$$D_{\mathrm{O}_2}\left(\frac{\mathrm{d}[\mathrm{O}_2]_\mathrm{f}}{\mathrm{d}x}\right) = \frac{l}{m}D_{\mathrm{vol}}\left(\frac{\mathrm{d}[\mathrm{vol}]_\mathrm{f}}{\mathrm{d}t}\right)_{x=0} =$$

$$K'[\mathrm{O}_2]_\mathrm{g}\sqrt{K_{\mathrm{O}_2}D_{\mathrm{O}_2}}\tanh\sqrt{\frac{K_{\mathrm{O}_2}}{D_{\mathrm{O}_2}}}l \text{ mol cm}^{-2}\text{ sec}^{-1} \quad (7'')$$

The total peroxide amount in the film is

$$\int_0^l [\mathrm{ROOH}]_\mathrm{f}\,\mathrm{d}x = K'[\mathrm{O}_2]_\mathrm{g}\frac{\sqrt{K_{\mathrm{O}_2}D_{\mathrm{O}_2}}}{C}\tanh\sqrt{\frac{K_{\mathrm{O}_2}}{D_{\mathrm{O}_2}}}l \text{ mol cm}^{-2} \quad (8'')$$

and the total volatiles in the film

$$\int_0^l [\mathrm{vol}]_\mathrm{f}\,\mathrm{d}x = mK'[\mathrm{O}_2]_\mathrm{g}\frac{D_{\mathrm{O}_2}}{D_{\mathrm{vol}}}l\left[1 - \left(\frac{D_{\mathrm{O}_2}}{K_{\mathrm{O}_2}l^2}\right)^{1/2} \times \tanh\left(\frac{K_{\mathrm{O}_2}l^2}{D_{\mathrm{O}_2}}\right)^{1/2}\right] \text{ mol cm}^{-2} \quad (9'')$$

If l is large, the following approximations hold

flux of volatiles =

$$mK'[\mathrm{O}_2]_\mathrm{g}\sqrt{K_{\mathrm{O}_2}D_{\mathrm{O}_2}} \text{ mol cm}^{-2}\text{ sec}^{-1} \quad (10'')$$

$$\text{total peroxide in film} = K'[\mathrm{O}_2]_\mathrm{g}\frac{\sqrt{K_{\mathrm{O}_2}D_{\mathrm{O}_2}}}{C} \text{ mol cm}^{-2} \quad (11'')$$

$$\text{total volatiles in film} = mK'[\mathrm{O}_2]_\mathrm{g}\frac{D_{\mathrm{O}_2}}{D_{\mathrm{vol}}}l \text{ mol cm}^{-2} \quad (12'')$$

The Glass Temperature of Linear Polyethylene[1]

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ABSTRACT: Transitions in linear polyethylene (LPE) samples encompassing a wide range of fractional crystallinity, 0.46–0.85, have been examined with the objective of ascertaining the glass transition temperature, T_g, of this polymer. Thermal expansion, calorimetric, and dynamic mechanical measurements lead to the conclusion that the γ transition at *ca.* −130° is the primary glass transition of LPE. At temperatures below the γ transition, the coefficient of thermal expansion, α, is almost independent of crystallinity, whereas at temperatures slightly above this transition, α increases systematically as the degree of crystallinity decreases. The quantitative behavior of α above and below the γ transition in LPE is very similar to that of other crystalline polymers at their respective glass temperatures. Furthermore, the value of α estimated for completely amorphous LPE below the γ transition is similar to that of completely amorphous polymers below T_g; and the value of α estimated for completely amorphous LPE slightly above the γ transition is similar to that of wholly amorphous polymers above T_g. Qualitative calorimetric measurements show that the heat capacity of LPE with low levels of crystallinity increases across the γ transition. The magnitude and character of the heat capacity change in the γ region for the least crystalline LPE sample is similar to that of semicrystalline polydimethylsiloxane at the T_g, −123°, of this polymer. Dynamic mechanical measurements show that the intensity of the γ relaxation increases as crystallinity decreases. The observed asymmetry of the γ relaxation is interpreted in terms of two overlapping relaxations arising from the noncrystalline domains of the polymer. A simple morphological model is suggested which satisfactorily accounts for the results of a large number of wide-line nmr and dynamic mechanical experiments made on melt and solution crystallized LPE. Since other investigators have proposed that the T_g of polyethylene is *ca.* −80° or *ca.* −20°, these temperature regions were also closely examined. However, even in the LPE samples with low levels of crystallinity, transitions in these temperature regions were, at most, barely detectible. Transitions in these temperature ranges, if they exist at all, do not have the typical characteristics of a primary glass transition.

The relaxations of linear and branched polyethylene have been extensively examined by numerous investigators, and the experimental results have been reviewed by Boyer,[2] McCrum, Read, and Williams,[3] and by McKenna, Kajiyama, and MacKnight.[4] Dynamic mechanical measurements made at low frequencies on branched polyethylene show loss maxima at *ca.* +70, −20, and −120° that have been termed the α, β, and γ relaxations, respectively. The α and γ relaxations have also been observed in all dynamic mechanical studies of linear polyethylene (LPE), but the β relaxation in LPE has been found to be either absent[5–7] or barely detectible.[8–11] Most investigators,

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although differing in their detailed interpretation, have concluded that the α relaxation arises from the crystalline regions of the polymer.[7,10,12–14] On the other hand, several conflicting interpretations have been given concerning the origin and molecular nature of the β and γ relaxations. The source of these relaxations is the subject of this paper.

The relation between the number of side-chain branches in high pressure polyethylene and the magnitude of the β and γ relaxations in dynamic mechanical measurements has been interpreted as indicating that the β relaxation corresponds to the primary glass transition of polyethylene. Kline, Sauer, and Woodward[11] showed that the intensity of the β relaxation increased markedly as the number of chain branches increased. The β relaxation was therefore attributed to the relaxation of chain branches. Furthermore, since the density and degree of crystallinity of polyethylene decreases as chain branching increases, this behavior is consistent with the view that the β relaxation arises from the amorphous domains of the polymer. These observations, together with dynamic mechanical measurement on ethylene-containing copolymers,[15] led to the proposal that the β relaxation corresponds to the glass transition of semicrystalline polyethylene[5,11,15] Thermal expansion measurements have also been used to detect the β transition in polyethylene. Comparison of the specific volume of LPE and the crystal unit cell of LPE as a function of temperature led Cole and Holmes[16] to propose that the glass transition temperature, T_g, of LPE was $-20°$. From the temperature dependence of the *d* spacing of the amorphous halo in the X-ray diffraction pattern of oriented branched polyethylene, Ohlberg and Fenstermaker[17] concluded that the T_g of branched polyethylene was $-28°$. In a careful examination of the thermal expansion of branched polyethylene, Simha, *et al.*, found a transition in the β region at $-22°$, in addition to transitions at -125, -60, and $0°$.[18]

