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

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

Introduction

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

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

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

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

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

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Table I
Characterization of Linear Polyethylene Samples

sample	crystallization condns	T_m,[a] °C	$(1 - \lambda)_{\Delta H}$	supermolecular structure	ν_1(D-LAM), cm^{-1}
Hifax-16	quenched, −70 °C	131	0.41	h	206
Hifax-28	quenched, −70 °C	132	0.42	h	204
Hifax-28	slow-cooled	135	0.48	h	206
Marlex 6009	quenched, −70 °C	130	0.59_5	a	204
Marlex 6009	124 °C (87 min)	135	0.72	a	210
Marlex 6009	128 °C (2510 min)	135.8	0.81		206
Marlex 6009	129 °C (2 weeks)	138.5	0.89	c	
Marlex 6009	scanned at 150 °C				206

[a] From DSC endothermic peak.

series of linear polyethylene samples that cover a wide range of crystallinities, as determined by conventional methods. In preparing these samples, advantage was taken of previous work that established the basis of how the level of crystallinity can be varied by proper choice of molecular weight and crystallization conditions.[11,17]

Experimental Procedures

Materials and Crystallization Procedures. Three unfractionated linear polyethylenes were the primary polymers used in this study. There were two very high molecular weight samples, Hifax-16 and Hifax-28 (manufactured by the Hercules Powder Co.) with viscosity-average molecular weights of 2×10^6 and 7×10^6, respectively, and Marlex 6009 (manufactured by the Phillips Petroleum Co) with $M_n = 7.5 \times 10^3$ and $M_w/M_n = 24.2$.

Films of approximately 1 mm thick were prepared by molding in a Carver press at temperatures between 160 and 180 °C for about 15 min. For nonisothermal crystallization, the films were either rapidly quenched from the hot press to −70 °C or allowed to crystallize slowly by turning the heaters off in the press (it usually takes between 5 and 6 h to cool to room temperature). For isothermal crystallization, the films were placed between aluminum foil and sealed in a glass tube under vacuum. After melting the sample, the tubes were quickly transferred to a silicone oil bath previously thermostated at a predetermined crystallization temperature.

Melting temperatures were determined with a Perkin-Elmer DSC 2B differential scanning calorimeter. The heating rate used was 5 °C/min, and the weight of the sample was approximately 5 mg. Melting points were identified with the maximum in the endothermic peak, and the instrument was calibrated with an indium standard. The enthalpies of fusion determined from the thermograms were converted to degrees of crystallinity by taking 69 cal g^{-1} to correspond to the enthalpy of fusion, ΔH_u, of a perfect polyethylene crystal.[19] The error in the degree of crystallinity thus calculated $(1 - \lambda)_{\Delta H}$ is estimated to be ±0.02.

Raman Procedures. The incident radiation for the Raman spectra was the 514.5-nm line of a Spectra-Physics Model 165 argon ion laser. The spectra were recorded with a SPEX 1403 spectrometer, which was controlled by a SPEX Datamate DMI computer. The computer allows for multiple scans, thus improving the signal-to-noise ratio of the final spectrum. The scattered light was collected in a direction perpendicular to the incident beam by a SPEX 1459 Uvisir illuminator. In the usual experiment, the samples were scanned for about 3 h with an effective power at the sample of $\simeq$300 mW and with a resolution of 5 cm^{-1}. Spectra were taken in the interval between 50 and 1450 cm^{-1}. Most of the spectra were measured at room temperature. In one specific set of experiments, the spectra were measured as a function of temperature between 30 and 150 °C. The temperature was determined with a thermocouple, and temperature variations were ±3 °C.

Background

For understanding the structural implications associated with the presence of D-LAM in the spectra of semicrystalline polyethylene, it will be helpful to examine briefly the origin and properties of this band. As has been previously reported, the D-LAM band is the dominant feature in the low-frequency Raman spectrum of a liquid *n*-alkane longer than about C_9.[9] D-LAM is comprised of an enormous number of overlapping bands that arise from the many different conformers existing in the liquid. We note that the Raman spectrum of each individual conformer will have many skeletal-bending modes of significant intensity in the D-LAM frequency region. This situation contrasts with that of a conformationally ordered chain, where essentially only one intense band, LAM-1, is found. In this latter case, the conformational regularity of the chain is conducive to a concerted "breathing", acoustic-like mode in which all CC stretching and CCC bending coordinates are displaced in-phase. For a conformationally disordered chain, an analogous in-phase mode is not possible. Instead, the in-phase mode breaks up, and a broad band, the D-LAM band, results.

