

## The Effect of Temperature on the Infrared Absorption Frequencies of Polyethylene and Ethylene-Propylene Copolymer Films

NORMAN F. BROCKMEIER, *Chemical Engineering Department,  
The University of Texas, Austin, Texas 78712*

### Synopsis

The frequency shifts of the six prominent infrared absorption bands were measured for films of polyethylene and ethylene-propylene copolymer as a function of temperature. Three bands (at 720, 731, and 1473  $\text{cm}^{-1}$ ) shifted to higher frequency, and three bands (at 1463, 2849, and 2918  $\text{cm}^{-1}$ ) shifted unexpectedly to lower frequency as the sample temperature was decreased. The greatest shift occurred with the  $\text{CH}_2$  rocking band, which increased from 730.2 to 734.2  $\text{cm}^{-1}$  as the temperature was decreased from 313 to 22°K. The shift usually ceased in the temperature range from 40 to 110°K, probably because some kind of molecular motion ceased. Four mechanisms are discussed in an attempt to account for the different frequency shifts: bulk contraction with decreasing temperature, an increase in dispersion forces between chains, variation in the length and coupling of the vibrating chain molecule, and a change in the planar zigzag conformation of the chain molecule. Thermal contraction is sufficient to explain most of the observed frequency shifts. The  $\text{CH}_2$  stretching modes (2849 and 2918  $\text{cm}^{-1}$ ) may be shifted to lower frequency by an increase in the dispersion forces between chains, caused by contraction. The displacement of the 1463  $\text{cm}^{-1}$  band-shift curve is an indication of the sample density. The displacements of the 1473 and 731  $\text{cm}^{-1}$  band-shift curves are indications of the proportion of propylene in the ethylene copolymer.

### INTRODUCTION

Some early investigators<sup>1</sup> have conducted infrared absorption measurements of polymers at very low temperatures in the hope that the broad absorption bands characteristic of these materials at normal temperatures would narrow down to a few sharp lines. This band structure, rather than a separate line spectrum, occurs because there are many rotational energy transitions near each vibrational transition at room temperature. The sharpening of the bands would simplify the problem of assigning the normal modes to the correct frequencies. However, the desired sharpening of the absorption bands, which normally occurs with relatively small molecules, did not occur to any large extent in the case of the polymers. The frequency of the maximum absorption shifted with temperature, arousing the curiosity of several investigators.

The IR absorption band shifts have been measured for the  $\text{CH}_2$  rocking bands (720 and 731  $\text{cm}^{-1}$ ) of polyethylene.<sup>2</sup> The slopes of these band-shift

curves rapidly diminished to zero at about 100°K. This cessation of the band shift implied that below this temperature some kind of structural change in the polymer could no longer occur. It was inferred that this structural change was related to one of the known mechanical relaxations, such as the gamma transition.<sup>2</sup> In the present study the six prominent absorption bands (CH<sub>2</sub> rocking, CH<sub>2</sub> bending, and CH<sub>2</sub> stretching) of polyethylene and ethylene-propylene copolymer were scanned in an attempt to discover the mechanism of the frequency shift.

## EXPERIMENTAL

### Apparatus

The infrared absorption frequencies for a number of polyethylene and ethylene-propylene copolymer films were measured with a Perkin-Elmer 225 grating spectrophotometer. The potential problem of interference fringes generated by such a film was overcome by casting the polymer directly on a salt window. Heat flux to the film was minimized by placing this coated window in a specially designed absorption cell, which was contained in a vacuum-insulated chamber. In addition, for all absorption measurements of bands below 1600 cm<sup>-1</sup> a AgS filter was used to cut off radiation above 1600 cm<sup>-1</sup>. Salt windows on each side of the vacuum