Numerous suggestions for the origin of the γ relaxation in polyethylene have been presented. Boyer,[19] Bohn,[5] and Schatzki[20] concluded from dynamic mechanical measurements that this relaxation was the consequence of the motion of a small number of methylene units in the amorphous domains of the polymer. Although these investigators consider the γ relaxation to arise from the amorphous regions of the polymer, they do not believe that this relaxation corresponds to the primary glass transition of polyethylene. Wada, *et al.*,[21] and Fischer and Peterlin[22] attributed the γ relaxation to the motion of disordered chain segments at the surface of polymer crystals. On the other hand, Sinnott,[7] Hoffman,[13] Pechold,[9] Illers,[10] and Takayanagi[14] concluded that this relaxation arises at least in part from motion of defects in the crystalline regions. In an examination of poly(ethylene-*co*-methacrylic acid), MacKenna, *et al.*, found that the γ relaxation in this copolymer consisted of two overlapping peaks.[4] One of these peaks was attributed to defects within crystals and the other peak was attributed to local motions of methylene units in the glassy amorphous domains of the polymer. Finally, Willbourn showed that the γ relaxation was found in any polymer which contained four or more contiguous methylene sequences.[23]

Willbourn concluded that dynamic mechanical data obtained on linear polymethylene and branched polymethylenes, together with brittle point temperature measurements and qualitative crystallization rate data, supported the assignment of the γ relaxation as the glass transition of LPE.[23] Dannis also concluded that the γ relaxation corresponded to the glass transition of polymethylene because thermal expansion measurements showed a distinct change in coefficient of thermal expansion at about $-118°$.[24] Faucher and Koleske arrived at the same conclusion by extrapolation of T_g data from the polymeric series $-[(CH_2)_mO]_x-$ to 100% CH_2 content.[25]

Thus, despite the extensive work that has been reported on polyethylene, there is no generally accepted explanation of the origin of the β and γ relaxations and no agreement concerning the glass temperature, T_g, of polyethylene. This lack of unanimity appears to be partly a consequence of the fact that the LPE samples that have been examined have generally been highly crystalline specimens that have encompassed only a small range of crystallinity. In such highly crystalline samples detection of the primary glass transition by the two most widely accepted methods, specific heat and specific volume measurements, is difficult because the disordered zones make only a small contribution to the total thermodynamic properties of the polymer.

In the present work we have taken advantage of recent reports that show that the degree of crystallinity of LPE can be varied over wide limits by control of molecular weight and crystallization conditions.[26,27] Hence, a wide range of crystallinity is accessible without introducing chain branches into the molecules. We have prepared LPE samples whose densities at room temperature range from 0.918 to 0.977, corresponding to degrees of crystallinity equal to 0.46 and 0.85, respectively; and we have examined the transitions in such LPE specimens by thermal expansion, calorimetric,

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Table I
Properties of Samples Examined

Polymer^b designation	$\bar{M}_v{}^c$	Degree of crystallinity, $1 - \lambda^a$		
		Thermal expansion specimen	DSC specimen	Torsion pendulum specimen
1	7,000^d	0.84	0.85	0.85, 0.84
2	46,000	0.74	0.73	0.73, 0.73
3	250,000	0.68		0.68
4	300,000	0.69		0.69
5	4,400,000^e	0.57 (0.53)^f	0.57	0.57
6	8,000,000		0.46^g	

[a] At 23° prior to initiation of experiment, except where indicated. [b] Except for polymer 5, all samples are molecular weight fractions. [c] Calculated from relation $[\eta] = 6.2 \times 10^{-4}\bar{M}_v{}^{0.7}$, decalin at 135°: R. Chiang, *J. Polym. Sci.*, **36,** 91 (1959). [d] $\bar{M}_n$ by infrared = 7100. [e] $\bar{M}_n$ = 192,000. [f] Indicated value of 0.53 is crystallinity of sample after quenching the melt to −196° and running thermal expansion test up to 25°. [g] Rapidly cooled from melt in ice water.

and dynamic mechanical measurements. The experimental results and the interpretation of the results are presented in this report.

Experimental Section

Polymers examined in this work are listed in Table I. With one exception, all of these polymers were molecular weight fractions obtained from Marlex-50 or Hifax-28 LPE by procedures described elsewhere.[28] The properties of the unfractionated Hifax-28 were also examined. Sample specimens were prepared by compression molding using a steel mold and a melt temperature of 170°. Specimens were cooled from the melt by placing the mold in contact with water-cooled platens whose temperature was maintained at *ca.* 20°. However, the sample with lowest level of crystallinity shown in the table was obtained by rapidly cooling a very high molecular weight fraction by immersion in ice water. Densities of the samples prior to initiation of the measurements were determined using a water–isopropyl alcohol density gradient column at 23°. The degree of crystallinity was calculated from the density, d, using the relation[29]

$$\frac{1}{d} = \frac{1 - \lambda}{1.00} + \frac{\lambda}{0.855}$$

where $1 - \lambda$ is the fraction crystallinity of the sample. Specimens are designated by two numbers. The first number refers to the polymer from which the specimen was prepared, and the second number is the fraction crystallinity of the particular specimen.

Thermal expansion measurements were made over the temperature range from −196 to +60° using a Du Pont 940 thermomechanical analyzer. The instrument was calibrated with a lead specimen using the coefficient of expansion values for lead given by Nix and MacNair.[30] The accuracy of the measurement was assessed by measuring the coefficient of thermal expansion of aluminum and comparing the measured values with literature values.[31] The average deviation of these values in the −160 to −80° temperature range where comparisons were made was 7.8%. Temperatures were measured using a chromel–alumel thermocouple, and the accuracy of the temperature scale to 1° was verified by obtaining expansion curves on frozen cylinders of compounds having known melting points. Since the emf–temperature curve of the thermocouple was nonlinear, especially below −100°, the recorded expansion curves were replotted on a linear temperature scale. Except for sample 5 (0.53), the compression molded cylindrical sample (0.25 in. diameter, 0.25 in. height) was cooled from room temperature to −195° by immersion in liquid nitrogen, and the thermal expansion curve was then obtained at a heating rate of 5°/min. In order to achieve the lowest possible degree of crystallinity, sample 5 (0.53) was examined as follows. The compression molded cylinder was placed in the instrument, heated to 170°, and then cooled by immersion in liquid nitrogen to −195°. The thermal expansion curve from −195 to 25° was then obtained at a heating rate of 5°/min. The degree of crystallinity measured after this procedure was 0.53. It is possible that some crystallization occurred upon raising the temperature from −195 to 25°. Consequently, the fraction crystallinity of the sample during the expansion measurement is uncertain and may have been less than 0.53.

The calorimetric measurements were made using the Du Pont 900 thermal analyzer equipped with the Du Pont differential scanning calorimeter (DSC) cell. Temperatures down to −190° were achieved after making minor modifications of the cell. Detailed operating conditions are given in the thermograms. With one exception, each LPE sample was run on a 32 ± 2 mg sample at a heating rate of 10°/min. Only a small quantity of sample 6 (0.46) was available, and the DSC scan of this sample was made at a threefold greater heating rate to compensate for the threefold smaller sample size. For comparison purposes, a semicrystalline sample of polydimethylsiloxane (PDMS) was run under the same conditions as sample 6 (0.46).