The frequency of D-LAM depends on the ratio, t/g, of the number of trans to gauche bonds, as well as on the number of carbon atoms, *n*, in the chain. This dependence, which will be presently discussed, suggests that D-LAM, in spite of its complexity, can in some ways be considered to be a single vibration. From this point of view, the D-LAM mode is associated with a hypothetical regular chain whose vibrational equations are defined in terms of the ensemble average. A model based on this concept has been used successfully to explain the dependence of the D-LAM frequency on t/g and *n*.[9] According to this model, the bandwidth of D-LAM is determined largely by the variance in the distribution of trans and gauche bonds.

The dependence of the D-LAM frequency on the number of carbons in the chain has been established experimentally for the liquid *n*-alkanes and the perfluoro-*n*-alkanes.[9] The relation found is $\nu = \nu_0 + B/n^2$, where ν_0 and B are constants and n is the number of carbons. We note that the $1/n^2$ dependence for D-LAM contrasts with the $1/n$ dependence observed for LAM-1 modes of ordered chains. The $1/n^2$ dependence observed for disordered chains reflects the fact that the vibrations associated with the D-LAM band are primarily not acoustic in character, although the intensity of the D-LAM band results from an acoustic component. This point is discussed in ref 9.

Results and Discussion

The observation of the D-LAM band in semicrystalline linear polyethylene will now be described and its significance discussed in terms of structure. A list of the samples studied, the different crystallization conditions, and the resultant properties is given in Table I. In addition to the melting temperatures and degree of crystallinity, the supermolecular structures are also given. These were obtained by small-angle light scattering and are designated by symbols previously defined.[17,21] Thus, in these studies, the supermolecular structure ranges from a random arrangement of lamellae "h" to well-developed and organized spherulites "a".

The D-LAM band was observed in the Raman spectra of all the polyethylene samples with a crystallinity less than

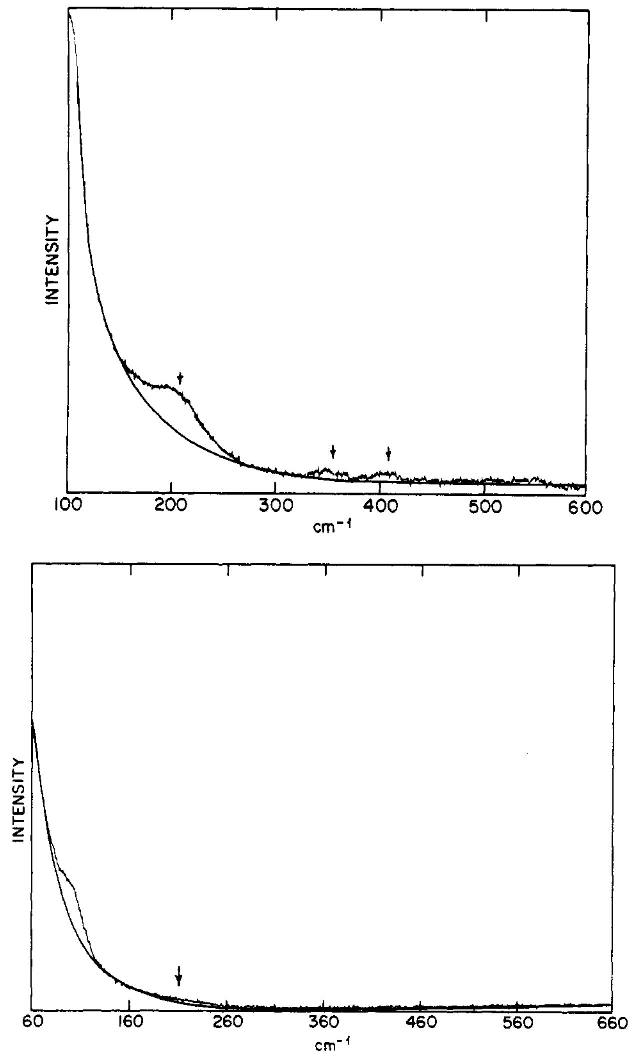

Figure 1. Low-frequency Raman spectra of two samples of semicrystalline linear polyethylene that differ in their level of crystallinity: (a) Hifax-28, $(1 - \lambda)_{\Delta H} = 0.42$; (b) Marlex 6009, $(1 - \lambda)_{\Delta H} = 0.72$. See Table I for sample characterization. Spectral resolution was 5 cm^{-1}. Laser power ≃300 mW. Temperature was 23 °C.