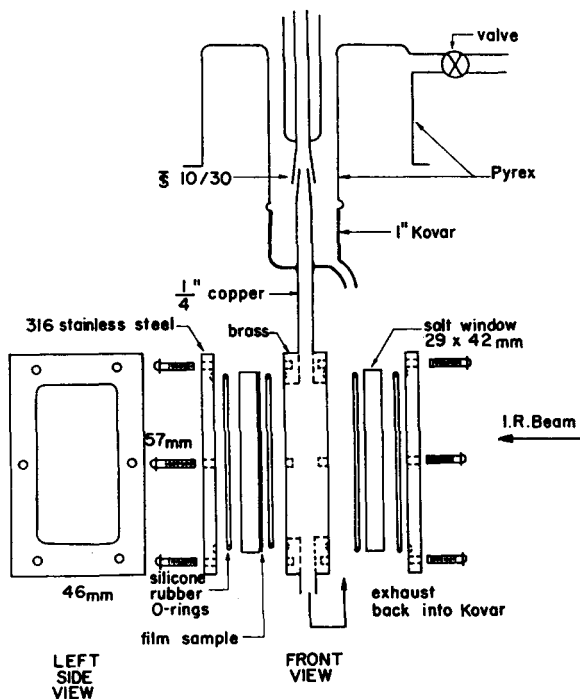


Fig. 1. Exploded diagram of infrared absorption cell. Note that the exhaust line for the nitrogen coolant is not drawn completely, to simplify the drawing.

chamber permitted passage of the IR beam through the cell. A drawing of the cell is shown in Figure 1. Silicone rubber O-rings sealed the cell windows effectively above 180°K. Below this temperature continuous pumping of the vacuum chamber was necessary, because the seals developed minor leaks.

The temperature of the film, located on the inside of one window, was controlled by blowing nitrogen gas through the cell. The nitrogen passed through 20 in. of copper tubing immersed in liquid nitrogen contained in a half-gallon Dewar vessel, through a vacuum-jacketed tube, and then into the cell. The flow rate of nitrogen provided a very sensitive ( $\pm 1^\circ\text{K}$ ) control of the film temperature, which could be decreased to 80°K by this technique. For experiments below 80°K a Cryotip brand cell was substituted for this cell. Liquid hydrogen cooled the film to 22°K in the Cryotip. The film temperatures above 77°K were measured with an iron-constantan thermocouple placed in contact with the sample. Below 77°K the film temperatures were measured with a gold-copper (gold-doped) thermocouple. A vacuum-tube millivoltmeter indicated the potential difference.

### Procedure

All of the film samples were cast from solution on either a KBr window or a NaCl window. A typical casting recipe was 2.1 g of polymer dissolved in 30 ml of *o*-dichlorobenzene at about 140°C under a nitrogen purge. The salt window was prepared to receive the casting by preheating to 120°C on a hot plate. The solution was poured onto the salt window and immediately spread with a preheated glass rod to a uniform thickness set by 20-gauge wire shims. The casting was placed in an oven preheated to 145°C, the oven was evacuated, and the film was cooled at a rate of less than 0.5 deg/min. The slow cooling rate allowed the film time to anneal. The amount of film oxidation caused by the casting procedure was negligible, as evidenced by the absence of any increased absorption for the carbonyl band in these spectra (carbonyl absorption was always very small or absent).

Each absorption band for a sample was scanned at constant temperature at a rate of 4 wavenumbers/min with 16:1 scale expansion on the recorder chart. The spectral slit width was 0.7  $\text{cm}^{-1}$  at 1463  $\text{cm}^{-1}$ . The frequency of maximum absorbance was read from the instrument dial while the drive was in slow motion, always toward decreasing wavenumbers. The scan for each band was repeated, and the mean frequency was recorded. A typical variation in these readings was  $\pm 0.05 \text{ cm}^{-1}$ . Ammonia, water vapor, and HCl were used to calibrate the spectrophotometer in the appropriate regions. All of the data have been corrected by using the frequencies reported in the IUPAC tables.<sup>3</sup>

### RESULTS

Experiments showed that all six prominent absorption bands of polyethylene shifted in frequency as the temperature of the sample was lowered.

TABLE I  
Some Vibrational Modes of Polyethylene<sup>a</sup>

Wavenumber, cm <sup>-1</sup>	Nominal descript. of mode	Phase involved <sup>b</sup>	Sign of band shift (slope)
720	CH <sub>2</sub> rock.	C, A	Neg.
731	CH <sub>2</sub> rock.	C	Neg.
1463	CH <sub>2</sub> bend.	C, A	Pos.
1473	CH <sub>2</sub> bend.	C	Neg.
2849	CH <sub>2</sub> sym. stretch.	A, C	Pos.
2918	CH <sub>2</sub> asym. stretch.	A, C	Pos.

<sup>a</sup> Reproduced, by permission, from Krimm.<sup>4</sup>

<sup>b</sup> C and A refer to crystalline and amorphous, respectively.