Dynamic mechanical tests were made with an inverted torsion pendulum constructed in this laboratory. Oscillations of the pendulum were followed by reflecting a light beam from a mirror attached to the pendulum onto a Giannini photopot. The signal from the associated bridge circuit was recorded using an analog–digital converter and computer, and the desired viscoelastic quantities (the shear storage modulus, G'; the shear loss modulus, G''; and the logarithmic decrement, Δ) were automatically calculated on a digital computer. Samples were in the form of compression molded strips with the dimensions 2 in. × 0.25 in. × 0.05 in. A run was made by rapidly cooling the mounted sample from 25 to −195° by passing cold nitrogen over the sample. The temperature was then increased in about 4° increments and the sample temperature was equilibrated for 5 min before making a measurement. The temperature range from −195 to +100° was scanned in about 10 hr, corresponding to an average heating rate of 0.5°/min. The temperature was measured using thermocouples calibrated to 1°. Low temperature gradients across the sample, less than 1° over the entire range of measurement, were achieved by housing the pendulum in a dewar cylinder. The fre-

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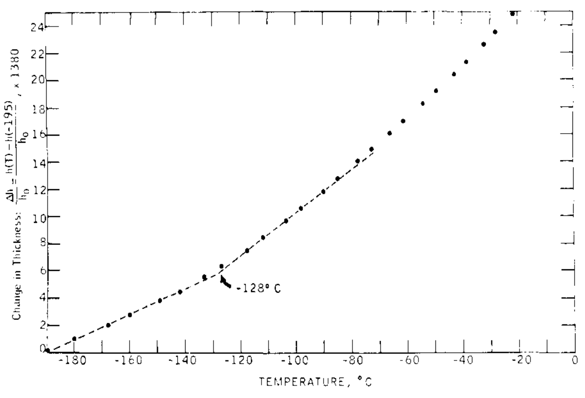

Figure 1. Thermal expansion curve for LPE with 0.57 degree of crystallinity.

quency of vibration of the pendulum at −195° was 5.25 ± 0.31 cps for all of the samples tested.

Results and Discussion

Thermal Expansion. The thermal expansion of an LPE sample, having $1 - \lambda$ equal to 0.57 at room temperature, is shown in Figure 1. The change in thickness *vs.* temperature plot is continuously curved over the temperature range −190 to −20° measured. Such behavior is typical of thermal expansion curves at low temperature in general and is accentuated by the crystalline character of the sample.[32–34] However, at temperatures less than −80°, the data can be represented by two straight lines which intersect in the region of the γ transition. There are perhaps also indications of transitions at higher temperatures. The visual examination of such expansion curves can, however, lead to rather subjective conclusions concerning the existence of transitions in a given temperature range. To determine whether transitions do in fact exist in various temperature regions we have made a detailed examination of the magnitude of thermal expansion coefficients at various temperatures as a function of degree of crystallinity.

Expansion curves for a series of samples encompassing a range of crystallinity are given in Figure 2. It is particularly noteworthy in this figure that all the curves are approximately parallel to one another at temperatures below about −140°, *i.e.*, the linear coefficient of expansion, α, is almost independent of the degree of crystallinity in this region. In contrast, the expansion curves are not parallel at temperatures above −140°, and the slope increases systematically as the degree of crystallinity of the sample decreases. These data clearly demonstrate the existence of a transition in the vicinity of −130° which arises from the amorphous domains of the polymer. The temperature of the transition could not, however, be determined with high precision. The average value obtained from duplicate measurements on five samples having different levels of crystallinity was −133° with a standard deviation of 7°. This value for the transition temperature obtained from quasi-static expansion measurements is in agreement with the temperature range of the γ relaxation observed by low-frequency dynamic mechanical measurements.[7,9,10]

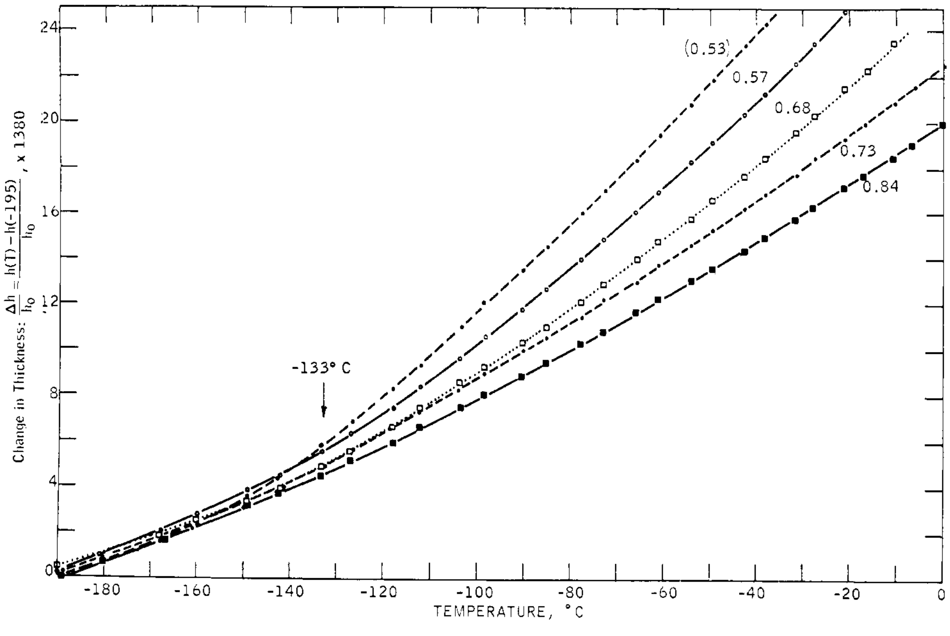

Figure 2. Thermal expansion curves from −190 to 0° for LPE samples with various degrees of crystallinity.

With the establishment of an amorphous transition in the vicinity of −130°, the question arises as to whether this is the primary glass transition of LPE or whether it is some type of secondary transition caused by the rotational motion of a small number of chain segments.[20,35] In addition to turning to other types of measurements to answer this question, pertinent information can be obtained from a detailed analysis of the data in Figure 2. In Figure 3, α at −160°,

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TABLE II

COMPARISON OF LINEAR COEFFICIENTS OF THERMAL EXPANSION FOR AMORPHOUS POLYMERS AND EXTRAPOLATED VALUES FOR AMORPHOUS POLYETHYLENE

	Coefficient of thermal expansion, 10^{-4}/deg	
Amorphous organic polymers[a]	$\alpha_g = 0.47\text{–}0.80$	$\alpha_l = 1.7\text{–}2.7$
Amorphous linear polyethylene, γ region	$\alpha_{-160} = 0.67 \pm 0.14^b$	$\alpha_{-105} = 1.77 \pm 0.12^b$
Amorphous linear polyethylene, β region	$\alpha_{-70} = 2.0 \pm 0.15^b$	$\alpha_{+15} = 3.3 \pm 0.14^b$

[a] See ref 41. [b] Indicated limit is standard deviation of the intercept of least-squares straight line.