about 90%. Representative low-frequency spectra are shown in Figure 1. These spectra are of two linear polyethylene samples that are significantly different in their levels of crystallinity, 42% vs. 72%. The prominent feature in the spectrum of the lower crystallinity sample is a broad band near 200 cm^{-1}. This is the D-LAM band. The spectrum of the more highly crystalline sample also shows this band, but it is much less intense. Both spectra show a band near 100 cm^{-1} that is characteristic of the crystalline component. This band is made up of an unresolved pair of bands that are associated with two lattice-mode fundamentals of the orthorhombic crystal. (These lattice modes involve restricted rotation of the chains about their long axis).[22] Two less intense bands near 350 and 410 cm^{-1} are found in the spectra of the semicrystalline polyethylenes, and, like the D-LAM band, these bands are associated with disordered chains.

For comparison with the spectra of the semicrystalline polyethylenes, the Raman spectrum of liquid polyethylene was measured under the same conditions used for the solids except, of course, for the sample temperature. This spectrum is shown in Figure 2. Another Raman spectrum of the liquid, which was obtained earlier,[23] is shown in Figure 3. This spectrum, unlike that in Figure 2, was measured with an analyzer so that the $I_{\parallel}$ and $I_{\perp}$ spectra are reported. We note that the D-LAM band is much stronger in $I_{\parallel}$ than in $I_{\perp}$, showing that D-LAM is strongly polarized.

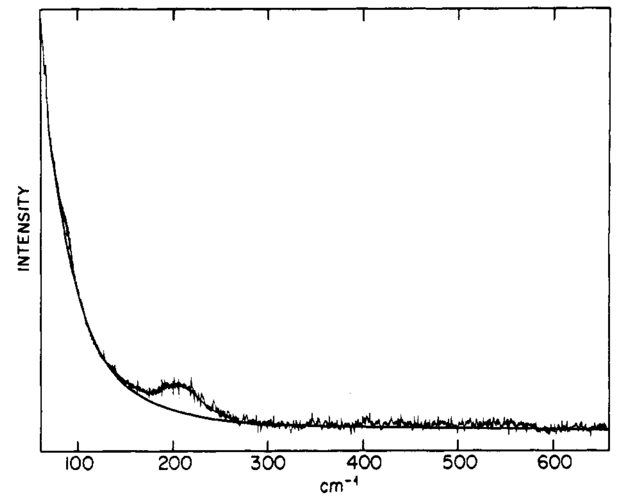

Figure 2. Low-frequency Raman spectrum of molten linear polyethylene at 150 °C.

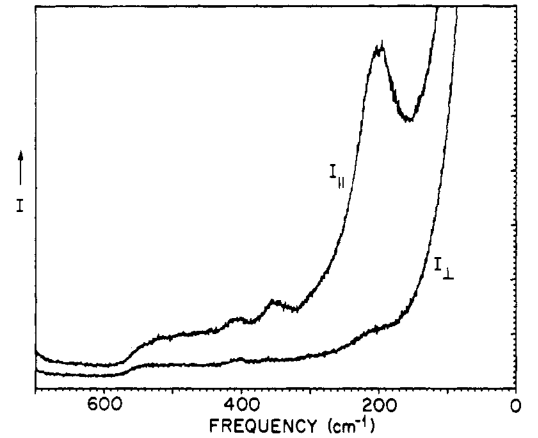

Figure 3. Low-frequency Raman $I_{\parallel}$ and $I_{\perp}$ spectrum of molten linear polyethylene at 150 °C.

Table II
Comparison of the Spectral Features in the Low-Frequency Raman Spectra of Semicrystalline and Molten Linear Polyethylene

	crystalline	liquid
ν(D-LAM), cm^{-1}	206 ± 4	202 ± 2
$\Delta\nu_{1/2}$(D-LAM), cm^{-1}	55 ± 7	60 ± 5[a]
ν (other bands), cm^{-1}	350	357
	409	412

[a] Measured from the $I_{\parallel}$ spectrum.

