Reviews

Glass Temperatures of Polyethylene

Raymond F. Boyer

The Dow Chemical Company, Midland, Michigan 48640. *Received July 3, 1972*

ABSTRACT: Combining the thermal expansion data of Stehling and Mandelkern (S–M) on polyethylene samples of varying crystallinity; the thermal expansion data of Illers on amorphous ethylene–vinyl acetate copolymers; and certain criteria developed by Simha and Boyer for thermal expansion quantities, α_g, α_l, $\alpha_l T_g$, and $\Delta\alpha T_g$, lead us to the following conclusions. (1) The S–M data appear correct but have been incorrectly interpreted by them in regard to assigned α_g and α_l values. (2) The glass temperature of amorphous polyethylene is 195 ± 10°K. (3) The 145 ± 10°K process in polyethylene is a $T < T_g$ relaxation commonly, and correctly, known as T_γ. (4) Partially crystalline ($\chi \cong 0.5$–0.8) polyethylenes exhibit two glass transitions: a T_g(L) around 195°K, and T_g(U) around 240°K but both increase linearly with crystallinity. (5) These are ascribed to the existence of two types of amorphous material. For example, T_g(L) may be associated with cilia and T_g(U) may arise from loose loops and/or tie molecules. (6) In-chain relaxation processes at T_γ involving -(CH_2)-$_n$ sequences of $n \geq 3$ are accompanied by higher than normal values of α_g (*i.e.*, $\alpha_g > 2 \times 10^{-4}$ deg^{-1}) and smaller than normal values of $\Delta\alpha$ and $\Delta\alpha T_g$. This is shown to be true for nylons, polyethylene, and ethylene–vinyl acetate copolymers. (7) What S–M refer to as α_l is really an α_g enhanced above its normal value by the in-chain γ relaxation. (8) There is a linear relationship between α_g and the strength, S_γ, of the γ relaxation at ≈150°K for a family of nylons and, by analogy, for ethylene–vinyl acetate copolymers. (9) The γ relaxation in polyethylene is strong compared to T_g(L) and T_g(U), possibly because of the simple structure of polyethylene. (10) Data on electron spin resonance probes collected by Rabold for a variety of polymers are reexamined. This method verifies our assignment of T_g(L) for semicrystal line polyethylene; lacks resolution to prove or disprove a T_g(U); and verifies that the 145°K relaxation is a T_γ rather than T_g. (11) Available evidence suggests that double glass transitions are fairly common in semicrystalline polymers.

Linear and branched polyethylenes, especially in the range of 50–75% crystallinity, exhibit three amorphous phase transitions or relaxation phenomena at the following temperature regions:[1,2] 145 ± 10, 195 ± 10, and 240 ± 20°K. Each of these regions has one or more characteristics of a true glass transition, *i.e.*, an abrupt increase, $\Delta\alpha$, in the coefficient of thermal expansion, and an abrupt increase, ΔC_p, in the specific heat; a dynamic mechanical loss peak whose magnitude increases with amorphous content; time effects; an increase in magnitude of $\Delta\alpha$ and ΔC_p with amorphous content. Each of these three amorphous transitions has been labeled by more than one group of investigators as the true T_g of polyethylene.

Stehling and Mandelkern,[2] after providing a general background for the problem, present thermal expansion, specific heat and dynamic mechanical loss data on well-characterized fractions of linear polyethylene ranging in fractional crystallinity from 0.47 to 0.87. From these data they conclude that T_g is 145°K. However, the controversy continues and even intensifies as new experimental methods and techniques (to be discussed later) are reported. In view of the experience and reputation of the various proponents of each of these three glass transition values, we decided that the experimental data could not be wrong. Instead an attempt must be made to reconcile these divergent views. In doing this, we rely mainly on the S–M paper for background except for certain key references which S–M seem to have omitted or ignored and except for specific conclusions. An earilier review will also be used.[1]

We have concluded, as illustrated in Figure 1, that semicrystalline linear polyethylene exhibits a double glass transition, T_g(U) and T_g(L) resulting from what is generally believed to be the chain-folded morphology of melt crystallized polyethylene.[3,4] In addition, the amorphous γ relaxation, T_γ, is shown. According to Figure 1, completely crystalline polyethylene must be free of amorphous transitions although a hypothetical transition temperature can be obtained by extrapolation. A completely amorphous (and thus far experimentally unrealizable) polyethylene will have two amorohous transitions, of which the upper is the true T_g and the lower is T_γ. At intermediate levels of crystallinity, the γ or $T < T_g$ relaxation as well as two true glass transitions exist.

The slopes of the upper line, T_g(U), and of the lower line, T_g(L), resulted from our estimates of changes in slopes of the thermal expansion data of S–M on either side of T_g(U) and T_g(L). We suggest tentatively that T_g(L) is associated with dangling cilia and with molecules rejected by the spherulites. T_g(U) is associated with loose loops or intercrystalline tie molecules. (We assume that increasing crystallinity means that the loops and tie molecules are under more constraints.) More generally, we suggest that there are two distinct types of amorphous material in bulk crystallized polyethylene, one of which is under more constraint than the other.

The circles in Figure 1 represent our estimates about the relative intensities of the several transitions as a function of crystalline content. These estimates are based on logical considerations augmented and supported by the S–M thermal expansion plots as well as thermal expansion data on isotactic polypropylene which also shows evidence for a double glass transition.[5]

It should be noted that Figure 1 represents a tentative hypothesis. We believe it reconciles the seemingly con-

---

[1] R. F. Boyer, *Rubber Chem. Technol.*, 36, 1303 (1963).

[2] F. C. Stehling and L. Mandelkern, *Macromolecules*, 3, 242 (1970).

[3] P. H. Geil, "Polymer Single Crystals," Interscience, New York, N. Y., 1963.

[4] A. Keller, *Rept. Progr. Phys.*, 31, 2, 623 (1968).

[5] D. L. Beck, A. A. Hiltz, and J. R. Knox, *SPE (Soc. Plast. Eng.) Trans.*, 3, 279 (1963).

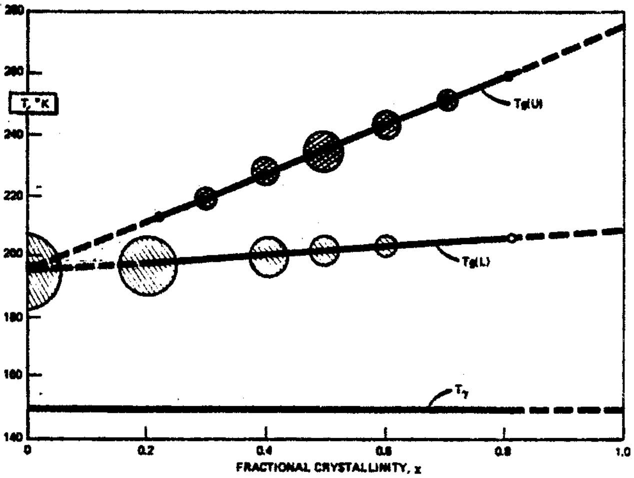

Figure 1. The double glass transition, T_g(L) and T_g(U), and the T_γ amorphous relaxation in linear polyethylene. The size of the circles indicate the intensity of the two glass transitions. Intensity of the T_γ transition increases continuously to the left. We associate T_g(L) with cilia and polymer chains rejected by crystallites; and T_g(U) with loose loops and/or tie molecules. This plot has been estimated by us from the thermal expansion data of Stehling and Mandelkern.[2]

flicting literature data of a large number of investigators. The evidence leading to this hypothesis for polyethylene will now be presented. Evidence for a double glass transition in other semicrystalline polymers is being described elsewhere.[6] This hypothesis suggests many experiments relating transition phenomena to detailed polymer morphology. Until such experiments are performed on polyethylene and other semicrystalline polymers, this hypothesis must remain tentative.