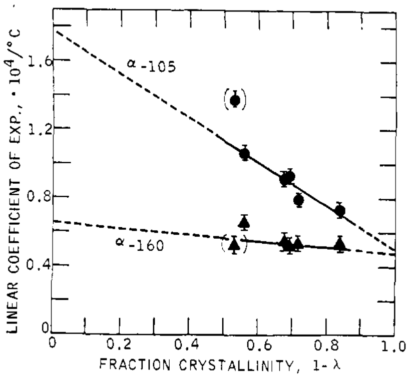

Figure 3. Linear coefficient of thermal expansion at −160 and −105° as a function of degree of crystallinity, 1 − λ.

α_{-160}, and at −105°, α_{-150}, is plotted as a function of 1 − λ. The temperatures, −160 and −105°, were selected because these values bracket the γ transition. The limits on the data points given in Figure 3 represent the maximum deviation of duplicate or triplicate measurements. Least squares straight lines have been drawn through the data points. Data for the least crystalline sample shown in the figure were not considered in constructing the lines because, as noted previously, the level of crystallinity of this sample during the expansion measurement is uncertain.

Inspection of the α_{-160} plot in Figure 3 shows that this quantity is nearly independent of the level of crystallinity. Since the expansion coefficient of a glass is only slightly greater than that of the corresponding crystalline polymer,[36–40] this would be the expected result if the amorphous domains of LPE were in a glassy state. This observation then establishes a lower limit to the glass temperature. In contrast, the line representing the α_{-105} data shows that α_{-105} increases considerably as the level of crystallinity decreases. A large increase in the expansion coefficient is expected for the glass to liquid transition while the expansion coefficient for the crystalline portion should not be affected in passing through the transition region. We also note in the figure that the α_{-160} and α_{-105} curves extrapolate to the same value, 0.50 ± 0.10 × 10^{-4}/deg for the coefficient of expansion for the 100% crystalline polymer. This value agrees with the directly measured expansion coefficient of the crystal unit cell in this temperature range, which is about 0.59 × 10^{-4}/deg.[16]

Results similar to those in Figure 3 have been reported in the literature for semicrystalline polymers whose glass transition temperatures are well accepted and have been established by other independent means. One example is polyethylene terephthalate, whose T_g is generally accepted to be 70°. Plots of the linear coefficients of expansion, slightly above and below this temperature, as a function of the degree of crystallinity give results virtually identical with Figure 3.[36] Similar results have also been reported for semicrystalline polypropylene[37] and poly-4-methylpentene-1,[38] whose glass temperatures are also well established. Thus, the quantitative behavior of the expansion coefficients above and below the γ transition for LPE is very similar to that of other crystalline polymers at their respective glass temperatures.

The expansion coefficients for completely amorphous LPE, as obtained by a linear extrapolation of the data in Figure 3, can also be compared with typical values for various noncrystalline polymers that have been reported by Kovacs.[41] This compilation is given in Table II. The value of α_{-160} estimated for 100% amorphous LPE is 0.67 × 10^{-4}/deg, which is in the range 0.47–0.80 × 10^{-4}/deg given by Kovacs for noncrystalline organic polymers below T_g. Similarly, α_{-105} for 100% amorphous LPE is 1.77 × 10^{-4}/deg, which is in the range 1.7–2.7 × 10^{-4}/deg given by Kovacs for noncrystalline polymers above T_g. This comparison strongly supports the conclusion that the amorphous transition in the vicinity of −130° is the primary glass transition of linear polyethylene.

It is also of interest to compare the change in α across the γ transition estimated for completely amorphous LPE with values reported for secondary transitions in noncrystalline polymers. In addition to the primary glass transition, some polyalkylethers have secondary transitions at temperatures lower than T_g.[42] The change in α across these secondary transitions ranges from 0.12 to 0.28 × 10^{-4}/deg. Our value of 1.1 ± 0.26 × 10^{-4}/deg for the change in α across the γ transition in 100% amorphous LPE is four- to ninefold greater than this range. If 0.12–0.28 × 10^{-4}/deg is representative of the change in α in the region of secondary transitions in amorphous polymers, then the proposal that the amorphous γ transition in LPE is a secondary transition involving conformational changes of a small number of chain units[20] does not account for the large observed change in thermal expansion coefficient in the γ region.

Since it has been postulated that the β transition in the vicinity −20 to −30° is the glass temperature of

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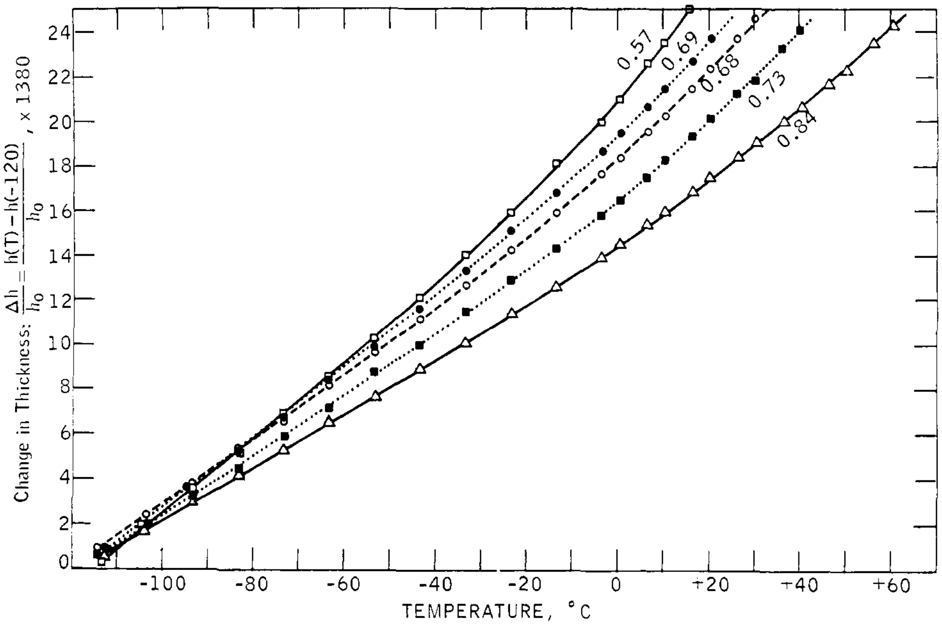

Figure 4. Thermal expansion curves from −120 to +60° for LPE samples with various degrees of crystallinity.

LPE,[5,15,16] an analysis similar to that described above has been made of the thermal expansion curves in this temperature region. Expansion curves over the temperature range −120 to +60° for samples of varying levels of crystallinity are shown in Figure 4. Visual examination of these curves gives little if any evidence for a transition in the β region. Nevertheless, coefficients of expansion at −70 and +15°, temperatures which encompass the β region, are plotted in Figure 5. Examination of Figure 5 shows that the expansion coefficient below the reported β transition temperature depends very strongly on the level of crystallinity and varies by a factor of more than three in going from the completely amorphous to the completely crystalline state. In contrast, the coefficient of expansion below T_g *in other semicrystalline polymers* that have been examined[36–40] is nearly independent of crystallinity. Thus, the large change in α_{-70} with the level of crystallinity of LPE is not consistent with a glassy state of the amorphous domains of the polymer.