TABLE II  
Polyethylene Samples Used

Sample no.	Density, g/cm <sup>3</sup>	Mol. wt. distrib.	Visc.-avg. mol. wt.
7	0.9525	Broad	91,500
9	0.9560	Narrow	41,700
11	0.932	—	—
12	0.915	—	—

Repetition of the runs gave identical results within experimental error. In addition, the band frequency at each temperature was the same whether the temperature was approached from above or below. The band at 731 cm<sup>-1</sup> shifted the most, going from 730.2 to 734.2 cm<sup>-1</sup> as the sample temperature was lowered from 313 to 22°K. Three of the bands (those at 1463, 2849, and 2918 cm<sup>-1</sup>) showed an unexpected shift to lower frequency as the temperature was lowered. The band shifts for the ethylene-propylene copolymer were similar to those observed for polyethylene.

Table I lists the vibrational modes for each of the six bands studied, together with the region in which the motion occurs, amorphous or crystalline.<sup>4</sup> The various polyethylene samples are identified in Table II.

### Detailed Results for Polyethylene

Figure 2 shows the frequency of the maximum infrared absorption plotted against absolute temperature for each of the six prominent bands. The band shifts for all four samples of polyethylene were identical for both CH<sub>2</sub> rocking bands, 720 and 731 cm<sup>-1</sup>. The dashed lines show the data of Hansen et al.<sup>2</sup> The 731 cm<sup>-1</sup> band shift ceases at 70°K, but at room temperature the frequency seems to be increasing rapidly. This band, which is split from the one at 720 cm<sup>-1</sup> by crystal interaction,<sup>5</sup> probably approaches the amorphous band at the crystalline melting point (≈410°K). The CH<sub>2</sub> bending band at 1473 cm<sup>-1</sup> probably does the same with its companion at 1463 cm<sup>-1</sup> as the temperature is increased. The temperatures at which

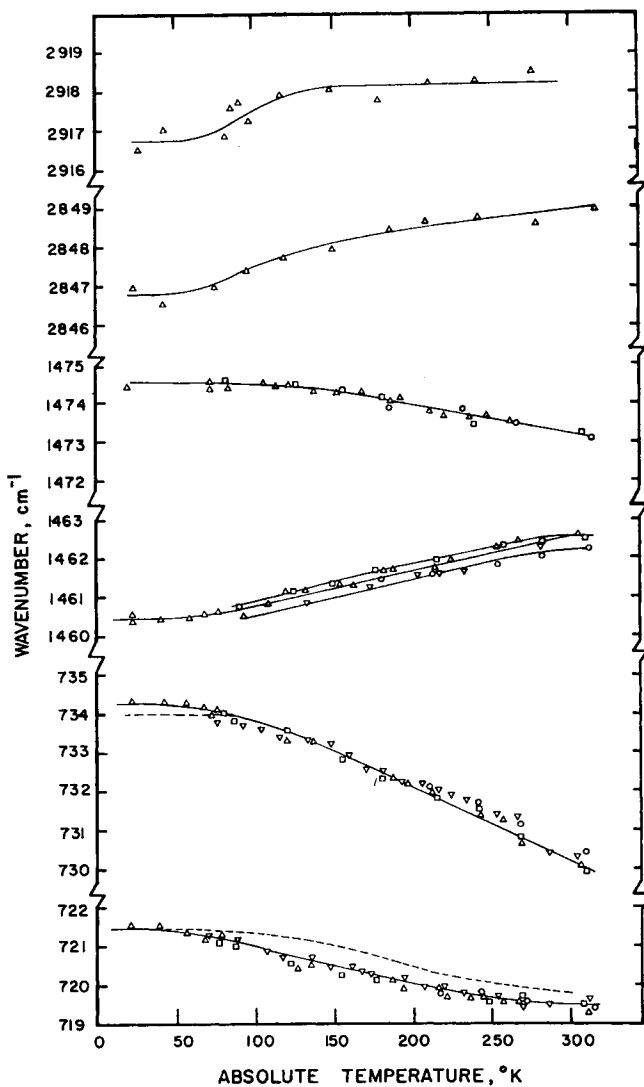


Fig. 2. Absorption band-shift curves for polyethylene film. Kinds of samples: ( $\nabla$ ) high density, broad molecular weight distribution (MWD); ( $\circ$ ) high density, narrow MWD; ( $\Delta$ ) medium density; ( $\square$ ) low density. The dashed lines show the data from Hansen et al.<sup>2</sup>

the band shifts cease are listed in Table III for all bands. These points were determined by extending the nearly straight-line portions until the intersections were reached.

