Observation of the Raman D-LAM Band in Ethylene Copolymers: Hydrogenated Polybutadiene

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ABSTRACT: The low-frequency Raman spectra of a series of hydrogenated polybutadienes have been studied. As has been previously reported for linear polyethylene, this spectral region is dominated by a broad band in the vicinity of 200 cm^{-1}, which has been designated as the D-LAM band and which reflects the regions of configurational disorder. The intensity of this band is shown to be a linear function of the degree of crystallinity when account is taken of the interfacial region. Thus, only the disordered, or liquid-like, regions contribute to the band intensity. The frequency of D-LAM increases with an increase in branching, indicating a decrease in the number of trans bonds in the chain backbone. Calculations based on rotational isomeric state theory demonstrate a decrease in trans concentration due to branching that is in accord with the spectroscopic results.

Introduction

It has been shown that in the low-frequency isotropic Raman spectra of liquid *n*-alkanes, as well as in completely molten polyethylene, there is a band that is well suited for the study of long-range conformational disorder.[1] This band, which appears in the vicinity of 200 cm^{-1} for polyethylene and which has been given the designation D-LAM, is predicted to occur in all disordered polymer chains. It has in fact been observed in a variety of noncrystalline polymers.[2] Recently, the same band has been observed in a series of semicrystalline linear polyethylenes where the level of crystallinity, on an enthalpy of fusion basis, ranged from 0.41 to 0.89.[3] It was found that the D-LAM band and other features in the low-frequency Raman spectra of this series of semicrystalline polymers are virtually identical with those observed for the molten polymer. Furthermore, a linear relation was found between the intensity of the D-LAM band and the level of crystallinity over the range of crystallinities attainable for linear polyethylene. This spectral evidence makes it quite clear that the disordered regions in the crystalline polymer are essentially liquid-like from the standpoint of conformation.

In the present work we have analyzed the D-LAM band of random type ethylene copolymers in order to extend the measurement to lower levels of crystallinity. Random copolymers are admirably suited for this purpose since it is possible to obtain completely noncrystalline samples even at room temperature.[4] Therefore, polymers which show a continuous decrease in level of crystallinity, including noncrystalline ones, can be conveniently studied at room temperature. We will also be concerned with the interesting question as to the extent the co-units, or branch groups, influence the disordered conformation, a question that can be addressed by this type of spectral analysis. It is also known that the interfacial content increases substantially as the co-unit content increases in ethylene copolymers.[4,5] Any influence that the interfacial region may have on the spectral analysis is also a matter of interest.

Therefore, to examine these questions and to expand the experimental base of low-frequency Raman spectra, we have studied a series of well-characterized hydrogenated polybutadienes with varying branching content. It is particularly advantageous to study this kind of polymer since the ethyl branches have a random or nearly random sequence distribution as well as a very narrow molecular weight and composition distribution.

Experimental Procedures

Raman Spectra. The basic procedures used to obtain the low-frequency Raman spectra have been described in the previous paper in this series.[3] The spectra were measured with a SPEX 1403 spectrometer, controlled by a SPEX Datamate DMI computer. Multiple scans were necessary to improve the signal-to-noise ratio. The effective power at the samples was $\simeq$100 mW, and the spectral resolution was 5 cm^{-1}. All but one of the spectra, which will be so indicated, were measured with the sample at ambient temperature. The observed intensity of the high-temperature spectrum was corrected for translucent effects and temperature by methods previously described.[3]

Materials and Crystallization Procedures. The properties of the hydrogenated polybutadienes used in this work are given in Table I. The basic synthesis involves the anionic polymerization of butadiene followed by hydrogenation. The sample labeled P108 was purchased from Phillips Petroleum Co. The other copolymers were kindly supplied to us by Dr. William Graessley. The synthesis and molecular properties of these copolymers have been given previously.[6-8] They are all characterized by narrow molecular weight distributions (M_w/M_n = 1.05–1.3) and narrow composition distributions. The overall branching content was determined by high-resolution, proton-decoupled ^{13}C NMR, using well-established procedures and methods of analysis.[9-11] The branching contents of these copolymers are given as the percent branches per 100 main-chain carbon atoms. From ^{13}C NMR analysis, Graessley et al.[7] have reported that the hydrogenated polybutadiene samples have essentially a random distribution of ethyl side groups at low co-unit content. The polymers have, however, a tendency to develop a slightly more ordered sequence distribution at high co-unit contents. We have analyzed our spectra following the methods described by Randall[10,12] and have come to the same conclusion. From the point of view of molecular constitution these samples clearly represent an ideal set of copolymers to study.