The values for α_{-70} and α_{+15} for the completely amorphous LPE, as extrapolated from the data in Figure 5, are given in Table II. The value for α_{-70} is much greater than α_g for completely amorphous polymers. Similarly, α_{+15} is also larger than typical α_l values given by Kovacs for completely amorphous polymers. Thus, if there is a transition in LPE in the β region, it can be concluded from the expansion data that the transition does not have the properties of a primary glass transition.

Calorimetric Measurements. Duplicate differential calorimetric measurements are given in Figure 6 for samples with various levels of crystallinity measured at room temperature. The duplicate curves demonstrate the good reproducibility that was obtained. The two samples with the highest levels of crystallinity show no evidence of a transition in the γ region. This result is in accord with specific heat measurements

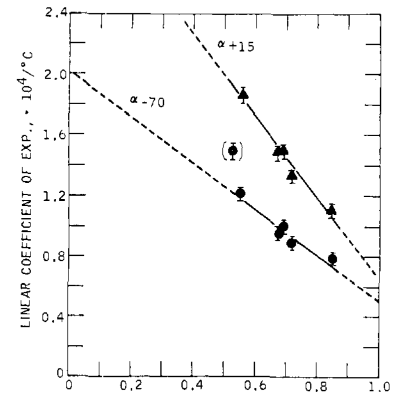

Figure 5. Linear coefficient of thermal expansion at −70 and +15° as a function of degree of crystallinity, 1 − λ.

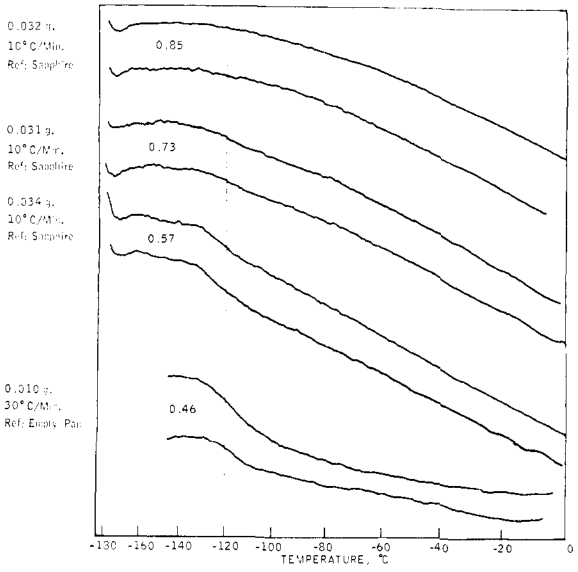

Figure 6. DSC runs on LPE samples with various levels of crystallinity.

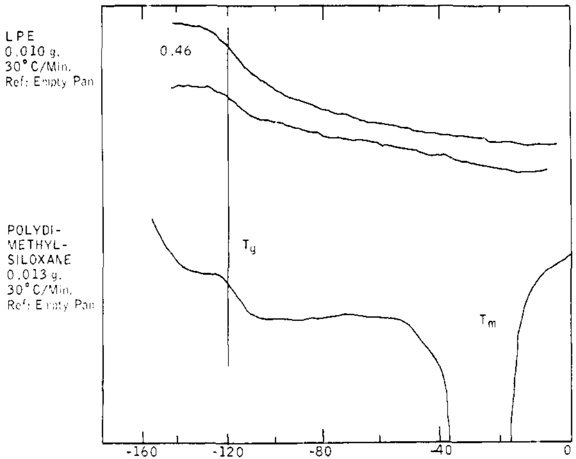

Figure 7. DSC runs on LPE sample with 0.46 fractional crystallinity and on semicrystalline polydimethylsiloxane.

made on highly crystalline LPE.[43,44] However, the sample with the lowest level of crystallinity displays a definite sigmoidal increase in heat capacity in the γ region. The form of the curve in this temperature range is similar to that of other polymers in the T_g region.

For purposes of comparison and as a further check on the technique, a DCS trace on a sample of semicrystalline PDMS is given in Figure 7. This polymer was chosen because its glass temperature is known to be −123°,[45] which is comparable to the γ transition temperature. As can be seen from the figure, the magnitude and character of the heat capacity change in the T_g region of this polymer is similar to that in the γ region for the least crystalline specimen of LPE. Hence, the calorimetric measurements support the assignment of the γ transition as the primary glass transition of LPE. In the −100 to −50° region of Figure 7, there appears to be a greater increase in heat capacity for LPE than for polydimethylsiloxane. This might be interpreted as an indication of a diffuse transition in LPE in this temperature interval. However, in view of the qualitative nature of our data, such a conclusion would be very tenuous.

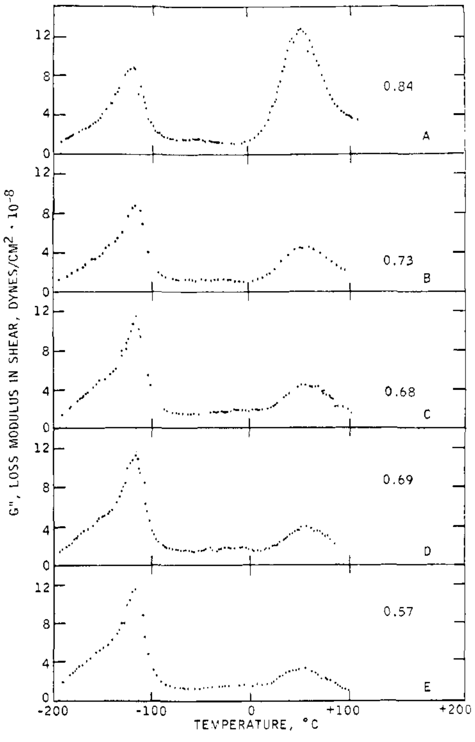

Figure 8. Loss modulus *vs.* temperature curves for LPE with various levels of crystallinity.

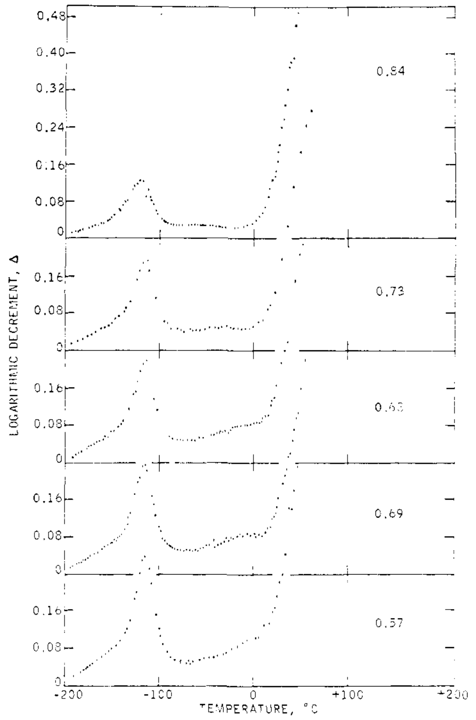

Figure 9. Logarithmic decrement *vs.* temperature curves for LPE samples with various levels of crystallinity.