The  $1463\text{ cm}^{-1}$  band-shift curves are displaced to the right in the order of increasing sample density. The position of this band for the ethylene-propylene copolymer (Fig. 3) is also sensitive to density or composition.

TABLE III  
Temperature at Which Band Shift Ceases

Band, $\text{cm}^{-1}$	Temperature limit, $^{\circ}\text{K}$	
	Lower	Upper
720	60	320
731	70	—
1463	40	330
1473	110	—
2849	50	340
2918	50	160

The measurements of the band shifts for the  $\text{CH}_2$  stretching modes (2849 and  $2918\text{ cm}^{-1}$ ) were limited to the medium-density sample. The amount of each frequency shift is comparable to the shifts for the other bands.

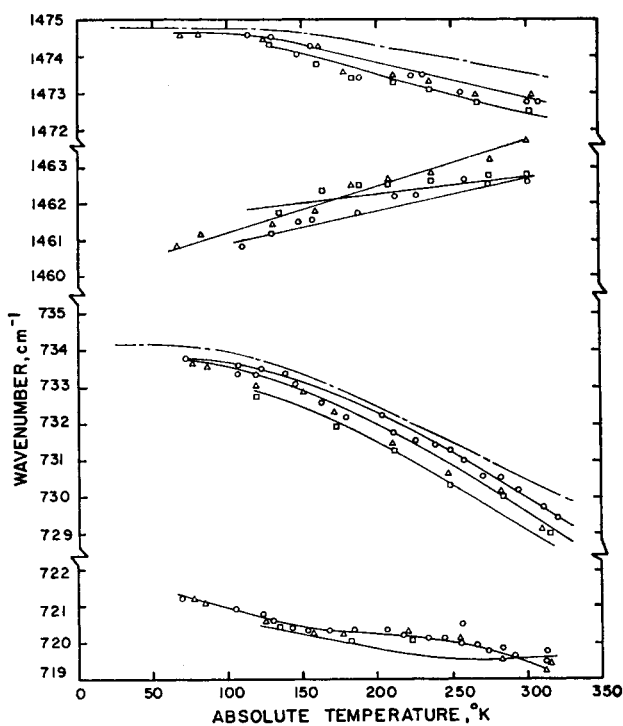


Fig. 3. Absorption band-shift curves for films of ethylene-propylene copolymer. Propylene in sample (mol-%); (O) 2.4%; ( $\Delta$ ) 6.8%; ( $\square$ ) 10.8%. The broken lines show the data for polyethylene from Figure 2.

### Detailed Results for Ethylene-Propylene Copolymer

Figure 3 shows the results for the  $\text{CH}_2$  rocking and bending modes, the only bands that were measured in the three copolymer samples. Table IV

TABLE IV  
Ethylene-Propylene Copolymer Samples

Sample no.	Ethylene, mol-%	Density, g/cm <sup>3</sup>	Crystallinity, %	Melt index
8	97.6	0.9184	35.7	1.40
13	93.2	0.8979	26.5	0.07
10	89.2	0.8890	19.5	0.35

summarizes some physical properties of the copolymer samples. The copolymer sample that contained 10.8 mol-% propylene gave a separate shift curve for each of the four bands.

The 731 cm<sup>-1</sup> band (Fig. 3) shows a regular displacement to lower frequency for each sample studied. Table IV shows that these three copolymer samples have a regularly decreasing density as the mole per cent of propylene is increased. The 1473 cm<sup>-1</sup> band which, like the 731 cm<sup>-1</sup> band, originates in the crystalline regions, shows a similar displacement for two of the copolymer samples. However, each of these bands yields only one shift curve for polyethylene (Fig. 2), even though these samples have a range of densities from a high of 0.956 to a low of 0.915 g/cm<sup>3</sup>. Moreover, the band-shift curves for the polyethylene samples (broken lines) are above the copolymer curves for both bands. The most likely reason for the displacement of these two crystalline bands is, therefore, the differing propylene composition of the samples.

The 1463 cm<sup>-1</sup> band shift is different for each copolymer sample. The relationship of the curves for 2.4 and 6.8 mol-% propylene is the same as for the three polyethylene shift curves at 1463 cm<sup>-1</sup> (Fig. 2): the curves for the higher-density samples lie below those for the lower-density ones. The curves of both kinds of polymer shift steadily as the sample density is increased, except for the sample of highest propylene composition (10.8%). The reason the latter sample does not fit the trend is unknown.