The D-LAM band observed for the semicrystalline polyethylenes (Figure 1) has a frequency and shape virtually identical with those of the D-LAM band observed for liquid polyethylene (Figures 2 and 3).

The values of the parameters describing the principal features in the low-frequency Raman spectra of liquid and solid polyethylene are summarized in Table II. The peak position of D-LAM for each of the semicrystalline polymers is given in the last column of Table I. The D-LAM frequency is essentially constant irrespective of the level of crystallinity over this wide range and the widely differing supermolecular structures. The average value for the six crystalline samples is 206 ± 4 cm^{-1}; for the liquid it is 202 ± 2 cm^{-1}. The latter frequency is for the liquid at 25 °C and was obtained by applying a Boltzmann correction to the high-temperature (150 °C) spectrum.[20] The half-width

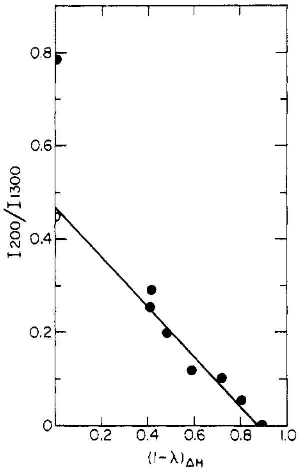

Figure 4. Relative intensity, $I(200)/I(1300)$, of the D-LAM band of linear polyethylene plotted against the degree of crystallinity, $(1-\lambda)_{\Delta H}$. Solid circle is the experimental value. Open circle is the corrected value for the completely molten polymer. See the text.

(full width at half-height) is 56 ± 7 cm^{-1} for the solid and 60 ± 5 cm^{-1} for the liquid. Finally, we note that the frequencies of the two less intense bands are 350 and 409 cm^{-1} for the semicrystalline polymers and 357 and 412 cm^{-1} for the liquid. Thus we can conclude that the D-LAM band and, in fact, the entire low-frequency Raman spectra of the liquid polymer and the noncrystalline component of the solid are virtually identical.

The striking similarity between the position and shape of the D-LAM band in the semicrystalline and liquid polyethylene spectra demonstrates that in the semicrystalline polymer there are regions of the chains over which the conformational structure is essentially that of liquid polyethylene. Any substantial differences in the trans–gauche ratio would be manifest in differences in the D-LAM band. Similarly, the reciprocal of the average length of the disordered sequence in the semicrystalline polymer must be close to that of the liquid. Estimated limits on the extent of any differences are discussed later.

It follows from the above that the intensity of the D-LAM band for the crystalline polyethylene samples should be closely related to their level of crystallinity. A comparison of these quantities is made in Figure 4. In this figure, the integrated intensity of D-LAM is plotted against the calorimetrically determined crystallinity for a series of linear polyethylene samples having crystallinities that vary from about 90% to 0%. The 0% value is for the molten polymer at 150 °C. The crystalline samples are characterized in Table I. Their spectra were measured at 25 °C. To establish the intensity of the D-LAM band, we use the intense methylene twisting band near 1300 cm^{-1} as an internal standard. Actually there are two twisting bands. One appears at 1295 cm^{-1} in the spectrum of the crystal and the other at 1306 cm^{-1} for the liquid. The 1306 cm^{-1} band also appears in the spectrum of semicrystalline polyethylene since this band arises from short-range conformational disorder. However, the sum of the intensities of the 1295 and 1306 cm^{-1} bands can be assumed to be independent of sample crystallinity. The combination of these two bands will be referred to as the 1300 cm^{-1} band. The D-LAM was separated from the baseline with the use of a flexible curve. The straight line drawn in Figure 4 is the result of a least-squares analysis of the seven experimental points for the samples having a finite level of crystallinity. The data are represented by a straight line with a correlation coefficient of 0.969. We note that the extrapolated value obtained for the molten polymer is substantially lower than the measured value. Corrections for sample transparency and temperature must be applied in order to compare with the data for the solids. These corrections will now be discussed.