We have been surveying the multiple transition literature on polyethylene and other polyolefins continuously since our earlier review appeared.[1] As a result of this survey, covering primarily thermal expansion, specific heat and dynamic mechanical loss data, we have developed a set of working hypothesis which are stated below for the convenience of the reader. These should in no way be considered as a set of *a priori* assumptions. Each of them will be justified at the appropriate place. (1) Thermal expansion data are sufficient in themselves to reach the desired reconciliation of conflicting results on the glass temperature of polyethylene. (2) A discontinuity, $\Delta\alpha$, in thermal expansion coefficient at T_g is a necessary but not a sufficient condition for T_g. Identical remarks hold for the discontinuity, ΔC_p, in specific heat. Likewise, dynamic mechanical loss peaks which are proportional in magnitude to amorphous content are a necessary but not a sufficient condition for T_g. (3) The amorphous state thermal expansion properties of linear polyethylene can be estimated by any or all of three different methods: (a) extrapolation of data on samples of different crystallinities, as demonstrated by S-M;[2] (b) extrapolation of amorphous copolymer data to pure polyethylene as done by numerous workers cited in the S-M article, which will be detailed later; (c) use of homologous series, $R(CH_2)_nR$, as with nylons, extrapolated to $n \to \infty$. (4) Certain semiempirical criteria apply to the amorphous state of all polymers at T_g, namely

$$\alpha_l T_g \cong 0.16 \tag{1}$$

$$\Delta\alpha T_g \cong 0.11 \tag{2}$$

$$\alpha_g \cong 2 \times 10^{-4}\ \mathrm{deg}^{-1} \tag{3}$$

in the absence of strong $T < T_g$ relaxations

$$\alpha_g > 2 \times 10^{-4}\ \mathrm{deg}^{-1} \tag{3'}$$

if strong $T < T_g$ relaxations are present. α_l is $(1/V_g)(\mathrm{d}V/\mathrm{d}T)_l$ immediately above T_g. α_g is $(1/V_g)(\mathrm{d}V/\mathrm{d}T)_g$ immediately below T_g. $\Delta\alpha$ is $\alpha_l - \alpha_g$. V_g is the specific volume at T_g. Gee,[7] who recommends thermal expansion as the primary criterion for deciding T_g, uses other numerical criteria involving thermodynamic quantities such as the discontinuities, ΔC_p, in specific heat and $\Delta\kappa$ in compressibility; and the pressure coefficient of T_g, namely, $\mathrm{d}T_g/\mathrm{d}P$. However, there is controversy about these thermodynamic relationships as well as a lack of data for amorphous polyethylene. (5) There is no reason to conclude that the simple chemical structure of amorphous polyethylene should exclude it from following the criteria in eq 1-3′ or cause it to differ in any radical manner from the expected behavior of polymer systems. (6) T_g values of ethylene copolymers can be reliably extrapolated to pure amorphous polyethylene *via* the Gordon-Taylor copolymer equation if the copolymers are random and amorphous. Thermal expansion data on such amorphous copolymers can be extrapolated linearly to give reliable values for amorphous polyethylene.

Thermal Expansion Data on Linear Polyethylene

Our emphasis on thermal expansion quantities is based on three factors: (1) the availability of a considerable body of experimental data; (2) the existence of semiempirical numerical criteria as in eq 1-3′; (3) the basic approach of Gee.[7]

S-M[2] measured coefficients of linear expansion on five fractions and one whole polymer of linear polyethylene with fractional crystallinity ranging from 0.53 to 0.84 over the temperature range from 83 to 338°K. They extrapolated linearly by least squares to zero crystallinity at four temperatures, 113, 168, 203, and 288°K, which they selected to bracket both sides of the three amorphous transition regions stated in the opening paragraph. From this they reached several conclusions: (1) $\alpha_{113°\mathrm{K}} = \alpha_g = 2.01 \times 10^{-4}\ \mathrm{deg}^{-1}$; (2) $\alpha_{168°\mathrm{K}} = \alpha_l = 5.31 \times 10^{-4}\ \mathrm{deg}^{-1}$; (3) $T_g = 145°\mathrm{K}$.

They justified their α_g value on the basis that it was a normal glassy state value when compared with values in a short table given by Kovacs.[8] This table listed two inorganic, two low molecular weight organic, and six organic polymer glasses. None of the latter had subgroup transitions. By examination of the more extensive table by Wood[9] or the Simha-Boyer paper to which they later refer,[10] or a paper by Rogers and Mandelkern,[11] it would have been immediately apparent that α_g can be substantially greater than 2×10^{-4}. They similarly justified their α_l value by noting that it was marginally above the α_l of poly(methyl methacrylate) in this same table by Kovacs,[8] thereby ignoring the fact that it is risky to compare a hydrocarbon polymer of low T_g with poly(methyl methacrylate) of high T_g, especially in view of eq 1 and the findings of Simha and Boyer.[10] They noted the product, $\Delta\alpha T_g$, was 0.046 and hence quite low compared with the Simha-Boyer value stated in eq 2. They excused this low value by stating that eq 2 was only an empirical average and that

---

(6) R. F. Boyer, manuscript submitted to *J. Macromol. Sci., Part B.*

(7) G. Gee, *Polymer*, 7, 177 (1966).

(8) A. J. Kovacs, *Advan. Polym. Sci.*, 3, 395 (1964) (Table I on p 404).

(9) L. A. Wood, *J. Poly. Sci.*, 28, 319 (1958).

(10) R. Simha and R. F. Boyer, *J. Chem. Phys.*, 37, 1003 (1962).

(11) S. S. Rogers and L. Mandelkern, *J. Phys. Chem.*, 61, 985 (1957).

many polymers fell below it. Unfortunately they chose a faulty reference, the work of Krause *et al.*,[12] in which all values were β's ($\beta = \mathrm{d}V/\mathrm{d}T = \alpha V_g$). The low values S-M emphasized in this reference[12] were for dense, highly polar polymers of low V_g, not strictly suited for comparison with polyethylene. More recently Sharma *et al.*[13] concluded that eq 2 was generally invalid. Simha and the writer have offered a factual refutation of this conclusion.[14]

S-M did not apply eq 1 to their results. The product $\alpha_l T_g$ is 0.077 and therefore less than half of the Simha-Boyer average value given in eq 1. Simha and the writer have concluded, severally and together,[10,14-20] that whereas there are a number of marked exceptions to eq 2, eq 1 appears to hold remarkably well for a wide variety of polymers. Hence it is my conclusion that

$$\alpha_{168°\mathrm{K}} = 5.31 \times 10^{-4} \text{ deg}^{-1} \neq \alpha_l$$

We return to the matter of α_g.

It is true that α_g was stated by Gordon and Taylor[21] to have a normal value of about 2×10^{-4} deg^{-1} which is amply confirmed by numerous examples in the literature. However, we have reached the general conclusion, to be documented later, that $\alpha_g > 2 \times 10^{-4}$ deg^{-1} for any polymer or copolymer which has a strong $T < T_g$ mechanical relaxation arising from side-chain or in-chain motion. This first became apparent to Simha-Boyer[10] on examining data of Rogers and Mandelkern[11] for poly(*n*-alkyl methacrylates). This was emphasized by us[10] as a reason why these polymers deviate from eq 2. For example, three polymers with *n*-hexyl side chains all have values of $\alpha_g > 2 \times 10^{-4}$, namely, poly(*n*-hexyl methacrylate), 3.9×10^{-4};[11] poly(*n*-hexyl vinyl ether), 3.75×10^{-4};[16] and poly(octene-1), 6.9×10^{-4} deg^{-1}.[22] Sharma, Mandelkern, and Stehling measured and reported[13] an α_g of 4.96×10^{-4} for poly(dimethylsiloxane). Two conclusions follow immediately: an α of 2×10^{-4} does not guarantee that one is in the glassy state immediately below T_g; and the S-M α_l of 5.3×10^{-4} is actually less than the α_g of poly(octene-1) and very close to that for the siloxane polymer. Hence, even if S-M reject eq 1 and 2 as criteria, their assignment of α_g and α_l values around $T_g = 145$ lacks conviction by the incomplete comparison method they employed. It should be noted that the concept of $T_\gamma = 145$°K as a $T < T_g$ transition has been in the literature since it was first discovered by Schmieder and Wolf[23] so that extra caution was indicated if one were to label it as T_g.

In addition, application of a straight edge to the data points of Figure 1 of S-M reveals two additional straight lines intersecting around 193 and 238°K. S-M do not totally ignore this but insist that there is continuous curvature so that any straight lines thus drawn are subjective. However, these multiple breaks are readily seen in published plots by Dannis[22] for branched and linear polyethylene. Zakin, Hershey, and Simha[24] found changes in slope of linear thermal expansion values at 148, 213, 251, and 273°K (as stated explicitly by S-M). Since Zakin *et al.* used a computer program to calculate first derivatives, there can be a minimum of subjective judgement. These multiple breaks seen in the data of S-M, Dannis and Zakin *et al.* are consistent with the three amorphous transitions of Figure 1. It is our contention that the S-M data consist of a series of four straight lines (three intersections if extended) connected by curved sections at the lowest level of crystallinity reported (0.57) with a tendency toward continuous curvature as crystallinity approaches the highest measured level (0.87).