The 1473 cm<sup>-1</sup> band shift is one of the few curves for the copolymer that was extended far enough to reach the region of zero slope, at 80°K. Compare this with Figure 2, in which this band shift ceases at 110°K. This temperature change may indicate a corresponding change in the location of some kind of mechanical relaxation.

## DISCUSSION

In the following sections four explanations of the observed IR absorption band shifts will be discussed in order to determine which mechanism or combination of mechanisms best accounts for the results. Most of the discussion will be stated in terms of the results for polyethylene. However, the similarity between the experimental results for polyethylene and ethylene-propylene copolymer indicate that the same mechanisms are probably in operation for both of these materials. The first part of the discussion will concentrate on the explanations of the direction of the

frequency shifts, and the second part will concentrate on the reason for the cessation of the shifts.

### Bulk Contraction with Decreasing Temperatures

As the polymer is cooled, the crystalline portion contracts, and the unit cell shrinks. For polyethylene the shrinkage perpendicular to the chain axis is greater than that in the direction of the axis (between bonded atoms).<sup>6</sup> As the unit cell shrinks, the interatomic distances (between nonbonded atoms) decrease. The greater crystalline interaction that results should cause vibrational modes already split to separate further.<sup>7</sup> Other things being equal, as the temperature drops, for each pair of "crystal split" modes the component at higher frequency should rise, and the component at lower frequency should drop even lower.

Figures 2 and 3 show that the  $731\text{ cm}^{-1}$  split pair or doublet and the  $1473\text{ cm}^{-1}$  doublet separated in frequency as the temperature was lowered for both polyethylene and ethylene-propylene copolymer (unless otherwise noted, both kinds of polymers gave the same results). The  $1473\text{ cm}^{-1}$  doublet of the  $\text{CH}_2$  bending modes separated by  $3.7$  wavenumbers, from  $10.4\text{ cm}^{-1}$  to a splitting of  $14.1\text{ cm}^{-1}$ . The  $731\text{ cm}^{-1}$  doublet of the  $\text{CH}_2$  rocking modes separated by about half as much over the same temperature interval,  $1.8$  wavenumbers, from  $10.9\text{ cm}^{-1}$  to a splitting of  $12.7\text{ cm}^{-1}$ . These results are consistent with an increase in crystalline interaction caused by the contraction of the unit cell. Note that the splitting of the two different  $\text{CH}_2$  stretching modes is much less than the resolution of the spectrophotometer.

However, the  $720\text{ cm}^{-1}$  component of the  $\text{CH}_2$  rocking doublet increased in frequency, rather than decreased. This could be explained if another phenomenon is superposed on the bulk contraction. In subsequent paragraphs three other phenomena that might account for this upward shift are discussed.

### Increase in Dispersion Forces between Chains

It is known<sup>8</sup> that for some types of compound containing C—H the absorption bands for CH stretching will shift to lower frequency if the C—H group forms a hydrogen bond. The hydrogen bond causes an effective lowering of the force constant for the C—H bond, which results in a lower vibration frequency. This bonding is known to shift the stretching frequencies more than the bending or rocking frequencies. In the case of polyethylene hydrogen bonds are not possible between the chains, but there is a type of weak attraction caused by London dispersion forces. The contraction of the polymer with cooling may result in a slight increase in the strength of these dispersion forces. This mechanism is a possible explanation of the downward frequency shifts of the two stretching modes ( $2849$  and  $2918\text{ cm}^{-1}$ ).



### Vibration Frequencies in a Chain of Coupled Oscillators

The polyethylene molecule may be modeled as a chain of  $N$  coupled methylene units in order to calculate the vibration frequencies for the normal modes. The solution of the secular equation which results from this kind of mathematical model has been presented in the literature.<sup>7,9-11</sup> One of these solutions<sup>7</sup> gives an equation for the  $N$  discrete values of the vibrational frequencies,  $\omega_s$ , for a chain with fixed ends:

$$\omega_s^2 = \omega_o^2 + 2\omega'^2 [1 \pm \cos s\pi/(N + 1)] \quad (1)$$

where  $s = 1, 2, 3, \dots, N$ ,  $\omega_o$  = frequency of the uncoupled oscillator ( $\text{cm}^{-1}$ ),  $\omega'$  = interaction parameter ( $\text{cm}^{-1}$ ), and  $N$  = number of  $\text{CH}_2$  units acting as a "coupled" oscillator. The plus sign in the parentheses is used to solve for those vibrations for which all dipole moment changes are parallel, such as the  $\text{CH}_2$  rocking modes; the minus sign is used to solve for those vibrations for which adjacent dipoles point in opposite directions (antiparallel), such as the  $\text{CH}_2$  bending and  $\text{CH}_2$  symmetric stretching modes.