The thermodynamic and structural features of these copolymers have recently been described in detail.[4] Of particular interest in the present work are the melting temperatures T_m, the degree of crystallinity $(1 - \lambda)_{\Delta H}$ obtained from the enthalpy of fusion, as well as the fraction crystalline α_c, the liquid-like portion α_a, and the interfacial content $\alpha_b \equiv 1 - \alpha_c - \alpha_a$. These latter quantities are obtained from an analysis of the internal mode region of the Raman spectra.[4,5,13] The instrumentation used and the method of analysis have been previously discussed and described in detail.[5,14]

Films approximately 1 mm thick were prepared by molding in a Carver press at temperatures between 90 and 120 °C for about

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Table I
Properties of Hydrogenated Polybutadienes[a]

sample	branches[b]	T_m, °C	$(1-\lambda)_{\Delta H}$	α_c	α_a	α_b	ν(D-LAM), cm^{-1}
P108	2.2	100	0.28	0.25 ± 0.03	0.63 ± 0.04	0.12 ± 0.07	207 ± 4
	2.2						206 ± 2[c]
HPBD 12	5.5	65	0.125	0.08 ± 0.02	0.75 ± 0.04	0.17 ± 0.06	208 ± 2
HPBD 11	7.25	57	0.065	0.05 ± 0.03	0.73 ± 0.04	0.22 ± 0.07	212 ± 2
HPBD 8	13.0	21	≃0.01				213 ± 3
HPBD 9	18.0		0				214 ± 2
HPBD 10	49.0		0				228 ± 4

[a] Quenched from the melt to −70 °C. [b] Per 100 main-chain carbon atoms. [c] Spectrum obtained at 130 °C.

10 min. The films were rapidly quenched from the hot press into a bath at −70 °C. Samples prepared in this manner were used for the thermal and spectral analysis.

Melting temperatures were determined with a Perkin-Elmer DSC2B differential scanning calorimeter. The instrument was calibrated with indium. A standard heating rate of 20 K/min was used, and the sample weights were approximately 3 mg. The melting temperatures were identified with the location of the endothermic peak. The measured enthalpies of fusion were converted to the degree of crystallinity $(1-\lambda)_{\Delta H}$ by taking 69 cal g^{-1} to correspond to the enthalpy of fusion of the perfect polyethylene crystal.[15] The error in $(1-\lambda)_{\Delta H}$ is estimated to be ±0.03.

Results and Discussion

General Considerations. In this section we will first make some general comments concerning the samples and the nature of the Raman spectra. We then consider the two principal findings that were derived from the spectroscopic measurements. These are (i) evidence for a more extensive interfacial region for the copolymers relative to linear polyethylene and (ii) evidence that branching affects the trans/gauche ratio of the polymer backbone.

Table I shows that the range of crystallinity for the copolymers is significantly greater than that of the linear polyethylenes previously studied.[3] If the branching mole fraction is about 13% or greater, the samples are noncrystalline at ambient temperature. We note parenthetically that if the degree of crystallinity was determined from density measurements, a small but significantly higher value would result.[16] The enthalpy of fusion measures the core crystallinity and is thus devoid of interfacial contributions. We, therefore, find that for these samples $(1-\lambda)_{\Delta H}$ is in good agreement with α_c obtained from analysis of the Raman internal modes. Similar results have been generally found for a wide variety of polyethylene samples.[16] The interfacial content of these copolymers is significantly greater than that of linear polyethylene samples of the same molecular weight and increases with increasing branching content.[5] The values of α_b for the samples studied here are similar to those previously reported.

Low-frequency Raman spectra are given in Figure 1 for two copolymer samples, 5.5 and 18 mol % branches, respectively. The spectra illustrated, as well as those of the other polymers, have some common features in the region from about 100 to 600 cm^{-1}. A major characteristic feature is a broad band in the vicinity of 200 cm^{-1}, which is the D-LAM band.[1-3] There are also discrete bands in the region from about 300 to 450 cm^{-1} that are associated with the branches.

The frequencies of the D-LAM band maxima were carefully measured with attention to the fact that the D-LAM bands sit on a sloping background. The measured frequencies are indluced in Table I along with the estimated errors.