The D-LAM intensity is measured by the ratio $I(200)/I(1295)$. However, the observed value of this ratio is influenced by the relative transparency of the sample. This occurs because polarization scrambling by the sample affects polarized and depolarized bands in a quantitatively different way. The bands of interest here represent such a pair since the 200-cm^{-1} D-LAM band is polarized[9] and the 1300-cm^{-1} reference band, being a methylene twisting motion, is depolarized. It will be sufficient to consider only the two limiting cases, a clear sample and an opaque (highly scattering) sample. The Raman intensity for such samples can be expressed in terms of an isotropic I_i and an anisotropic I_a component. With randomly oriented molecules and no polarization analyzer, our sampling arrangement gives $I_{\mathrm{clear}} = I_i + I_a$ for the clear sample and $I_{\mathrm{scatt}} = I_i + {}^{10}/_{7}I_a$ for the highly scattering sample.[24] For the D-LAM band, $I_a < 0.2I_i$, and for the 1300-cm^{-1} band, $I_i = 0$. Therefore, the value of $I(200)/I(1300)$ observed for liquid polyethylene should be reduced by 30% for comparison with the highly scattering samples. The temperature correction (the Boltzmann term[20]) results in an additional reduction by 19.4%. The open-circle data point for the liquid in Figure 4 represents the intensity ratio corrected for both the translucency and temperature. The relative D-LAM intensity measured for the liquid is now in excellent agreement with the value anticipated by extrapolation from the results for finite levels of crystallinity.

Some of the solid samples, especially those of low crystallinity, tended to be translucent, and, therefore, the possibility must be considered that the measured values of the D-LAM intensity for these samples might be affected in the manner observed for the liquid. We have concluded that this is not the case. This conclusion is based on intensity ratio measurements for a pair of bands at 1130 and 1295 cm^{-1}. These bands have polarization properties that are analogous to those of the 200- and 1300-cm^{-1} bands but are associated with the crystalline component rather than the disordered component. Their intensity ratio, being a property of the crystal, will have a value that is independent of the actual crystalline content. Therefore the observed value of the ratio will be constant for all samples unless there is an effect from the translucency of the samples. The constancy observed for this intensity ratio is indicated in Figure 5, where the ratio is plotted against crystallinity for the various samples. Translucency effects are not measurable, and thus a correction is not needed. Another relevant quantity, an estimate of the experimental error involved in measuring intensity ratios, is afforded by plotting the intensity ratio I_{1060}/I_{1295} against crystallinity. The bands involved in this ratio are both depolarized and both belong to the crystalline component so that the value of the ratio will be independent of both crystallinity and translucency. The observed values vary by about ±10%, and this variation probably represents the experimental error in the D-LAM intensities shown in Figure 4.

From these considerations we conclude from Figure 4 that the fraction of the sample consisting of highly disordered chains, as measured by the D-LAM intensity, is linearly related to the degree of crystallinity.

In a specifically designed multiple-scan measurement, the D-LAM band could not be detected in the spectrum of the 90% crystalline sample (Figure 6). We note that

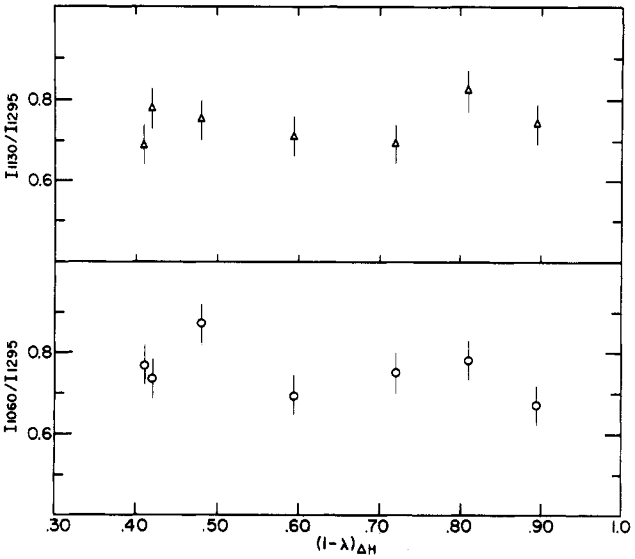

Figure 5. Plot of intensity ratios $I(1060)/I(1295)$ and $I(1130)/I(1295)$ against degree of crystalinity $(1-\lambda)_{\Delta H}$.