For the  $\text{CH}_2$  rocking modes the frequency given by  $s = N$  is by far the strongest observed with infrared absorption. Thus eq. (1) takes the form

$$\omega_{\text{strongest}}^2 = \omega_o^2 + 2\omega'^2 [1 + \cos N\pi/(N + 1)] \quad (2)$$

The interaction parameter may be expected to increase as the temperature is lowered because of the bulk contraction. This alone could account for the upward shift of the rocking frequencies. If the coupled length  $N$  of the oscillator were to decrease, this would also increase the rocking frequencies. For a typical value of  $\omega' = 200 \text{ cm}^{-1}$  a decrease in  $N$  from 200 to 15 would result in an upward shift of  $2 \text{ cm}^{-1}$ . However, it seems more probable that, if anything,  $N$  would increase as the temperature was lowered, because the chain could assume a more regular configuration. Equation (2) is valid only for an isolated chain, and thus it applies only to the  $720 \text{ cm}^{-1}$  band, a part of which originates in the amorphous regions of the polymer. The measured shift for this band was  $2 \text{ cm}^{-1}$  upward. One explanation consistent with eq. (2) is that the value of  $\omega'$  increased, while there was no significant change in  $N$ . Another possibility is that  $\omega'$  increased more than enough to offset an increase in  $N$ , resulting in a net upward shift.

For the  $\text{CH}_2$  bending modes the strongest observed frequency occurs at  $s = 1$ . Thus, eq. (1) takes the form

$$\omega_{\text{strongest}}^2 = \omega_o^2 + 2\omega'^2 [1 - \cos \pi/(N + 1)] \quad (3)$$

The interaction parameter for  $\text{CH}_2$  bending is in general different from the one for the rocking modes. Equation (3) is valid only for an isolated chain, so it applies only to the  $1463 \text{ cm}^{-1}$  band, a part of which originates in the amorphous regions of the polymer. If the bending interaction does not change significantly with temperature, and if  $N$  increases from a magnitude of 10 to 100 or more, the strongest bending frequency would shift downward  $2 \text{ cm}^{-1}$ . The measured shift was  $2 \text{ cm}^{-1}$  downward, so the mechanism

described above seems plausible. However, one expects the crystalline bending frequency ( $1473\text{ cm}^{-1}$ ) to shift in the same direction, but it does just the opposite. Perhaps an additional mechanism is in operation.

It has been shown that the frequency shift predicted by eq. (3) is proportional to the third power of the wavelength.<sup>7</sup> Thus, the short-wavelength  $\text{CH}_2$  stretching modes should not have shifts large enough to be observed. Although eq. (3) predicts the correct direction for the  $2849\text{ cm}^{-1}$  band shift, this mechanism cannot account for the observed magnitude, about  $2\text{ cm}^{-1}$ .

### Possible Change in the Helical Conformation of the Chain Molecule

A vibrational analysis of the isolated polyethylene molecule has been made by utilizing the fact that repeat units of a polymer are equivalent to each other under a screw (helical) symmetry operation.<sup>9</sup> This reduces the secular determinant to a tractable size, facilitating the calculation of the phonon or vibrational spectrum. This vibrational spectrum is a plot of  $\theta$ , the phase difference between adjacent oscillators, versus frequency  $\omega$ , in reciprocal centimeters.<sup>9</sup> The frequencies that are infrared-active are those for  $\theta = 0$  and for  $\theta$  equal to integral multiples of the screw angle per repeat unit,  $\psi$ . The active frequencies can be determined by the intersection of the spectrum curve with a line drawn perpendicular to the  $\theta$  axis at  $\theta$  of  $0, \psi, 2\psi$ , etc.