There is a significant monotonic increase in the D-LAM frequency with branching content as is indicated in Figure 2, where ν(D-LAM) is plotted against the mole percent

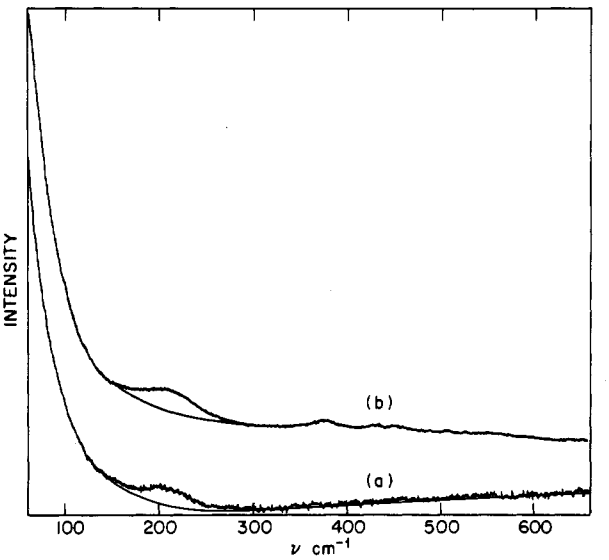

Figure 1. Typical Raman spectra for hydrogenated polybutadienes in the low-frequency region: (a) 5.5 mol % branches; (b) 18 mol % branches.

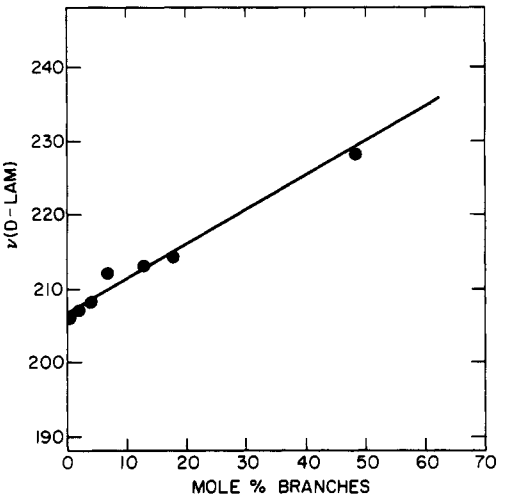

Figure 2. D-LAM frequency, ν(D-LAM), plotted against the mole percent branches for the hydrogenated polybutadienes.

branches. The frequency of D-LAM for linear polyethylene is 206 cm^{-1} [3] but a value of 228 cm^{-1} is found for a sample with 4% branches. Before discussing the significance of these results, we shall first analyze the intensities of the D-LAM band as a function of branching content.

D-LAM Intensity and the Crystallinity Level. The intensity of the D-LAM band was determined by procedures similar to those previously described.[3] To establish the intensity of the band so that comparison can be made between the different samples, we used the intense methylene twisting band near 1300 cm^{-1} as an internal standard.[3] In the case of the unbranched chain there are

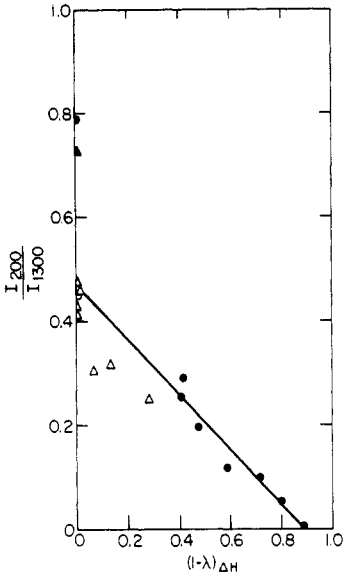

Figure 3. Plot of relative intensity $I(200)/I(1300)$ of the D-LAM band for linear polyethylene and hydrogenated polybutadiene against the degree of crystallinity $(1 - \lambda)_{\Delta H}$: (●, ○) linear polyethylene from ref (3); (△) hydrogenated polybutadiene at ambient temperature; (▲) 2.2 mol% hydrogenated polybutadiene at 130 °C.