Inspection of Figure 6 shows no indication of a transition in the region of the β transition.

Dynamic Mechanical Results. Loss modulus *vs.* temperature, *T*, plots for the LPE samples of various levels of crystallinity are shown in Figures 8A–E. The corresponding plots of the logarithmic decrement, Δ, *vs.* *T* are given in Figures 9A–E, while the storage modulus, *G'*, *vs.* *T* data are given in Figure 10. The γ relaxation is manifested in Figures 8 and 9 by an intense peak in the vicinity of −120° and by a large decrease in *G'* at about this same temperature in Figure 10. Inspection of Figures 8A–E and Figures 9A–E shows that the peak intensity in the γ region decreases as degree of crystallinity increases. This observation becomes quantitatively more apparent from Figure 11, where the peak heights $G''_{\max}$ and $\Delta_{\max}$ for the γ relaxation are plotted against degree of crystallinity. Data from Iller's work[10] are also included in the figure, and good agreement is obtained between the two studies for samples of the same level of crystallinity. It is presently uncertain whether the loss modulus, the logarithmic decrement, or the loss compliance is the preferred measure of the loss in a semicrystal-

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(43) F. S. Dainton, D. M. Evans, F. E. Hoare, and T. P. Melia, *Polymer*, 3, 277 (1962).

(44) E. Passaglia and H. K. Kevorkian, *J. Appl. Polym. Sci.*, 7, 119 (1963).

(45) C. E. Weir, W. H. Leser, and L. A. Wood, *J. Res. Nat. Bur. Stand.*, **44**, 367 (1950).

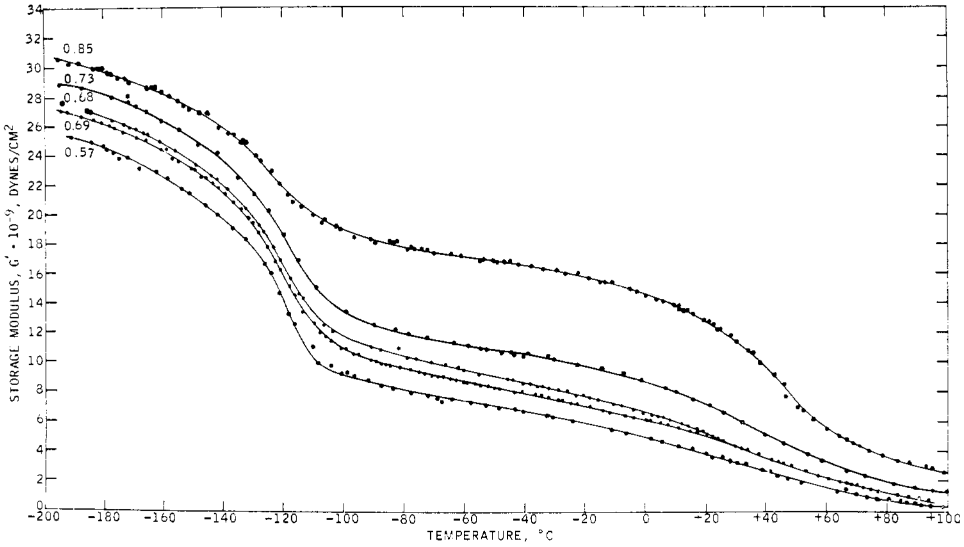

Figure 10. Storage modulus *vs.* temperature curves for LPE samples with various levels of crystallinity.

line polymer.[46,47] Irrespective of which of these criteria is adopted, however, the loss increases as the degree of crystallinity decreases. The same conclusion is obtained if the area under the γ peak rather than the peak intensity is used as a measure of the loss. Consequently, the γ relaxation originates, at least in part, in the amorphous domains of the polymer. This conclusion was previously reached by Illers[10,48] and by Gray and McCrum,[49] who studied LPE samples which encompassed a smaller range of crystallinity and did not include samples having such low levels of crystallinity.

Inspection of the curves for the samples with lower levels of crystallinity in Figures 8 and 9 shows that the γ band is very asymmetric. This is especially evident in Figures 8D and E where a shoulder is seen on the low-temperature side of the maximum. The appearance of these curves suggests that the γ relaxation has two components, one centered at *ca.* $-120°$ and the other at a lower temperature, whose relative intensities vary with level of crystallinity. In a study of poly(ethylene-*co*-methyacrylic acid), MacKnight, *et al.*, found that the γ relaxation in this copolymer could be partially resolved in a G'' *vs.* $1/T$ plot into two overlapping peaks.[4] However, treatment of the LPE data in Figure 8 by the method suggested by MacKnight does not further clarify the nature of the asymmetry since separate peaks cannot be resolved. Sinnott's dynamic mechanical measurements on solution precipitated LPE specimens also provide support for this interpretation of the asymmetry of the γ relaxation peak.[7] G'' *vs.* T curves for solution-precipitated samples show a symmetrical band centered at $-140°$. After melting and recrystallization of the crystals, *i.e.*, annealing at 130°,[50] an asymmetric band with a peak at about $-120°$ and a shoulder at around $-140°$, similar to our Figure 8E, was observed.

A different interpretation of the asymmetry of the γ peak has also been given.[13] It has been proposed that the γ relaxation arises from a single source, namely, the reorientation of chains in the vicinity of polymer chain ends trapped in the crystal lattice. A theoretical analysis has been developed which shows that such a model can give an asymmetric relaxation peak.[13] However, the view that chain ends in crystals are the source of the γ transition is not supported by experiment. Recent results, which substantiate earlier theory and experiments[51,52] on other polymers, have demonstrated that polymer chain ends are almost completely excluded from the crystalline phase of LPE.[53] Furthermore, Iller's data in Figure 11 were obtained on unfractionated LPE whereas, except for one sample, our data were obtained on molecular weight fractions. Nevertheless, the two sets of data fall on a common curve. Finally, for the molecular weight fractions, the intensity of the γ relaxation actually increases as the molecular weight increases, *i.e.*, as the concentration of chain ends decreases. Hence, defects caused by chain ends trapped in the

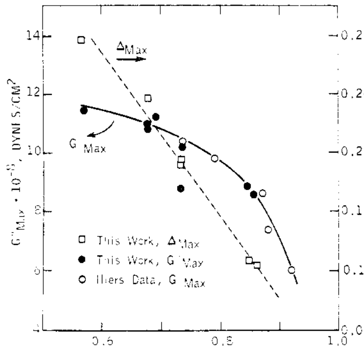

Figure 11. Variation of peak intensity of γ relaxation in LPE as a function of degree of crystallinity, $1 - \lambda$.

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(46) E. Passaglia and G. M. Martin, *J. Res. Nat. Bur. Stand.*, **68**, 519 (1964).