Under most conditions the value of  $\psi$  for polyethylene is equal to  $\pi$  radians, or  $180^\circ$ , as evidenced by x-ray diffraction experiments. However, Huggins<sup>12,13</sup> has suggested that the carbon chain in crystalline polyethylene departs slightly from the well-known planar zigzag as a result of intramolecular hydrogen-hydrogen interactions. The value of  $\psi$  was assumed to have the same magnitude and direction for each carbon atom in the chain. The resulting chain conformation would be a helix of relatively long pitch. If the crystalline lattice were unable to accommodate such a helix beyond a certain distance along the chain axis, the helix might be accommodated by folding back on itself. This was given as the reason for the chain folding observed in single crystals of polyethylene. Until now there has been no experimental evidence of such a long-pitch helix in polyethylene.

The frequency shifts in the present study may be interpreted within the framework of this helix formation mechanism. The vibrational spectrum plot<sup>9</sup> shows that, if  $\psi$  shifts in either direction from  $180^\circ$  as the temperature of polyethylene is lowered, the  $720\text{ cm}^{-1}$  band will shift upward, whereas the  $1463, 2849$ , and  $2918\text{ cm}^{-1}$  bands will shift downward. By analogy, one expects the crystalline bands to shift in the same direction as the amorphous bands above. The  $731\text{ cm}^{-1}$  band does this; however, the  $1473\text{ cm}^{-1}$  band shift opposes that of the  $1463\text{ cm}^{-1}$  band. Except for the  $1473\text{ cm}^{-1}$  band, the experimental results agree with the predictions of this theory.

There seems to be no single mechanism that can account for all six band shifts observed in this study.

### Cessation of Band Shift May Indicate Limit to Mechanical Relaxation

Table III shows that in most cases there are both upper and lower limiting temperatures, which define a range in which some kind of molecular change occurs, as evidenced by the frequency shift. Even for the two crystalline bands one may set an upper limit at the crystalline melting point. Note that for five of the bands the lower limits are near 50°K. This is significantly lower than the two temperatures given for the gamma transition peaks, at 130 and 160°K.<sup>14</sup> Some investigators have inferred that the cessation of the motion responsible for the gamma transition causes the band shift to cease.<sup>2</sup> However, it seems unlikely that the same mechanism that is responsible for the gamma transition is important in causing these frequency shifts. It is more probable that below 50°K the distance between the polymer chains does not decrease much, the van der Waals interaction is nearly constant and, therefore, the frequency shift approaches zero.<sup>15</sup>

The temperature at which the frequency shift ceased for the 1473  $\text{cm}^{-1}$  crystalline  $\text{CH}_2$  bending mode was strongly influenced by composition. This band shift ceased at 110°K for polyethylene, whereas it continued down to 80°K for the copolymers containing 2.4 and 6.8% propylene. This change is comparable to the magnitude and direction of the change in the glass transition temperature. There can be little doubt that this frequency shift ceases because some kind of molecular motion can no longer occur.

### CONCLUSIONS

(1) The mechanism of thermal contraction is sufficient to explain most of the observed frequency shifts in polyethylene as the polymer is cooled. The following observations are consistent with this mechanism: the bending doublet, at 1473  $\text{cm}^{-1}$ , separated further, the rocking doublet, at 731  $\text{cm}^{-1}$ , separated further, and the two  $\text{CH}_2$  stretching modes (2849 and 2918  $\text{cm}^{-1}$ ) decreased in frequency. The last result depends on the increasing dispersion forces caused by contraction.

(2) The upward frequency shift for the 720  $\text{cm}^{-1}$  component of the rocking doublet cannot be explained by crystalline interaction caused by contraction. There is probably at least one additional phenomenon superposed on the crystalline interaction for the rocking modes.

(3) The displacement of the 1463  $\text{cm}^{-1}$  band-shift curve is an indication of the sample density. The curves for the samples of higher density are displaced to lower frequency.

(4) The displacement of the 731  $\text{cm}^{-1}$  band-shift curve is an indication of the proportion of propylene in the ethylene copolymer. These curves are shifted to lower frequency as the mole per cent of propylene in the sample is increased.

(5) The displacement of the 1473  $\text{cm}^{-1}$  band-shift curve is also an indication of the proportion of propylene in the ethylene copolymer. These

curves are shifted in the same direction as the curves for the  $731\text{ cm}^{-1}$  band.

(6) The cessation of the frequency shift at certain temperatures probably indicates that some kind of molecular motion has ceased.

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