two twisting bands, one at 1295 cm^{-1} that is associated with ordered chains in the crystalline component and another at 1306 cm^{-1} that is associated with disordered chains. The sum of the intensities of the 1295- and 1306-cm^{-1} bands was assumed to be independent of the sample crystallinity. However, there is a further complication for the branched chain. If the methylene twisting band is to be used as an internal intensity standard, the number of methylenes represented by the band must remain constant. This condition is satisfied by a poly(methylene) chain with ethyl branches. The complication arises because the frequency of the twisting mode of the ethyl methylene, being vibrationally decoupled, is displaced to lower values and will appear in the region 1290–1250 cm^{-1}. Moreover, the frequencies of the twisting modes of the backbone methylenes will undergo similar displacements as the concentration of branches increases since this leads to short sequences and to isolated methylenes. The intensity of the D-LAM band is measured by the ratio $I(200)/I(1300)$, where $I(1300)$ is understood to include all the intensity in the region 1310–1250 cm^{-1}.

In Figure 3 this ratio is plotted against the degree of crystallinity determined from the enthalpy of fusion, $(1 - \lambda)_{\Delta H}$. Also plotted in this figure (solid circles) are the values reported earlier for the linear polyethylene at ambient temperature.[3] The solid line is identical with the straight line given previously for linear polyethylene.[3] The open triangles are new data points for the six hydrogenated polybutadiene samples at ambient temperature. The three ambient-temperature, noncrystalline samples fall on the terminus of the straight line that represents linear polyethylene. However, the intensities of the three crystalline samples fall well below this line.

Before discussing the significance of this point, we will first consider the data for the sample at high temperature. The solid circle at $(1 - \lambda)_{\Delta H} = 0$ represents the previously reported intensity of the linear polyethylene D-LAM at 150 °C.[3] When this datum is corrected for translucent and temperature effects the open circle results. As was previously noted, this datum point falls on the straight line.[3] Similarly, the solid triangle at $(1 - \lambda)_{\Delta H} = 0$ represents the observed intensity of the D-LAM band for the 2.2 mol % hydrogenated polybutadiene sample at 130 °C. When corrected for translucent and temperature ffects (from 130 °C to ambient temperature),[3] the intensity is reduced to 0.43. When plotted in Figure 3, (as an open triangle), this datum point falls very close to the straight line at $(1 - \lambda)_{\Delta H} = 0$. Therefore, essentially the same intensity values are found for the completely noncrystalline linear and branched samples. Moreover, these values join the linear extrapolation of the data for the much more crystalline linear polyethylenes.

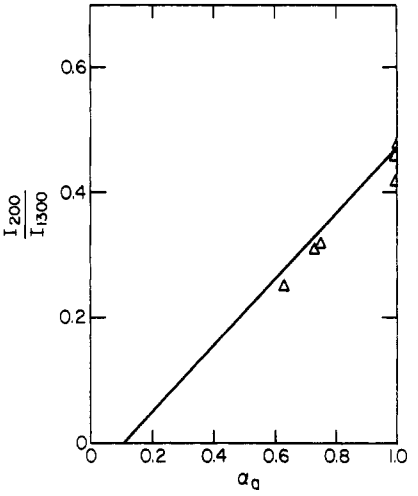

Figure 4. Plot of relative intensity $I(200)/I(1300)$ of the D-LAM band of hydrogenated polybutadiene against the liquid-like fraction, α_a. The solid line is for the linear polymer.[3]

Returning to the observed D-LAM intensities of the crystalline hydrogenated polybutadienes, we have noted that in Figure 3 these fall significantly below the intensities of the unbranched polyethylenes. There is a straightforward explanation for this result which involves the interfacial region. A linear relation between core crystallinity and D-LAM intensity should exist only if the D-LAM band represents the entire noncrystalline fraction. As we have emphasized, however, the D-LAM band at 200 cm^{-1} only measures the highly disordered component and does not include the interfacial region, which has some elements of intermediate order. Linearity occurs for unbranched polyethylenes because the interfacial region represents a small fraction of the sample (10% or less).[15,16]

For the random copolymers studied here the interfacial content becomes high and needs to be taken into account. The appropriate plot would therefore be the intensity against the liquid-like fraction, α_a, which is obtained directly from the Raman internal modes.[5] The data analyzed in this manner are plotted in Figure 4. The solid line represents the linear polymer and is taken from Figure 3. The open triangles are the copolymer data. When the data are treated in this manner, we find that within experimental error, the intensity data for the branched polymers are in excellent agreement with those for the linear polymer over the complete range of crystallinity. Once it is recognized that only the conformationally disorganized regions contribute to the D-LAM, the analysis quantitatively points out the importance of the interfacial region to the crystallite structure. Contributions have also been observed to other properties when this region is the order of 10% or greater. It has been shown to be an important factor in dynamic mechanical relaxation transitions[17,18] and thin-section transmission electron microscopic studies[19] for random type copolymers. In the latter case the differential staining techniques indicate that the stain does not penetrate the interfacial region.