In addition to the above representative thermal expansion results, there are various results revealing a glass-like transition around 250°K. We cite only two of these.[25,26] In one case[26] a mercury dilatometer was used so that the data do not go below 234°K. Also in this case, branched and linear polyethylenes of different crystallinities were used, showing a larger $\Delta\alpha$ for the more amorphous sample. Hence whatever one concluded about lower temperature events, we see no way that one could logically discard the existence of a glass-like transition at 240 ± 20°K. This glass transition has been confirmed conclusively recently by Chang[27] who measured drifts of C_p with time near this temperature; by Davis and Eby[28] who report drifts in volume with time near this same temperature region; and by Illers[29] with dynamic mechanical loss and time effects. This is our T_g(U) of Figure 1.

We conclude then that the S-M data, especially at 0.57 crystallinity, clearly reveals all three amorphous transitions and provides a sound basis for Figure 1. This includes the existence of the transitions, the slopes of the lines, and the sizes of the circles. S-M's erroneous assignment of T_γ transition as T_g was based on insufficient consideration of thermal expansion data and criteria readily available in the open literature.

They noted, correctly, that the $\Delta\alpha$ of 3.3×10^{-4} deg^{-1} observed at 145°K was larger than any reported in the literature for a $T < T_g$ transition. However, a $\Delta\alpha$ is only a necessary but not a sufficient condition for glass transitions. This has been demonstrated repeatedly by Simha and his collaborators who measured thermal expansion on amorphous poly(alkyl methacrylates)[15] and poly(alkyl vinyl ethers).[16] Secondary or $T < T_g$ mechanical relaxations are generally accompanied by a sharp $\Delta\alpha$ which is always smaller than the $\Delta\alpha$ at T_g. If $\Delta\alpha T_g < 0.11$, then the assignment of T_g, α_l, and α_g should be suspect. This is especially so if $\alpha_l T_g < 0.164$. We shall devote a later section to considering the strength of T_γ compared to T_g(L) and T_g(U) transitions in polyethylene.

S-M Dynamic Mechanical and DSC Results

S-M reported dynamic mechanical loss data on four of their samples, showing that the loss peak height at 145°K increases with amorphous content and that the loss peak has a low-temperature shoulder. Illers[30] had previously demonstrated that the γ peak in linear polyethylene has three components: an amorphous peak at 163°K corresponding to the S-M value, another amorphous peak at 138°K and a crystalline loss peak at 108°K.

---

(12) S. J. Krause, J. J. Gormley, N. Roman, J. Shetter, and W. H. Watanabe, *J. Polym. Sci., Part A*, **3**, 3573 (1965).

(13) S. C. Sharma, L. Mandelkern, and F. C. Stehling, *J. Polym. Sci., Part B*, **10**, 345 (1972).

(14) R. F. Boyer and R. Simha, *Polym. Lett.*, in press.

(15) R. A. Haldon and R. Simha, *J. Appl. Phys.*, **39**, 1890 (1968).

(16) R. A. Haldon, W. J. Schell, and R. Simha, *J. Macromol. Sci., Phys., Part B*, **1**, 759 (1967).

(17) R. Simha and C. E. Weil, *J. Macromol. Sci., Phys., Part B*, **4**, 215 (1970).

(18) R. F. Boyer, *J. Macromol. Sci., Part B*, in press.

(19) R. F. Boyer and R. Simha, *Polym. Lett.*, in press.

(20) R. F. Boyer and R. Simha, Manuscript in preparation.

(21) M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **2**, 1 (1952).

(22) M. L. Dannis, *J. Appl. Polym. Sci.*, **1**, 121 (1959).

(23) K. Schmieder and K. Wolf, *Kolloid-Z.*, **134**, 149 (1953).

(24) J. L. Zakin, R. Simha, and H. C. Hershey, *J. Appl. Polym. Sci.*, **10**, 1455 (1966).

(25) F. Dannuso, G. Moraglia, and G. Talamini, *J. Poly. Sci.*, **21**, 139 (1956).

(26) M. G. Gubler and A. J. Kovacs, *J. Polym. Sci.*, **34**, 551 (1959).

(27) S. S. Chang, *Polym. Prepr.*, **13**, 1, 322 (1972).

(28) G. T. Davis and R. K. Eby, *Bull. Amer. Phys. Soc.*, **17**, BL-3 (1972).

(29) K.-H. Illers, *Kolloid-Z. Z. Polym.*, **250**, 426 (1972).

(30) K.-H. Illers, *Kolloid-Z. Z. Polym.*, **231**, 622 (1969).

Now a mechanical loss peak increasing in intensity with amorphous content is a necessary but not a sufficient condition to establish a T_g. This can be seen quite readily, for example, in the dynamic mechanical loss data of Woodward *et al.*[31] for Nylon 6,6, Nylon 6,10, and an amorphous 6,6–6,10 copolymer. Both the T_g peak at 300°K and the T_γ peak at 170°K are more intense for the amorphous copolymer than for the two semicrystalline homopolymers. Here is a clear-cut case of a T_γ peak increasing in intensity with amorphous content and yet clearly not being the glass temperature peak.

S–M pointed out that their amorphous peak at 145°K is the only one of any prominence to be seen. However, Illers[30] presented evidence to indicate that the glass peak in polyethylene would be so weak as to be hidden under the background loss. Illers has recently refined his techniques so that he can pick up the β peak.[29] It increases in magnitude and decreases in temperature with amorphous content essentially according to the T_g(U) line of Figure 1. In fact, these data, available to us prior to publication, furnished extra assurance in drawing the T_g(U) line of Figure 1. These results must be added to the thermal expansion[25,26] and time effect[27,28] data mentioned earlier to demonstrate conclusively the existence of a T_g(U).

We wish to continue the dynamic loss discussion with reference to two pertinent copolymer references. McKenna, Kajiyama, and MacKnight[32] studied dynamic mechanical loss in the γ region of poly(ethylene-*co*-methacrylic acid) containing 4.1 mol % methacrylic acid. They found that the γ peak was not sensitive to the presence of metal salts or degree of ionization, in distinct contrast to the $\beta = T_g$ process. They state that the amorphous γ peak "mechanism appears to arise only from short-range local motions of polyethylene segments in the amorphous phase." It is difficult to believe that only 4.1 mol % of a comonomer would so alter polyethylene that what is clearly a $T < T_g$ peak in the copolymer becomes a T_g peak in polyethylene. We realize the copolymer is a high-pressure product with 25 branches/1000 carbon atoms of broad molecular weight distribution in contrast to the linear fractions used by S–M.

Very similar conclusions were reached by Hammer[33] by blending poly(vinyl chloride) with a series of ethylene–vinyl acetate copolymers which showed a characteristic γ peak and a glass temperature. Hammer concluded that ethylene–vinyl acetate copolymers exhibit two kinds of motion: one very local in nature, the other larger and more characteristic of that at glass transitions.

S–M found a glass like ΔC_p using a DSC method on a polyethylene sample of 0.46 fractional crystallinity. Unfortunately, they did not obtain an extrapolated ΔC_p for amorphous polyethylene to facilitate checking with any of the several criteria which might be used, such as the bead model of Wunderlich[34]

$$\Delta C_p/\text{mol of beads} = 2.60 \tag{4}$$

or the Simha-Boyer relation[10]

$$\Delta C_p T_g = 25 \tag{5}$$

which has recently been modified by us[35] to

$$\Delta C_p T_g = 15 + 4.0 \times 10^{-2}\, T_g \tag{6}$$

Illers[29] has DSC C_p–T plots at several levels of crystallinity from which we have extrapolated a ΔC_p of 0.07 which is only one-third of what one calculates from eq 6 for a T_p of 145. The adiabatic calorimeter measurements of Beatty and Karasz[36] do not permit an estimate of ΔC_p (amorphous) at their claimed T_g of 145°K. However, indications are that the extrapolated ΔC_p, when obtained, will prove to be small.