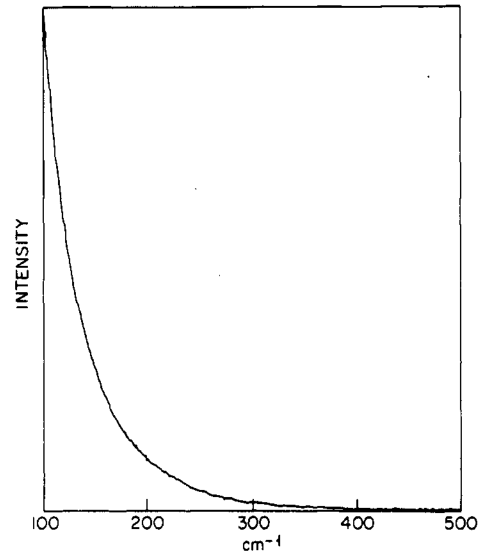

Figure 6. Low-frequency Raman spectrum of a highly crystalline polyethylene, $(1-\lambda)_{\Delta H} = 0.89$.

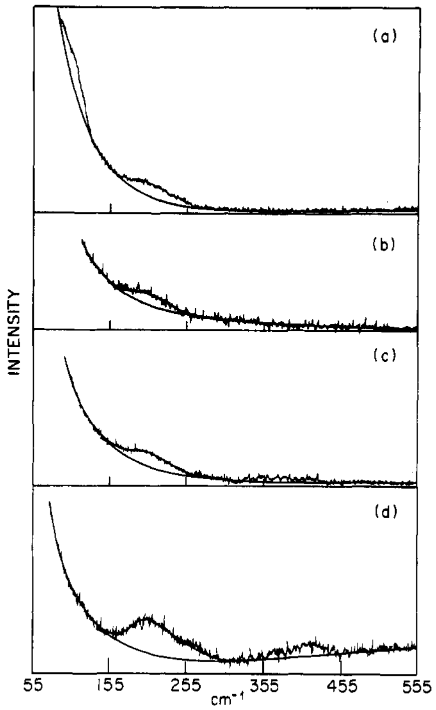

Figure 7. Low-frequency Raman spectra of linear polyethylene as a function of temperature, sample Hifax-28 initially quenched at −70 °C. Spectra obtained at (a) room temperature, (b) 57 °C, (c) 87 °C, and (d) 147 °C.

this result would be expected solely on the basis of the data plotted in Figure 5. The absence of the D-LAM for this sample indicates that at such very high levels of crystallinity the conformational structure of the disordered regions deviates from that of polyethylene in the liquid state. This change in structure would be expected at some high level of crystallinity, found here to be at about 90%. Under these conditions the disordered sequences will be shorter and strained and also influenced by the interface. Thus the trans–gauche ratio will be changed.[25]

The fact that the D-LAM band in the crystalline polymer arises from pure liquidlike structure can be further demonstrated by temperature studies. In Figure 7 we show a series of spectra at different temperatures for the same polymer, Hifax-28, which was initially quenched at −70 °C. At room temperatures the D-LAM band is well-defined for this 42% crystalline sample. As the temperature of the solid is initially increased, the intensity of this band increases slightly while the frequency of the band peak remains constant. In the melting range, there is a slight increase in intensity. In the melt at 147 °C, the D-LAM band is now much more intense but is still at the same frequency. Thus there is no indication of a discontinuity in the position or shape of D-LAM in going from the crystalline state to the melt.

Some limits can be placed on the differences between the conformational structures of the pure liquid and the liquidlike component in the crystalline polymer. Both the theoretical and experimental results indicate that a shift in the D-LAM frequency of ±10 cm^{-1} away from the 200-cm^{-1} value found for the liquid corresponds to a change of less than 10% in the concentration of trans bonds.[9] Since the frequency difference between the liquid and the solid is observed to be less than 5 cm^{-1}, we estimate that there is less than a 5% change between the liquid and amorphous component. Concerning the length of the conformationally disordered region, we note that a decrease in this length results in an increase in the D-LAM frequency: a length change from $n = \infty$ to $n = 20$ carbons results in an increase of 12 cm^{-1} in the position of D-LAM.[9] Because the frequency change is observed to be no more than 5 cm^{-1} higher for the solid, the average number of carbon atoms in a disordered sequence in the semicrystalline polymer must be well above 20.