D-LAM Frequency, Degree of Branching, and Trans Content. We next discuss the observed increase in the D-LAM frequency with increasing branching content. The simplest explanation is that the shift to higher frequency occurs because the trans-to-gauche ratio decreases with the increase in ethyl branch content since it is known that ν(D-LAM) increases with gauche concentration.[1] On the other hand, the mass effect of the C_2H_5 group by itself would be to decrease ν(D-LAM). However, at the low levels of branching, which are of concern here, this shift can be ignored. An estimate of the change in the gauche concentration can be obtained from rotational isomeric state theory.[20]

To calculate the t/g ratio we seek the probability for a trans placement in the chain backbone by formulating the configuration partition function, Z. All chains are assumed to have the structure $CH_3CH_2CH_2CH_2CHRCH_2CHR$-$CH_2$...$CHRCH_2CHRCH_2CH_3$. There is an even number, n, of C–C bonds in the main chain. Each R is either H or CH_2CH_3. Ethyl groups may be attached to the main chain in either the d or l configuration. We consider first a chain of defined composition where all of the R groups are assigned as H or ethyl, and all ethyl groups are assigned as d or l. From the rotational isomeric state approach to branched-chain molecules, the configuration partition function for a chain of defined composition can be written as[21]

$$Z = [1 \quad 0 \quad 0]\mathbf{U}(2)\mathbf{U}(3)...\mathbf{U}(n-1)\ \text{col}\ (1, ..., 1) \quad (1)$$

where col (1, ..., 1) denotes a column of ones in which the number of elements is identical with the number of columns in $\mathbf{U}(n-1)$. This number will be 3 or 9, depending on whether the last R is H or CH_2CH_3.

The statistical weight matrices used take account of all first- and second-order interactions, including those interactions generated by methylene and methyl groups in the articulated ethyl side chains. The statistical weight matrix appropriate for an internal C–C bond in unperturbed linear polyethylene[22] is

$$\mathbf{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \quad (2)$$

This statistical weight matrix is used for all internal C–C bonds in the ethylene–1-butene copolymers except for the three main-chain bonds in the sequences CH_2–CHR–CH_2–CH_2 and CH_2–CHR–CH_2–CHR. The statistical weight matrices that are used for these bonds depend on the stereochemistry of the CH_2CH_3 groups. The matrices used are formulated in the manner described in ref 21.

For the CH_2–CHR bonds (R = CH_2CH_3) in which the preceding unit is ethylene, and therefore does not contain a branch, the statistical weight matrix is

$$\mathbf{U}(Ed) = \begin{bmatrix} 1 & \tau & 1 \\ 1 & \tau\omega & \omega \\ \omega & \tau\omega & 1 \end{bmatrix} \quad (3)$$

when the ethyl branch is in the d configuration. It is

$$\mathbf{U}(El) = \begin{bmatrix} 1 & 1 & \tau \\ \omega & 1 & \tau\omega \\ 1 & \omega & \tau\omega \end{bmatrix} \quad (4)$$

if the ethyl branch is in the l configuration. Statistical weight matrices for CH_2–CHR bonds (R = CH_2CH_3) which follow a 1-butene unit are given below.

Statistical weight matrices for CHR–CH_2 bonds (R = CH_2CH_3) are of dimensions 3×9.[21] If the ethyl group is in the d configuration, the statistical weight matrix is

$$\mathbf{U}(d) = \begin{bmatrix} \omega & \tau & \omega & 1 & \tau & \omega & \tau & \tau^2\omega & \tau\omega \\ \omega & \tau\omega & 1 & 1 & \tau\omega & 1 & \tau\omega & \tau^2\omega^3 & \tau\omega \\ \omega & \tau & 1 & \omega & \tau\omega & \omega & \tau & \tau^2\omega & \tau \end{bmatrix} \quad (5)$$