There is, however, a more basic point at issue. O'Reilly and Karasz[37] had proposed, from the then available experimental absence of a ΔC_p at a $T < T_g$ transition, that a measured ΔC_p was both a necessary and a sufficient condition for a glass transition. Beatty and Karasz[36] now report a small ΔC_p for the $T < T_g$ cyclohexyl ring relaxation in poly(cyclohexyl methacrylate). The apparently small ΔC_p at $T_{145°\text{K}}$ in polyethylene would then be consistent with the status we have assigned it as a $T < T_g$ process. We are aware that Beatty and Karasz warn against linear extrapolation of C_p data to zero crystallinity. As we have shown elsewhere,[35] especially by comparing heat capacity and thermal expansion values, DSC results on polyethylene strongly suggest a $T < T_g$ relaxation at 145°K.

Whereas S–M conclude that the dynamic mechanical loss data and DSC results support their assignment of T_g = 145°K, we think the data merely prove, once again after numerous prior proofs in the literature,[23,30,38,39] that the relaxation event at 145°K occurs in the amorphous phase. The S–M experiments do provide polymer scientists for the first time with a numerical measure of its strength in pure amorphous polyethylene.

T_g Data on Ethylene Copolymers

S–M review literature data concerning T_g measurements on ethylene copolymers. They note that the extrapolated amorphous state values of T_g range from 163 to 198°K. They conclude that copolymer data cannot be interpreted with confidence at present. In reaching this conclusion they ignore or reject the precise and explicit findings in their ref 75 (to Maurer).

Maurer[40] has offered a critical review of T_g for ethylene–propylene copolymers prepared by low-pressure methods. He found that such copolymers are amorphous for ethylene contents of less than 60 mol %. He further showed that if data on truly random amorphous copolymers are used, there is no ambiguity about the Gordon–Taylor-Wood extrapolation to a T_g of 193°K for amorphous linear polyethylene. Maurer further noted that as 100% polyethylene is approached, T_g goes through a minimum and then increases before crystallinity sets in, finally approaching the value which we call T_g(U) for pure semicrystalline polyethylene.

S–M likewise ignore or reject the careful study by Illers[41] (their ref 15) on high-pressure copolymers of ethylene with acrylic acid, methyl and *n*-butyl acrylates, vinyl acetate, and vinyl propionate. His plot of V_{sp} at 20° on all of these systems show that all lines extrapolate to a common value of 1.16 cm^3 g^{-1} for amorphous polyethylene. We interpret this to mean additivity of specific volumes which is one requirement for using the Gordon–Taylor copolymer equation.[21] Illers kept his compositions in the

---

(31) A. E. Woodward, J. A. Sauer, C. W. Deeley, and D. E. Kline, *J. Colloid Sci.*, 12, 363 (1957).

(32) L. W. McKenna, T. Kajiyama, and W. J. MacKnight, *Macromolecules*, 2, 58 (1969).

(33) C. F. Hammer, *Macromolecules*, 4, 69 (1971).

(34) B. Wunderlich and I. D. Jones, *J. Polym. Sci., Part B*, 13, 67 (1969).

(35) R. F. Boyer, *J. Macromol. Sci., Phys., Part B*, in press.

(36) C. L. Beatty and F. E. Karasz, *Bull. Amer. Phys. Soc.*, 16, AC-12 (1971).

(37) J. M. O'Reilly and F. E. Karasz, *J. Poly. Sci., Part C*, 14, 49 (1966).

(38) A. H. Willborn, *Trans. Faraday Soc.*, 54, 717 (1958).

(39) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," Wiley, New York, N. Y., 1967.

(40) J. J. Maurer, *Rubber Chem. Technol.*, 38, 979 (1965).

(41) K.-H. Illers, *Kolloid-Z. Z. Polym.*, 190, 16 (1963).

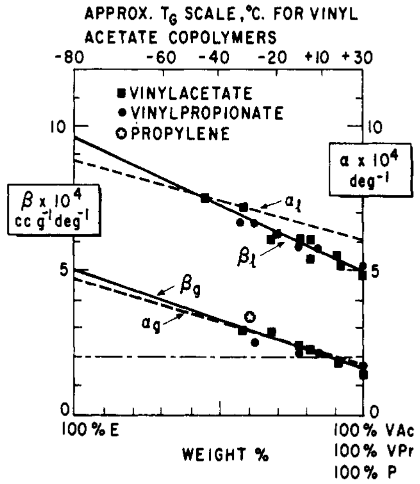

Figure 2. Thermal expansion quantities as indicated for three ethylene copolymer systems to obtain extrapolated values for amorphous polyethylene.

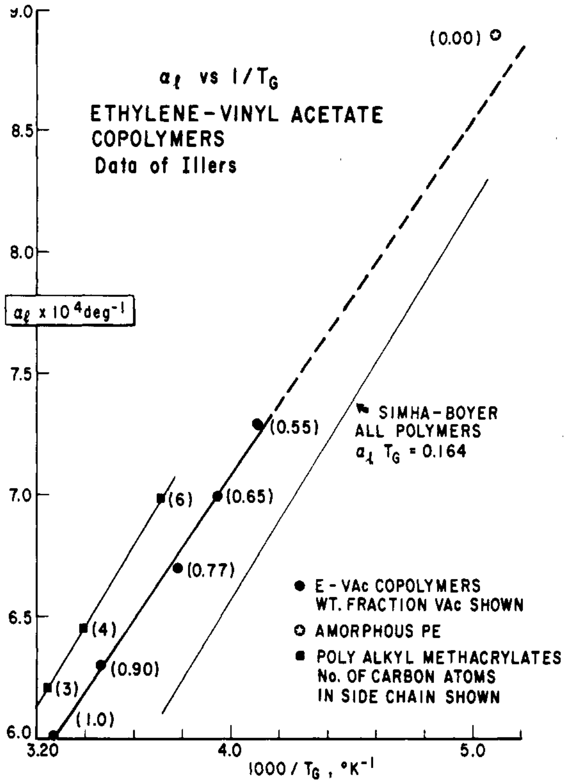

Figure 3. α_l *vs.* $1/T_g$ for ethylene-vinyl acetate copolymers extrapolated to that for amorphous polyethylene. Comparison with all polymers and with alkyl methacrylate polymers are shown.

amorphous range. For vinyl acetate copolymers this has been reported by Nielsen[42a] as less than 54 wt (73 mol) % propylene.

It might be argued, as S-M seem to imply, that crystallites of a size too small to be seen by X-rays exist in such copolymers and/or possibly develop at lower temperatures as T_g is approached. It remains, therefore, to demonstrate this experimentally and to show that if such crystallites exist, they have a sizeable effect on T_g. Illers[30] has presented several examples showing the effect of X-ray crystallinity on T_g in homopolymers. Except for isotactic polystyrene, the effect tends to be small. The T_g(L) line of Figure 1 is an example of the situation for polyethylene, even at high levels of crystallinity. We should also note that Illers extended his refractive index-temperature plots as much as 70° above T_g with no evidence of any other transition phenomena. Illers[42b] has shown that the melting point and heat of fusion decrease linearly with vinyl acetate content, reaching a melting point of 50° at 0.2 mol fraction (0.43 wt fraction) vinyl acetate after which no melting point or heat of fusion is noted. The highest temperature at which refractive index was measured by Illers[41] was 58° which is well above any of his glass temperatures. Illers advises us that DSC runs on his copolymers gave no evidence of crystallinity.[43]

Illers published refractive index temperature plots for both the vinyl acetate and vinyl propionate systems. Breaks in these plots indicate T_g as is well known. Extrapolation of T_g values to 100% amorphous polyethylene by the Gordon-Taylor equation gives a T_g of 196°K. Values of $\beta = \mathrm{d}V/\mathrm{d}T$ can be calculated by eq 5 in the Illers paper. Illers calculated but did not publish β-T values for the vinyl acetate and vinyl propionate systems. On our request he has placed his curves at our disposal.[43] Figure 2 shows both α and β values *vs.* temperature above and below T_g. We have added a point for an equimolar ethylene-propylene copolymer from the data of Zakin *et al.*[24] We also added an approximate T_g scale for the vinyl acetate copolymers. Three features of the Illers thermal expansion data in Figure 2 are noteworthy. (1) α_l increases regularly with decreasing T_g as required by eq 1, reaching an extrapolated limiting value of 8.9×10^{-4} deg^{-1} and thus giving for amorphous polyethylene an $\alpha_l T_g$ of 0.174, only slightly above the average for all polymers. Figure 3 is a plot of α_l *vs.* $1/T_g$ which we calculated for 5 of the ethylene-vinyl acetate copolymers. The point for amorphous polyethylene is slightly above the linearly extrapolated line. Also shown for comparison is the Simha-Boyer trend line and three points for poly(alkyl methacrylates) using data of Rogers and Mandelkern.[11] Data for the lower methacrylates ($n = 1$ and 2) fit on the line, if extended down. (2) α_g increases with weight fraction of ethylene, becoming abnormally high compared with the expected glassy state value of 2×10^{-4} deg^{-1}. This is suggestive of a strong $T < T_g$ relaxation around 113°K for ethylene-vinyl acetate copolymers. Reding, Faucher, and Whitman[44] earlier found the γ relaxation in ethylene-vinyl acetate copolymers containing 15-78 wt % vinyl acetate but did not show actual loss curves. S-M failed to cite this reference with its important conclusion that high ethylene copolymers have two glass transitions, 248 and 148°K. Hammer[33] reported dynamic loss curves. (3) The fact that β_g and α_g increased linearly with weight fraction of ethylene seemed intuitively surprising. All three points will receive detailed attention in the following sections.