(47) R. W. Gray and N. G. McCrum, *J. Polym. Sci., Part B*, **4**, 639 (1966).

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crystal lattice cannot be a major source of the γ relaxation. The interpretation of the γ relaxation in terms of two overlapping relaxations is in better accord with experiment. To facilitate discussion, we will hereafter refer to the two components of the γ relaxation observed in the dynamic mechanical experiments as the γ_{-120} and the $\gamma_{<-120}$ relaxations.

The interpretation of the asymmetry of the γ relaxation in terms of two unresolved relaxations is also consistent with wide-line nmr experiments. From a careful analysis of samples of different density and mode of crystallization, Bergman and Nawotki[54] have shown that the wide-line nmr spectrum of LPE consists of three superimposed bands having different widths. These three bands were interpreted as deriving from (a) crystalline domains in which segmental motion is highly restricted, giving rise by a broad nmr band, (b) a disordered domain in which segmental motion is relatively unrestricted, giving rise to a narrow band, and (c) a disordered domain in which chain segments have an intermediate degree of mobility, giving rise to a band of medium width. This three-component analysis of the nmr spectrum is strongly supported by the fact that, for LPE samples crystallized in different fashions and encompassing a range in the level of crystallinity, the fractional area under the broad band is equal to the degree of crystallinity calculated from density and heat of fusion measurements.

In the nmr experiments the medium-width component was first detected at $-100°$ and the narrow component was first detected at $-70°$. These two temperatures were originally identified with the γ and β relaxation temperatures, respectively.[54] However, since nmr is a high frequency measurement, the γ and β relaxations should be observed at considerably higher temperature in an nmr experiment than in low-frequency mechanical measurements. Therefore, the $-70°$ temperature at which the narrow nmr band is first detected cannot be related to the temperature of the β relaxation. Rather, we suggest that the temperatures at which the medium and narrow width components of the nmr spectra are first detected, -100 and $-70°$, respectively, should be related to the two components of the γ relaxation. We further propose that the medium-width nmr band and the dynamic mechanical $\gamma_{<-120}$ relaxation have a common morphological origin, and that the narrow-width nmr band and the dynamic mechanical γ_{-120} relaxation have a common morphological origin. This interpretation is supported by the observation that in solution crystallized LPE samples there is a sizeable medium-width nmr band and a very small narrow band,[54] while dynamic mechanical measurements on similarly prepared specimens show a distinct peak at $-140°$ but none at $-120°$.[7] In addition, for melt crystallized LPE, both the medium and narrow nmr bands are observed, the latter being more intense;[54] correspondingly, according to our interpretation, in dynamic mechanical measurements made on melt-crystallized LPE both the $\gamma_{<-120}$ and γ_{-120} relaxations are observed, the latter being more intense.

A simple morphological model can be developed to account for the foregoing nmr and dynamic mechanical observations. In this model the system consists of three zones; namely (a) a crystalline zone with the chain units in an ordered conformation; (b) a disordered, amorphous interzonal region where the chain units are in a nonordered conformation, and (c) an interfacial zone, many chain units thick, which is located at the diffuse boundary between the crystalline and disordered regions. A model of this type has been successful in explaining in a consistent manner, over a wide range of molecular weights and crystallization conditions, a variety of thermodynamic, spectroscopic, mechanical, and morphological properties as well as the very high interfacial free energy associated with high molecular weight samples of low density.[26,55] In this model the intermediate-width nmr component and the $\gamma_{<-120}$ mechanical relaxation would arise from the interfacial zone. The narrow-width nmr component and the γ_{-120} mechanical relaxation would result from the disordered zone. The material in the interfacial and disordered zones constitute the noncrystalline portion of the polymer.

In the preceding model the γ relaxation is attributed solely to the noncrystalline component of the polymer. It has also been proposed that the γ relaxation in LPE includes a contribution arising from within the crystalline domains of the polymer.[7,8,10,13] This view is based largely on a comparison of low temperature relaxations in *n*-alkanes[10] and solution crystallized LPE.[7] This comparison suggested that the relaxation mechanism in the solution precipitated LPE crystals was the same as that in crystalline *n*-alkanes.[7] However, contradictory experimental results on solution crystallized LPE have been recently reported.[48] Furthermore, in order to obtain the data on the *n*-alkanes it was necessary to precipitate the samples in a polystyrene matrix. It is thus possible that the observed relaxation arises from paraffin molecules which remain molecularly dispersed in the polystyrene matrix rather than from the paraffin crystals which are formed in the matrix. A careful examination of the transition temperature–molecular weight relation for the *n*-paraffins indicates the possibility that this relaxation could be the result of an end group effect. Unfortunately, the reported data are not sufficiently precise to resolve this point unequivocally. If this view were correct then the corresponding relaxation in polymers would be undetectably weak. If a crystalline contribution to the γ relaxation is eventually established, the morphological model proposed could be easily modified. At the present time there does not appear to be sufficient reason to complicate the model.

Dynamic mechanical measurements on both branched polyethylene,[5,11] prepared under high pressure, and ethylene-containing copolymers[15] show an intense relaxation peak in the β region. These results have provided the chief basis for the view that the β relaxation corresponds to the glass temperature of polyethylene.[5,11,15] As long as most studies of LPE were restricted to samples of high density and high degree of crystallinity, this proposition could not be critically examined. We are now, however, in a position to examine this question. A study of the -80 to $0°$ region

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in the G''–T plots in Figure 8 reveal that if maxima exist in this temperature region, they are barely detectable. The level of G'' is approximately the same in all the samples in this temperature region. The Δ–T plots in Figure 9 show, at most, very weak and poorly defined maxima and only low loss levels in this temperature region. Finally, the G'–T plots in Figure 10 in this region show a small linear decrease in G' as T increases, with no manisfestation of a transition in this temperature range. This contrasts with analogous curves obtained on branched polyethylene samples which show a large decrease in G' at around $-20°$.[11] Considering the rather low levels of crystallinity of some of the samples studied here, the virtual absence of a β relaxation in LPE appears to be inconsistent with the view that the β relaxation corresponds to the glass transition of LPE. Other investigators, working with higher density LPE have also found the β relaxation to be either absent[5–7] or barely detectable.[9–11] However, Moore and Matsuoka found a small but defined loss peak in the β region.[8]

Conclusions

The thermal expansion, calorimetric, and dynamic mechanical measurements on the LPE samples, possessing the lowest levels of crystallinity heretofore reported, have clearly demonstrated that the γ transition arises principally from contributions of the noncrystalline regions of the polymer. Furthermore, the thermal expansion and calorimetric data have shown that despite its complex character this transition can also be identified with the glass temperature of LPE. The fact that the impact strength of this polymer increases markedly in the γ region[56,57] is consistent with and further supports this conclusion.