If the configuration is l, the statistical weight matrix is

$$\mathbf{U}(l) = \begin{bmatrix} \omega & \omega & \tau & \tau & \tau\omega & \tau^2\omega & 1 & \omega & \tau \\ \omega & 1 & \tau & \tau & \tau & \tau^2\omega & \omega & \omega & \omega \\ \omega & 1 & \tau\omega & \tau\omega & \tau\omega & \tau_2\omega & 1 & 1 & \tau\omega \end{bmatrix} \quad (6)$$

For CH_2–CHR bonds (R = CH_2CH_3) where the preceding unit is 1-butene (and therefore has an ethyl branch), the statistical weight matrix depends on the stereochemistry of both ethyl groups. The possible statistical weight matrices are

$$\mathbf{U}(dd) = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} \omega & \tau\omega & 1 \\ 1 & \tau\omega & \omega \\ \omega & \tau\omega^2 & \omega \end{bmatrix} \quad (7)$$

$$\mathbf{U}(ld) = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 & \tau\omega & \omega \\ \omega & \tau\omega^2 & \omega \\ \omega & \tau\omega & 1 \end{bmatrix} \quad (8)$$

$$\mathbf{U}(dl) = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 & \omega & \tau\omega \\ \omega & 1 & \tau\omega \\ \omega & \omega & \tau\omega^2 \end{bmatrix} \quad (9)$$

$$\mathbf{U}(ll) = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} \omega & 1 & \tau\omega \\ \omega & \omega & \tau\omega^2 \\ 1 & \omega & \tau\omega \end{bmatrix} \quad (10)$$

In the symbolism $\mathbf{U}(ab)$, b denotes the stereochemistry of the ethyl group at the CH_2–CHR bond (R = CH_2CH_3), and a denotes the stereochemistry of the ethyl branch that precedes this unit. The direct product is denoted by $\otimes$.

Finally, the statistical weight matrices for the second C–C bond in CHR–CH_2–CH_2 are

$$\mathbf{U}(d...) = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 & \sigma\omega & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma\omega \end{bmatrix} \quad (11)$$

$$\mathbf{U}(l...) = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \quad (12)$$

for the cases where R is an ethyl branch attached in the d or l configuration, respectively.

The probability for a trans placement, $p(t)$, in the main chain of specified composition is given by

$$p(t) = (n-2)^{-1}Z^{-1}[1 \quad 0]\hat{\mathbf{U}}(2)\hat{\mathbf{U}}(3)...\hat{\mathbf{U}}(n-1)\ \text{col}\ (\mathbf{0}, \quad 1) \quad (13)$$

Here the **0** in [1 0] is a null row of five elements, and col (**0**, 1) is a column of 6 or 18 elements in which the first half of the elements are 0 and the second half are 1. The dimension of col (**0**, 1) is dictated by the number of columns in $\hat{\mathbf{U}}(n-1)$. Each of the $\mathbf{U}$ is

$$\hat{\mathbf{U}}(i) = \begin{bmatrix} \mathbf{U}(i) & \mathbf{U}'(i) \\ \mathbf{0} & \mathbf{U}(i) \end{bmatrix} \quad (14)$$

where $\mathbf{U}(i)$ is the statistical weight matrix used for bond i in eq 1, **0** is a rectangular null matrix, and $\mathbf{U}'(i)$ is obtained from $\mathbf{U}(i)$ by nulling several of the columns. If $\mathbf{U}(i)$ has three columns, it is the second and third columns that are rendered null. If $\mathbf{U}(i)$ has nine columns, it is the fourth through ninth columns that are rendered null.

We seek the value of $p(t)$ for a long chain of random composition where p(b) denotes the fraction of units that are derived from 1-butene.

A representative chain is generated from a sequence of random numbers. Successive units are assigned as 1-

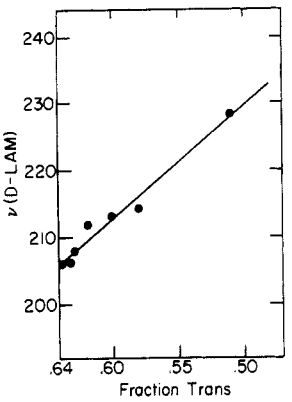

Figure 5. D-LAM frequency ν(D-LAM) plotted against the fraction trans bonds in the backbone.

butene or ethylene, depending on whether a random number is less than or greater than p(b). A second set of random numbers is used to assign the stereochemistry of the ethyl branches. It is assumed that the stereochemistry is completely random; i.e., an ethyl branch is d if the random number is less than $^1/_2$ and l otherwise. The desired $p(t)$ at a particular p(b) is the ensemble limit as the number of representative chains increases.