Comparison of S-M and the Illers' Thermal Expansion Data

It is thus apparent that S-M disagree with Illers not only on an assignment of T_g but on their α_g and α_l values. It was extremely difficult to reconcile this conflict in an unambiguous manner. To facilitate this task we show in Figure 4 a graphical comparison of the two sets of results (data points omitted) plotted in such a manner that the vertical center line represents amorphous polyethylene. We were faced with a double dilemma. (1) Whereas the

---

(42) (a) L. E. Nielsen, *J. Poly. Sci.*, 42, 357 (1960). (b) K.-H. Illers, *Eur. Polym. J., Suppl.*, 133ff (1969).

(43) K.-H. Illers, BASF, Ludwigshafen, West Germany, private communication.

(44) F. P. Reding, J. A. Faucher, and R. D. Whitman, *J. Polym. Sci.*, 57, 483 (1962).

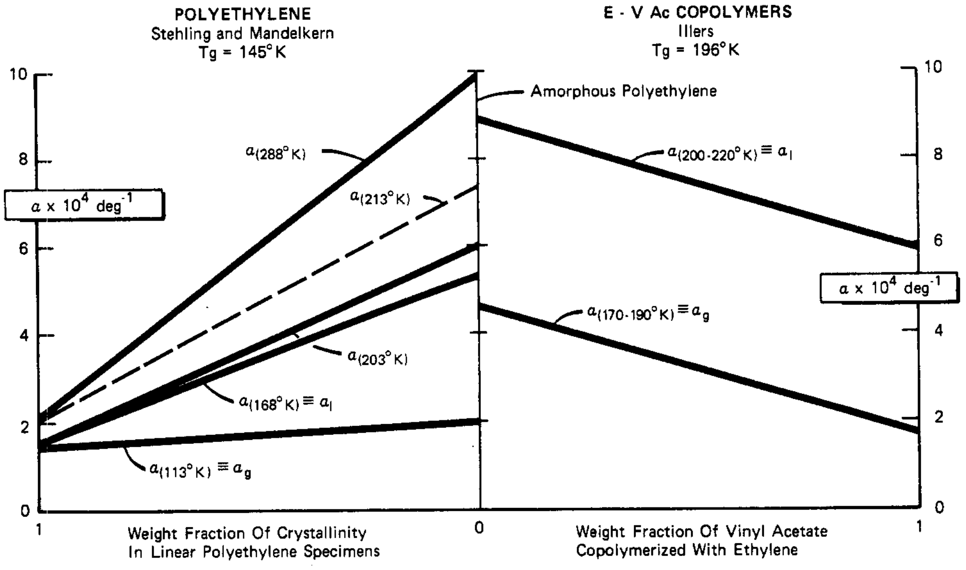

Figure 4. Comparison of Illers[41] and S-M[2] data. The dashed line was calculated by us from the length-temperature plots of S-M. We consider it the true α_l according to the S-M data.

S-M value of α_g appeared normal, α_l was too low for reasons already stated. (2) Whereas the Illers α_l value was normal, as shown in Figure 4, the α_g value was abnormally high. The principal task, in our opinion, was to explain the linear increase in α_g of ethylene copolymers with an extrapolated value of 4.7×10^{-4} for amorphous polyethylene. Once this is accomplished, reconciliation of the two sets of data shown in Figure 4 will be apparent.

Incidentally, S-M extrapolated thermal expansion data at 203°K to get an amorphous state value of 6.0×10^{-4} deg^{-1}. This was an unfortunate choice of temperature because it is too close to $T_g(L)$; as seen in Figure 1, and hence in a region where the length-temperature plots tend to have the normal curvature associated with a glass transition. The dashed line in Figure 4 was estimated by us from S-M data at 213°K which is always above $T_g(L)$. We estimate an amorphous $\alpha_{213°K}$ as 7.5-7.8 $\times 10^{-4}$ deg^{-1} or a midpoint of 7.65×10^{-4} which we consider to be more nearly the α_l just above the T_g of 196°K. This gives an $\alpha_l T_g$ of 0.15.

Interpretation of the Illers' α_g Values for Ethylene-Vinyl Acetate Copolymers

The rationale employed in trying to understand the high values of α_g observed by Illers is as follows. (1) We assume that some minimum number of CH_2 units is required for the T_γ relaxation process in order to cause α_g to be greater than its base value of 2×10^{-4} deg^{-1}. Hence we study data on nylons as model systems and calculate sequence lengths of ethylene units for ethylene-vinyl acetate copolymers. (2) We started out believing, in line with the teachings of Willbourn[38] and Schatzki[45] that at least four in-chain CH_2 units, or two monomer units, would be necessary for a γ relaxation. We had to modify this downward as we continued our analysis and survey of the literature. This does not rule out the importance of longer sequences. (3) There is no formal theory connecting a sequence length of CH_2 units and the strength of a mechanical relaxation or a coefficient of expansion. We therefore investigated nylons for which sequence lengths, relaxation strengths, and α_g values are available in the literature. (4) We next note generic formulas for ethylene-vinyl acetate copolymers and for nylons as

$$CH_2CHR(CH_2CH_2)_NCH_2CHR \qquad (7)$$

$$CO(CH_2)_nNH \qquad (8)$$

and assume that α_g of these two classes of polymers approaches the α_g of amorphous polyethylene as N or n, respectively, approach infinity. (5) We then assume a one to one relationship between the calculated sequence lengths and α_g values in ethylene-vinyl acetate using the nylon data as model polymer systems. (6) We suggest that both the nylon family and the ethylene-vinyl acetate copolymers are ideal model systems for studying polyethylene because they have unambiguous glass transitions in addition to an amorphous transition in the same temperature region which S-M call the T_g of polyethylene, *i.e.*, 145°K. We recognize that the procedure just proposed is not free from objections. For example, for any given composition in an ethylene-vinyl acetate copolymer, there is a wide distribution of sequence lengths about the average value; as contrasted with an exactly known sequence length in the nylons. With the above assumptions and limitations in mind, we can proceed with the analysis.

Willbourn proposed[38] that the T_γ relaxation at about 150°K would occur for any polymer or copolymer containing an in-chain sequence of four or more methylene units. This was based on data for a number of polymers including various polyethylenes. Schatzki later developed[45] a specific crankshaft model for the γ relaxation in polyethylene which also seemed to require a minimum of four methylene units. Wunderlich suggested[46] a model requiring $-(CH_2)-_3$ as a minimum and Boyer suggested a $-(CH_2)_2-$ model.[47] Redding, Faucher, and Whitman[44] concluded from their study of various ethylene copolymers that the T_γ relaxation is found experimentally for n = 3-5. We will get some further insight after studying the nylon data.

Schmieder and Wolf[23] demonstrated that all nylons exhibit a well-defined dynamic mechanical T_g in the region of 325°K and an amorphous phase γ relaxation near 150°K. We have already alluded to the amorphous copolymer data of Woodward *et al.*[31] Kawaguchi,[48] using nylons quenched from the melt and cooled down to low tempera-

---

(45) T. F. Schatzki, *Polym. Prepr.*, **6**, 646 (1965).

(46) B. Wunderlich, *J. Chem. Phys.*, **37**, 2431 (1962).

(47) R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).

(48) T. Kawaguchi, *J. Appl. Polym. Sci.*, **2**, 56 (1959).

