, which melts at 100 °C, the value of $\partial \ln x_c/\partial T$ at 80 °C is about (–0.2 ± 0.1) × 10^{-3} K^{-1}. This value is much less than that observed for the polymer samples at comparable temperatures below the melting points (Figure 7). We should, however, at this point distinguish between two types of partial melting. In one case, partial melting, or premelting as it is often termed, involves the disappearance of imperfect crystallites at temperatures below the melting temperature of the complete system.[19] The other case is best illustrated by the *n*-alkanes. Here, at low temperatures, molecular crystals are favored; the chains assume a planar zigzag structure, and the terminal groups lie in parallel planes. Prior to complete melting, disorder develops from the ends of the individual chains. This type of premelting has been predicted theoretically[20] and observed experimentally.[14,21]

The magnitude and temperature behavior of $\partial \ln x_c/\partial T$ observed for the PE samples indicates that this coefficient plays an important role in determining the temperature dependence of the specific volume of semicrystalline polyethylene. It has been previously observed[22] that a temperature plot of the specific volume for a sample[23] similar to sample A in the present paper and a temperature plot of the specific volume of the *crystalline fraction* for a similar sample have essentially the same slopes from −150 to about 0 °C. However, at higher temperatures, the slope for the semicrystalline sample becomes increasing larger than that for the crystalline fraction alone. This observation has been interpreted to mean that above 0 °C the amorphous regions expand more rapidly than the crystalline regions.[22]

An alternative explanation is supported by the measurements reported here. We propose that, as the temperature increases, premelting becomes an increasingly significant factor so that, at temperatures above ~0 °C, the increase in specific volume with temperature is largely due to an increase in the amount of the amorphous component. We have estimated the value of the coefficient $\partial \ln x_c/\partial T$ necessary to reproduce the measured values of the specific volume of the semicrystalline polymer. The temperature coefficient for the specific volume of the amorphous component was assumed *constant*. The value of the coefficient was obtained from the V_{sp} versus T plot given in ref 23 for the molten polymer. The values of $\partial \ln x_c/\partial T$ needed to account for the upward slope in V_{sp} observed for the sample ranged from around $(0.5 \pm 0.4) \times 10^{-3}$/K at 12 °C to around $(1.8 \pm 0.4) \times 10^{-3}$/K around 87 °C. These values of the temperature of crystallinity are near those estimated for sample A (see Figure 7) and thus provide strong supporting evidence for this proposal.

Acknowledgment. We gratefully thank the National Science Foundation Polymers Program, Grant DMR 87-01586 to the University of California, Berkeley, and Grant DMR 86-13007 to Florida State University, Tallahassee, for supporting this research. H. H. thanks the Swiss National Science Foundation for a postdoctoral fellowship.

Registry No. PE, 9002-88-4.

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