In summary, we have demonstrated the presence of a conformationally liquidlike component in a variety of crystalline polyethylene samples as is indicated by the appearance of the unique D-LAM band in the low-frequency Raman spectra. Earlier studies on the D-LAM band in the Raman spectra of liquid n-alkanes and molten linear polyethylene have shown this band to be characteristic of conformational disorder that extends over long sequences of the chain.[9] These studies have also shown that the frequency and shape of D-LAM depends on the trans to gauche ratio and the average number of carbon atoms in the disordered sequences. In the present study, we have found that the D-LAM band as well as other features in the low-frequency Raman spectrum of crystalline polyethylene are virtually identical with those for the molten polymer. Thus the disordered regions in the crystalline polymer are essentially liquidlike from the standpoint of conformation.

There is a linear relation, within the accuracy of our measurements, between the intensity of the D-LAM band and the level of crystallinity over the range of crystallinities 0–90%. The liquidlike content as measured by the D-LAM approaches zero concentration in the crystallinity region of about 90%. This result indicates that the disorder in such very high crystalline regions is significantly different either in the trans–gauche ratio or in the lengths of the sequences or in both.[25]

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Registry No. Polyethylene, 9002-88-4.

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(25) It has been established that the degree of crystallinity that is obtained calorimetrically is always less than that found by density, the difference being attributed to the interfacial structure.[11] Hence the crystallinity value of 90% should be considered to be a lower limit for the loss of the D-LAM band since it arises from the liquidlike structure.

Mesophase Formation and Polymer Compatibility. 4. Cellulose/Cellulose Acetate/Diluent Systems

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ABSTRACT: The phase diagram of a system composed of a rigid polymer (cellulose), a flexible polymer (cellulose acetate, CA), and a diluent (*N,N*-dimethylacetamide (DMAc) + 7.8% LiCl) was investigated. A series of samples covering a range of degree of polymerization (cellulose) and degree of substitution (CA) were analyzed. The binary cellulose/diluent system exhibits a mesophase above a critical volume fraction $v_2' = 0.065$ (DP = 460). The CA/diluent system is always isotropic, in line with a small value of the persistence length (~40 Å) attributed to the presence of the salt. The ternary systems show incompatibility of the two polymers even in rather diluted solution, when two isotropic phases are observed. Above a combined polymer volume fraction of ~0.1, one anisotropic and one isotropic phase coexist. The anisotropic "phase" may actually be an intimate mixture of two phases. Analysis of the composition of each phase reveals a complete exclusion of CA from the mesophase and of cellulose from the conjugated phase. These findings cannot be represented by Flory's theory of phase equilibria between a rigid and flexible polymer due to the assumption of athermal behavior. The role of mutual interaction parameters for a quantitative interpretation of the results is pointed out.

In the first paper of this series[1] we reported the behavior of two ternary systems composed of a solvent, a rigid mesogen, and a more flexible polymer. The systems were poly(*p*-benzamide) (PBA)/polyterephthalamide of *p*-aminobenzhydrazide (X-500)/*N,N*-dimethylacetamide (DMAc) + 3% LiCl and PBA/poly(acrylonitrile) (PAN)/DMAc + 3% LiCl. We found that the flexible polymer was invariably excluded from the mesophase formed above a critical concentration of the two solutes. The rigid polymer was, however, mixed with the flexible one in the conjugated isotropic phase, and a fractionation of the former polymer in the latter phase was also observed. These observations were in satisfactory agreement with a theory[2] which predicts that the incompatibility is due to the interference of the random coil with the mutual orientation of the rigid polymer in the mesophase.

Table I
Characteristics of Samples Investigated

sample	origin	$[\eta]^{25\,°\mathrm{C}}$, dL/g	$\bar{M}_{\mathrm{v}}$	DP
A, CA, DS = 2.84	Fluka Buchs SG	3.63[a]	214 000	781
B, CA, DS = 2.30	Eastman Kodak 4655	1.90[a]	115 000	447
C, CA, DS = 0.9	Courtanz DS = 2.5 deacetylated[7]	1.74[a]	86 000	421
I, cellulose	SSCC, Milan (regenerated cellulose II)	2.45[b]	74 500	460
L, cellulose	SNIA Fibre (regenerated cellulose II)	1.62[b]	47 000	290

[a] In DMAc; cf. ref 7. [b] In 0.5 cupric ethylenediamine.

The above theory does not include the role of the interaction based on enthalpy parameters χ_{23} for the polymer pair. The latter is the basis for the compatibility, or incompatibility, between conventional polymers in the isotropic state.[3] In fact, we evaluated the χ_{23} parameter for the PBA/X-500 and PBA/PAN pairs and showed that

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