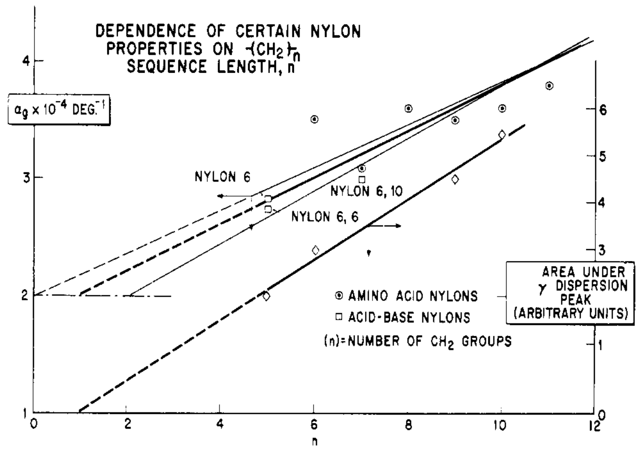

Figure 5. Area under the $T < T_g$ dynamic mechanical γ dispersion peak[48] and α_g for various nylons[52] as a function of CH_2 sequence length. It is suggested that free volume generated at the γ relaxation increases α_g.

ture, from 20°, which is below their T_g's, showed that the area under the γ peak increased linearly with n as n increased from 5 to 12. The area extrapolates to zero for $n = 1$ and is presumably finite for $n \leq 2$. Lawson *et al.*[49] have measured a well defined γ peak for $n = 3$. Papir[50] has measured a similar loss peak for $n = 2$.

We recognize that area under a tan δ *vs.* T dynamic loss curve is not necessarily an adequate measure of the molecular strength of the relaxation process.[39] Heijboer,[51] for example, recommends using the area under a G'' *vs.* $1/T$ plot after substracting background. G'' is the imaginary loss modulus and is equal to G' tan δ, where G' is the real modulus. We suggest that the good correlation found by Kawaguchi between area and n may result from the facts that, while the loss peak broadens, T_γ does not change much with n (thus eliminating a major $1/T$ effect) and that the modulus, G', at T_γ decreases regularly with n.

Champetier and Pied[52] reported thermal expansion values, α_l and α_g, for the lactam series n = 6–12. α_g was greater than 2×10^{-4} in all cases (even with crystallinity present) and increased generally with n but exhibited an even–odd effect. Figure 5 is a plot of area under the γ relaxation and α_g, both as a function of n. Included are α_g values for Nylons 6, 6,6, and 6,10 found in the literature.[53a] Three lines were drawn through the α_g data corresponding to α_g reaching a limiting value of 2×10^{-4} at n = 0, 1, and 2. An unambiguous choice is not possible.

Using a device employed by Illers[30] for extrapolating the strength of the T_g relaxation in nylons to $n = \infty$ we show in Figure 6 of the plot of α_g *vs.* $1/n$. The value of α_g at $1/n = 0$ is the Illers' value for amorphous polyethylene from Figure 2. The line was arbitrarily drawn to go through this point. α_g reaches the normal value of 2×10^{-4} at $n = 3$.

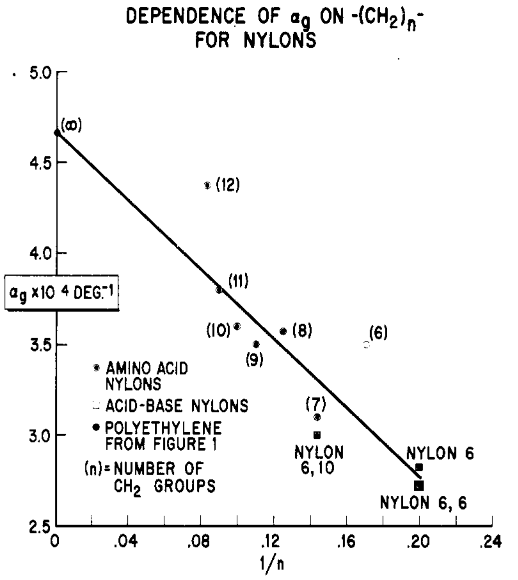

Figure 6. α_g *vs.* $1/n$ for various nylons. The line is forced through the point for amorphous polyethylene taken from Figure 2. α_g reaches a normal value of 2×10^{-4} deg^{-1} for $n \simeq 3$.

Recognizing that different sets of nylons of unknown crystallinity were used, one can still make a general correlation from Figure 5 that the difference, $\alpha_g - 2 \times 10^{-4}$, increases linearly with area under the dynamic loss curve. This is both a qualitative and a semiquantitive confirmation of our view that α_g in Figure 2 might increase regularly because of a T_γ relaxation.

Next we must attempt to explain the observed linear increase of α_g in Figure 2 with composition and also to justify the linear extrapolation employed by Illers. To do this, we have calculated the expected distributions of sequence lengths of N for ethylene–vinyl acetate copolymers. Since $r_1 = 1.07$ and $r_2 = 1.08$,[53b] we assume $r_1 = r_2 = 1$ for this system, and consider the copolymers to be random. We could not locate in the literature all of the needed expressions, but Alfrey[53c] derived them for us in terms of the mole fraction, f, of ethylene in the copolymer.

The number average, $\bar{N}_N$, the weight average, $\bar{N}_W$, sequence lengths of ethylene units in the copolymer are

$$\bar{N}_N = 1/(1 - f) \tag{9}$$

$$\bar{N}_W = (1 + f)/(1 - f) \tag{10}$$

The weight fraction, $W(N)$, of all ethylene units found in sequences of length N is given by:

$$W(N) = (1 - f)^2 N f^{N-1} \tag{11}$$

$$W(N \geq 1) = 1 \tag{12}$$

$$W(\geq N) = 1 - (1 - f)^2[1 + 2f + 3ft^2 + \\ \ldots.(N - 1)f^{N-2}] \quad (\text{for } N \geq 2) \tag{13}$$

$$W(N \geq 2) = 1 - (1 - f)^2 \tag{14}$$

Multiplying eq 11–14 by the weight fraction of ethylene corresponding to f gives the weight fraction of ethylene in the copolymer. Figure 7 is a plot of several of these quantities. Since $\alpha_g - 2.0 \times 10^{-4}$ deg^{-1} in Figure 2 increases linearly with weight fraction of ethylene in the copolymer, we are interested in the plots which increase linearly. The plot for $N \geq 1$ is exactly linear, as it must be. That for $\bar{N}_N$ starts out linearly but then starts to swing up sharply, as does the plot for $\bar{N}_W$. (It is recognized that eq 11 gives a well-known distribution of sequence lengths, not shown in Figure 7: for $N = 1$, $W(N)$ drops rapidly from a value of 1 for $f = 0$; for $N \geq 2$, $W(N)$ goes through a maximum which shifts to higher values of f as N increases; the

---

(49) Lawson, Sauer and Woodward, *J. Appl. Phys.*, **34**, 2492 (1963).

(50) Y. Papir, Ph.D. Thesis, Case Western Reserve Univ., Cleveland, Ohio (1971); see also *J. Macromol. Sci., Phys., Part B*, **6**, 761 (1972).

(51) J. Heijboer, "Mechanical Properties of Glassy Polymers Containing Saturated Rings," Vitgeverij Waltman, Delft, Holland (1972); see also K. H. Illers and H. Breuer, *J. Colloid Sci.*, **18**, 1 (1963).

(52) G. Champetier and J. P. Pied, *Makromol. Chem.*, **44**, 64 (1961).

(53) (a) R. M. Ogorkiewicz, Ed., "Engineering Properties of Plastics," Wiley-Interscience, New York, N. Y., 1970, p 177. (b) R. D. Burkhardt and N. L. Zutty, *J. Polym. Sci., Part A*, **1**, 1137 (1963). (c) T. Alfrey, The Dow Chemical Co., private communication.

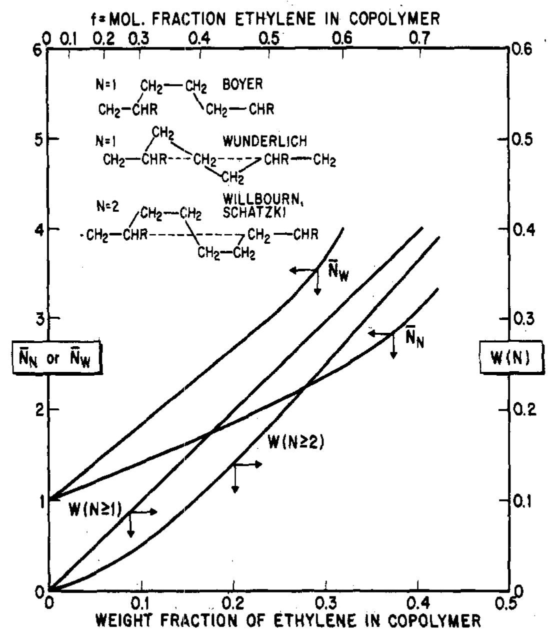

Figure 7. From top to bottom. Weight- and number-average sequence lengths, $\bar{N}_W$ and $\bar{N}_N$; and weight fraction of ethylene units in the copolymer having sequence lengths as indicated, all as a function of weight fraction of ethylene in an ethylene-vinyl acetate copolymer. The inset shows the several structural units which have been proposed as giving rise to the γ relaxation.

height of the maximum, $W(N)_{\max}$, decreases as N increases.) Some improvement in linearity is obtained by weighting the sequences in proportion to their length by any of several options but this exercise hardly seemed worth pursuing.