Without invoking the thermal expansion and calorimetric results, the dynamic mechanical results taken by themselves suggest that the γ relaxation in LPE corresponds to the primary glass transition of this polymer. Thus, the dynamic mechanical data reported here and by others[10,48] demonstrate the existence of an amorphous relaxation in the γ region. On the other hand, other loss peaks which could be attributed to the amorphous regions are virtually absent even for LPE samples whose level of crystallinity has been reduced to close to 0.50. In contrast, well-defined loss peaks which have been independently identified with the glass transition have been observed in other semicrystalline polymers with levels of crystallinity of about 0.50, *e.g.*, polychlorotrifluoroethylene,[58] polypropylene,[59] poly(ethylene oxide),[60] poly(propylene oxide),[60] poly(4-methyl-1-pentene),[38] and poly(ethylene terephthalate.[61] Hence, relying solely on the mechanical data, we can be default assign the amorphous γ relaxation to the primary glass transition of LPE. This assignment is in accord with the conclusion obtained from the thermal expansion and calorimetric measurements.

It is also of interest to consider the temperature–frequency dependence of the γ relaxation in LPE. The temperature at which the primary glass transition is observed in completely amorphous polymers varies with the measuring frequency in accordance with the WLF equation.[62,63] Secondary transitions, on the other hand, generally have an Arrhenius temperature dependence.[63] Unfortunately, literature reports on the frequency–temperature dependence of the γ relaxation in LPE are discordant. It has been variously reported that (a) the γ relaxation in LPE has an Arrhenius temperature dependence,[48] (b) the γ relaxation in LPE has a WLF–temperature dependence but the parameters differ somewhat from the so-called universal WLF values,[64] and (c) the γ relaxation in LPE is anomalous and has neither an Arrhenius nor a WLF dependence.[9] However, irrespective of the functional form of the frequency–temperature relation, the γ relaxation in LPE for the samples reported in the literature has an apparent energy of activation, ΔH_a, which is smaller than that generally found for primary glass transitions. For primary glass transitions ΔH_a is usually between 30 and 100 kcal/mol.[2] However, ΔH_a of the γ relaxation in polyoxymethylene, the relaxation which corresponds to the glass transition of this polymer,[65,66] is about 20 kcal/mol. In comparison, ΔH_a for the γ transition in LPE has been reported to vary from 5 to 18 kcal/mol,[9,48] depending on the crystallinity of the specimen. The discrepancy between ΔH_a reported for the γ relaxation in LPE and the glass relaxation in other polymers is possibly a consequence of the composite nature of the γ relaxation, which makes it difficult to accurately determine ΔH_a for the individual relaxations. More important perhaps is the fact that the appropriate frequency dependent experiments on LPE samples containing low levels of crystallinity have not yet been reported. It is for such samples that the classical behavior, approaching that for an amorphous polymer, would be expected.

We should also consider before concluding some arguments that could be raised against the γ transition being identified with T_g. Boyer[67] and Beaman[68] found that the ratio of T_g to the melting temperature, T_m, for many polymers falls in the range 0.5–0.8. This ratio for LPE, based on our assignment of T_g, is $\backsim$0.37, which is outside this range. However, exceptions to the Boyer–Beaman generalization are known.[69] Two examples are poly(2,6-dimethyl 1,4-phenalene ether) and polyoxymethylene, whose T_g/T_m ratios are 0.88[70] and 0.42,[65,66] respectively. Hence, the fact that this ratio is outside the usual range is not unique to LPE and cannot be used as a serious argument against the assignment made.

From the examination of data for a restricted number

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(70) F. E. Karasz, *Amer. Chem. Soc., Div. Polym. Chem. Preprints*, **9**, 822 (1968).

of polymers, Simha and Boyer[71] have proposed the relation

$$3(\alpha_l - \alpha_g)T_g = 0.11$$

where the constant 0.11 is supposed to be universal for all polymers. Krause and coworkers have pointed out many exceptions to this rule[72] and an analysis of her data for amorphous polymers indicates that the quantity $3(\alpha_l - \alpha_g)T_g$ ranges from about 0.055–0.15. Haldon, *et al.*, have also noted deviations from the Simha–Boyer relation.[42] For LPE, using the values of α_{-105} and α_{-160} which were obtained by extrapolation to the completely amorphous polymer and $T_g \backsim 140$°K, we obtain $3(\alpha_l - \alpha_g)T_g = 0.046 \pm 0.011$. This value is marginally below the range observed for some other polymers.

Data obtained on copolymers of ethylene have led to a diversity of interpretations by different investigators. Baldi and Zannetti[73] showed that the T_g of completely amorphous ethylene–propylene copolymers decreased systematically from *ca.* −10 to −75° as ethylene content increased from 0 to 75 mol %. Linear extrapolation of the T_g–composition curve obtained on such amorphous samples to 100% ethylene content yielded a value of *ca.* −95°. Analogous results have been obtained by other investigators who have examined amorphous ethylene copolymers. However, the transition temperature so derived depends on the copolymer system examined and the extrapolation procedure used, with reported values ranging from −75 to −110°.[15,74–79] The extrapolated transition temperature has been considered by some investigators to represent the T_g of completely amorphous polyethylene.[57] Baldi and Zannetti and others[75,78] have found, however, that crystalline copolymers do not fall on the T_g–composition curve defined by completely amorphous copolymers. Rather, at high ethylene content the transition temperature is either independent of the overall composition[73,78] or increases with ethylene content.[75,79] From such measurements some investigators have concluded that the T_g of semicrystalline LPE is about −30°.[57,74] This interpretation of the copolymer data has been criticized by McCrum, *et al.*[79] It should also be emphasized that it is the composition of the noncrystalline regions of the copolymer and not the overall composition that is important in the analyses of T_g–composition relations.[2,32] This is an uncertain quantity in most cases, and the situation is complicated by the possibility of crystallization, with attendant compositional changes, at the low temperatures involved. In view of the uncertain composition of the noncrystalline portions of such semicrystalline copolymers and the complex experimental results obtained, it appears that the copolymer data cannot be interpreted with confidence at present.

An Esr spin probe method for examining the spectrum of a paramagnetic molecule in a host matrix has recently been applied using various polymers, including LPE, as the matrix material.[80] The spectrum of the paramagnetic molecule is sensitive to the motion of the host polymer and, for various polymers whose T_g's are uncontroversial, a major change in band width occurs in the T_g region. In the case of LPE, there is a large change in band width in the β region and no change in width in the γ region. This observation favors the assignment of the β transition rather than the γ transition as the primary glass transition of LPE.

Further work is necessary to reconcile the results of all the experimental data reported on transitions in polyethylene. Nevertheless, the new experimental data presented in this report clearly demonstrate that the γ transition in LPE arises principally from the amorphous domains of the polymer. The thermal expansion and calorimetric measurements strongly support the conclusion that this transition can be identified with the primary glass transition of linear polyethylene.

Acknowledgments. We are grateful to Mr. J. O. Brewer and Mr. D. J. Krisher for obtaining most of the experimental data and to Mr. E. Ergoz for preparing the lowest density LPE sample that was examined. We also wish to thank Mr. Charles Russ of the Du Pont Instrument Co. for the use of the DSC equipment. The torsion pendulum was designed by Mr. John Heigl.

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