The calculations were carried out for a chain of $n = 1000$. The values of the statistical weights were $\sigma = 0.43$ and $\omega = 0.034$, which are appropriate for unperturbed polyethylene at 300 K.[22] The value of τ, which is an additional statistical weight that is employed at each trifunctional branch point, was taken to be zero. The numerical results are not very sensitive to plausible variations in τ. Similar trends are found with $\tau = 0$ and $\tau = 0.43$. In terms of the mole fraction of 1-butene units, $p(t)$ monotonically decreases from 0.64 for linear polyethylene to 0.50 for poly(1-butene).

The chain becomes atactic poly(1-butene) in the limit where p(b) goes to one. Wittwer and Suter[24] have computed the characteristic ratio of poly(1-butene) using a more complicated model (with five rotational isomers for each internal bond) than the one employed here. They obtained a characteristic ratio of about 4.5 for the atactic chain. When our model is combined with the customary generator matrices, plausible variations in τ give characteristic ratios of 4.5 ± 0.3.[25] Therefore, the three-state model used here yields unperturbed dimensions for atactic poly(1-butene) that are indistinguishable from those obtained with the five-state model.

From these calculations we can estimate the dependence of ν(D-LAM) on the trans concentration in the chain backbone. A plot of ν(D-LAM) against trans concentration is given in Figure 5. The data can be represented by a straight line so that it appears ν(D-LAM) decreases approximately linearly with the fraction of trans placements in the chain backbone. The slope derived from this plot indicates that a 10% change in the trans bond concentration in the chain backbone results in a 16-cm^{-1} frequency shift. This value is in good agreement with a shift of about 13 cm^{-1} derived from D-LAM spectra that were synthesized numerically.[23]

The results described above substantiate the previous conclusion[3] that the D-LAM band reflects the regions of configurational disorder in the semicrystalline polymer. It has been shown to be quantitatively sensitive to the amount of the liquid-like region and to the structural changes which influence the t/g ratio in this region and affect the average chain configuration.

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References and Notes

(1) Snyder, R. G. *J. Chem. Phys.* **1982**, *76*, 3921.
(2) Snyder, R. G.; Wunder, S. L. *Macromolecules* **1986**, *19*, 496.
(3) Snyder, R. G; Schlotter, N. E.; Alamo, R.; Mandelkern, L. *Macromolecules* **1986**, *19*, 621.
(4) Alamo, R.; Domszy, R.; Mandelkern, L. *J. Phys. Chem.* **1984**, *88*, 6587.
(5) Glotin, M.; Mandelkern, L. *Colloid Polym. Sci.* **1982**, *260*, 182.
(6) Rachaperdy, H.; Smith, G. G.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1211.
(7) Krigas, T. M.; Carella, J. M.; Struglinski, M. J.; Crist, B.; Graessley, W. W.; Schilling, F. C. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 509.
(8) We sincerely thank Dr. Graessley for supplying us with these samples and for many helpful discussions with regards to their properties.
(9) Dorman, D. E.; Otocka, E. P.; Bovey, F. A. *Macromolecules* **1972**, *5*, 574.
(10) Randall, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 275.
(11) Axelson, D. E.; Mandelkern, L.; Levy, G. C. *Macromolecules* **1977**, *10*, 557.
(12) Randall, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1975.
(13) Strobl, G. R.; Hagedorn, W. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1181.
(14) Glotin, M.; Domszy, R.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 285.
(15) Flory, P. J.; Vrij, A. *J. Am. Chem. Soc.* **1963**, *85*, 3548.
(16) Mandelkern, L. *Polym. J.* **1985**, *17*, 337.
(17) Popli, R.; Mandelkern, L. *Polym. Bull.* **1983**, *9*, 260.
(18) Popli, R.; Glotin, M.; Mandelkern, L.; Benson, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 407.
(19) Voigt-Martin, I. G.; Alamo, R.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1283.
(20) Flory, P. J. *Statistical Mechanics of Chain Molecules* Interscience: New York, 1969.
(21) Mattice, W. L. *Macromolecules* **1975**, *8*, 644.
(22) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.
(23) Snyder, R. G., to be published.
(24) Wittwer, H.; Suter, U. W. *Macromolecules* **1985**, *18*, 403.
(25) Mattice, W. L. *Macromolecules*, submitted for publication.