While it is not possible to make fine distinctions between the several molecular models for the γ process, it does appear that all ethylene sequence of $N \geq 1$ make a contribution. These results, especially in view of Kawaguchi,[48] suggest that the Schatzki-Willbourn -$(CH_2)_4$- crankshaft corresponding to $N \geq 2$ is not required but that the simpler -$(CH_3)_3$- of Wunderlich may suffice. This should not be construed as an argument against the existence of the crankshaft or against its possible role in the γ relaxation. It is recognized that crystallization sets in when $\bar{N}_N \geq 4$.[19] We suggest, but do not consider it a rigorous proof so much as a consistency test, that the results of Figure 7 along with the nylon data of Figure 5, lend strong justification to the linear extrapolation employed by Illers in Figure 2. We further conclude that the high value of $\alpha_g = 4.7 \times 10^{-4}$ for amorphous polyethylene is a consequence of the fact that the transition at 145°K is a $T < T_g$ relaxation involving ethylene sequences of $N \geq 1$.

Final Reconciliation of S-M and Illers' Thermal Expansion Results

Several conclusions can now be expressed with confidence; referring to Figure 4. (1) What S-M label as α_g is really $\alpha_{113°K}$, an expansion coefficient below $T < T_g$ and appropriate to the temperature selected. Its numerical correctness may be judged by comparing it with the Zakin *et al.*[24] value for an equimolar ethylene-propylene copolymer at the same temperature, *i.e.*, 1.8×10^{-4} deg^{-1}. This copolymer has a sharp T_g at 213°K. (2) What S-M label α_l is really an α_g enhanced over the normal value of 2.0×10^{-4} by the T_γ relaxation, and agreeing reasonably well (within 10%) of the Illers' value for α_g. (3) What S-M call $\alpha_{288°K} = 9.3 \times 10^{-4}$ agrees rather well with the Illers α_l value. Both values are actually high when compared with $\alpha = 6.60 \times 10^{-4}$ deg^{-1} for polyethylene at 150°.[26] Our extrapolated value, based on the S-M data, of $\alpha_{213°K} \equiv \alpha_l = 7.5\text{-}7.8 \times 10^{-4}$ deg^{-1} is probably a preferred value. With it, $T_g = 196°K$, $\alpha_l T_g = 0.15$, and, calling $\Delta\alpha = 7.65\text{-}2.01 \times 10^{-4}$, $\Delta\alpha T_g = 0.111$.

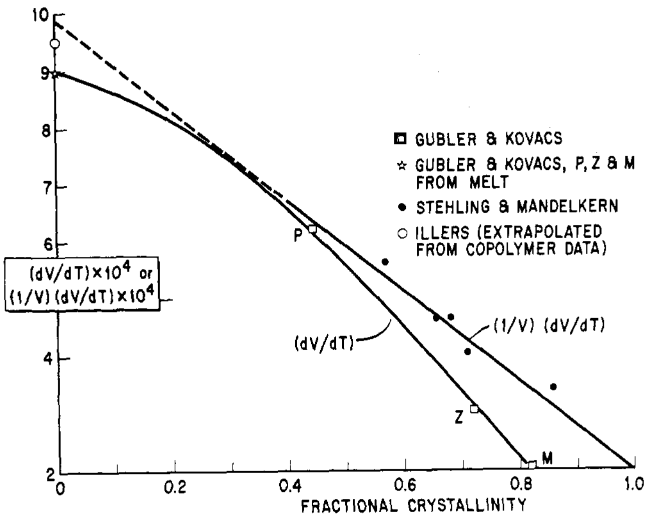

Figure 8. Thermal expansion quantities at 15° *vs.* fractional crystallinity for the three commercial polyethylenes of Gubler and Kovacs:[26] P = high pressure, Z = Ziegler, M = Marlex; and the linear polyethylene fractions plus one whole polymer of Stehling and Mandelkern.[2] Also indicated is the value calculated by Illers[41] for amorphous polyethylene.

Because of this concern about extrapolation procedures, we have estimated slopes of the V-T plots for three polyethylenes using the data of Gubler and Kovacs.[26] Accuracy is not high but the trends are clear. Figure 8 is a plot of the Gubler-Kovacs slopes at 15° as estimated by us, as well as the liquid state expansion extrapolated down to 15° from the melt. While the points for the three different polymers having the level of crystallinity indicated are on a straight line, the extrapolation to zero crystallinity must be curved. Also shown for comparison are values for $(1/V)(dV/dT)$ at 15° from Stehling and Mandelkern, including the linear extrapolation which they recommend.

Electron Spin Resonance Data

S-M in the final two paragraphs of their paper, comment on results by Rabold[54] who used an esr probe method to study transition phenomenon in a variety of polymers. S-M apparently confused the sharp drop in line width, $T_{\Delta w=50}$, with the glass transition region, even though the effective frequency at this temperature is about 10^7 Hz. Actually, as Rabold showed quite clearly in his Figure 16, T_g is some 30-75° below $T_{\Delta w=50}$ values. This difference is greater the lower is T_g, consistent with the trend for activation energies.[1] As a result of studying the Rabold paper we realized that he had measured $T_{\Delta w=50}$ values for several copolymers but did not know the corresponding T_g values. However, T_g could be readily estimated by reference to literature data. Secondly, in discussing this problem with Rabold[55] we found that he had an unpublished $T_{\Delta w=50}$ value for polybutadiene (Diene 55) whose T_g value can be estimated with reasonable confidence.[56]

Table I assembles all such $T_{\Delta w=50}$ data, together with estimated values of T_g. Figure 9 is a plot of T_g *vs.* $T_{\Delta w=50}$.

---

(54) G. P. Rabold, *J. Polym. Sci., A-1*, 7, 1203 (1969).

(55) G. P. Rabold, The Dow Chemical Co., private communication.

(56) G. Krause, G. W. Childers, and J. T. Gruver, *J. Appl. Polym. Sci.*, 11, 1581 (1967).

TABLE I
Correlation of T_g with Electron Spin Resonance Data[a]

Polymer	T_g (°K)	$T_{\Delta w=50}$[b]	Ref[c]
Polybutadiene (Diene 55)	179	249	*d*
Low-density polyethylene	196[e]	277	Illers[41]
High-density polyethylene	196[e]	278	Maurer[40] Illers[41]
High-density polyethylene	145[e]		S-M[2]
High-density polyethylene	240[f]		Natta *et al.*[25] Gubler and Kovacs[26]
Ethylene–propylene (50:50, wt)	217	289	*g*
Polypropylene	253	315	*h*
Styrene–Butadiene Copolymers			
0.42 wt fraction styrene	240	312	*i*
0.52 wt fraction styrene	253	325	*i*
0.57 wt fraction styrene	262	320	*i*
0.62 wt fraction styrene	272	337	*i*
Poly(vinyl chloride)	350	393	*j*
Polystyrene	373	403	*h*

[a] Electron spin resonance data by Rabold.[54, 55] [b] Temperature at which extreme separation is 50 G.[54, 55] [c] Reference for T_g. [d] Diene 55 has a nominal content of cis-35%, trans-55%, and 1,2-10% from which T_g was calculated using the method of ref 56. [e] Extrapolated to amorphous state. [f] Semicrystalline state. [g] Estimated from Figure 3 of Maurer.[40] [h] "Polymer Handbook."[59] [i] Calculated from formula by Wood.[60] [j] Average of three values in "Polymer Handbook."[59]

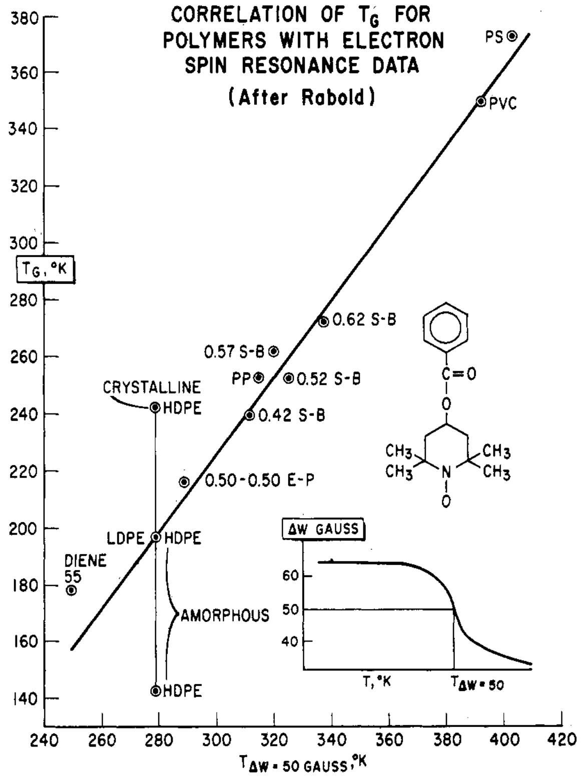

Figure 9. Correlation of T_g with temperature at which the esr line width reaches 50 G (see inset) for the free-radical probe molecule shown. The esr apparently "sees" T_γ faintly at about 243–263°K but lacks the resolving power to see T_g(U). This plot is a modification of the original one by Rabold.[54]

This is an extension of Rabold's Figure 16 greatly strengthened by six more data points including that for Diene 55 and the styrene–butadiene copolymers, all of which serve to bracket the $T_{\Delta w=50}$ value of polyethylene. We plot the three commonly held values of T_g for polyethylene. It is obvious that only the one near 195°K is compatible with all other data.

We have discussed Figure 9 with Rabold[55] and asked why the esr probe does not respond to all three amorphous transitions. He states that the sensitivity of the method is not sufficient to resolve T_g(U) because of the much higher frequency that prevails around 320°K where one might expect T_g(U) to be found by the esr probe. The apparent drop in line width at about 350°K seen in his Figure 5 for linear polyethylene is an artifact caused by a change in the temperature control system.[55]

Because of the relatively high frequency of the test at $T_{\Delta w=50}$, estimated by Rabold[55] at about 2 × 10^7 Hz, the T_γ peak would appear at a temperature considerably above that in Figure 1. Relaxation maps of log frequency $-1/T$ prepared by Schatzki[45] and by Pechhold[57] predict T_γ (at 2 × 10^7 Hz) of *228* and *210*°K, respectively. Now Rabold commented as follows (page 1215 of ref 54). "There is a second aspect of the temperature-dependent spectral changes which is of considerable interest. Inspection of the −30 (243°K) and −10° (263°K) spectra of Figure 2 shows that each is a superposition of two spectra, one corresponding to the probe in a restrictive environment and one corresoonding to the probe in a looser structural network. This is quite similar to what we showed earlier for BzONO phases in a latex. In the present case it is possible that the two environments reflect contributions from the probe in those regions of the polymer where crankshaft chain motion is occurring and from other regions where lower frequency chain motion is dominant."

It thus appears that Rabold did see evidence for T_γ in about the expected temperature region. Rabold believes[55] that his probe molecule is too large (mol wt 261 ≅ 20 methylene units) to tumble freely if the γ process involves a local mode type of notion with sequences of three to four methylene units.

Rabold did use a smaller probe (mol wt 155 ≅ 13 methylenes) but it had an anomalous behavior which he attributed to either crystallization or dimerization. Kusumoto *et al.*[58] used this smaller probe and found a $T_{\Delta w=50}$ at 243°K but did not comment on any other relaxations.

We conclude that Figure 9 has a simple and precise meaning. The γ process is not a glass transition whereas T_g(L) is real and exists in a semicrystalline polymer as indicated in Figure 1. The method cannot confirm or disprove the existence of T_g(U).

(57) W. Pechhold, *Kolloid-Z. Z. Polym.*, 228, 1 (1968).

(58) N. Kusumoto, H. Uchida, and M. Takayanagi, *Rep. Progr. Polym. Phys. Jap.*, **XIV**, 219 (1971).

A closely related conclusion follows from the work of DeVries and Williams[61] who measured free radical population as a function of temperature during the mechanical fracture of crystalline polymers. A plot of number of spins *vs.* T/T_g shows a sharp drop at $T/T_g = 1$ for nylon and polypropylene. Polyethylene behaves in similar fashion if T_g is chosen as 195°K but not for T_g of 148°K which these authors used as the handbook value.[59] In this case the esr signal arises from a free-radical-bearing chain end which finds itself in an amorphous environment frozen below and free above T_g(L). (It should be noted that whenever a polymer chain (probably a tie molecule) is ruptured, two dangling ends or cilia will result. These would presumably act like other cilia and participate in T_g(L).)

Other Arguments for T_g = 195 ± 10°K

In addition to the thermal expansion, dynamic mechanical loss and esr evidence for a T_g of 195 ± 10°K, there are some indirect lines of approach which should be mentioned.

We have presented elsewhere[62] in more detail the following reasoning. Goldstein has developed a theory[63] which concludes that every glass transition should have a $T < T_g$ glassy transition frequently called a β relaxation. Experimentally, most, but not all polymers exhibit such a T_β relaxation, as can be seen in the extensive tabulation of McCrum *et al.*[39] Moreover, Matsuoka and Ishida[64] have shown that

$$T_\beta = 0.75\,T_g \tag{15}$$

when both temperatures are in °K. If T_g for polyethylene is 145°K, as S-M assert, then there is no lower amorphous transition. However, if T_g is 195°K, and $T_\gamma \equiv T_\beta = 145$°K then eq 15 is followed exactly by amorphous polyethylene.[62]

Secondly, Miller[65] has made calculations, using melt viscosity data on normal alkanes, and extrapolated to infinite molecular weight. He estimates T_g of polyethylene to be 200°K.

Other Arguments for T_g = 145°K

S-M are certainly not alone in their conclusion that T_g of amorphous polyethylene is 145°K. We have already noted, and questioned, the conclusion of Beatty and Karasz[36] based on a glass-like ΔC_p at 145–150°K. Fischer and Kloos[66] found evidence for amorphous transitions in polyethylene by low-angle X-ray scattering (LAXS). They conclude that T_g is 143–153°K for linear polyethylene but 247°K for branched polyethylene. This is almost self-defeating in view of our Figure 1. Fortunately, Hara,[67] using a similar technique, finds breaks in his curves on linear polyethylene at 143 and 253°K. There is also a break at 283°K. We believe the Hara plot justifies drawing the curve so as to indicate a break around 200°K. As Fischer and Kloos point out, LAXS responds to differences in density as a function of temperature. Hence it should "see" the three amorphous transitions of Figure 1 which were deduced primarily from thermal expansion data.

There are several sets of examples in which the T_g of a homologous series of polymers or copolymers containing $(CH_2)_n$, sequences in the side chain or the main chain is extrapolated to $n = \infty$.[68-70] The results range widely from approximately 108 to 180°K. With the exception of the DiMarzio-Gibbs[68] copolymer theory (T_g = 180°K), these extrapolations are on an empirical basis. This is unlike the Gordon-Taylor (G-T) copolymer extrapolation[21] whose results we have accepted at least for ethylene-propylene and ethylene-vinyl acetate copolymer systems. The G-T copolymer equation is amenable to checking over the complete composition range from homopolymer A to homopolymer B. With homologous series, the highest member we have found is $(CH_2)_{12}$. On a weight per cent of methylene, the highest value was 78%.[70]

We plan to discuss this extrapolation problem at some future time. The essence of our observations can be stated briefly: one is usually going from a highly polar situation (polyamide, polyester, polyether) to a completely nonpolar amorphous polyethylene. The general fallacy of this is best seen with nylon data. Plotting T_g *vs.* $1/n$ leads to the conclusion that the T_g of polyethylene ($n = \infty$) is 290°K. Even with Gordon-Taylor copolymer results, we have relied most heavily on the completely nonpolar ethlene–propylene data of Maurer[40] and the relatively mild ethylene–vinyl acetate situation of Illers.[41] As Illers showed so clearly,[41] the T_g of ehtylene–acrylic acid systems with the certain hydrogen bonding, is rather deviant so far as Gordon–Taylor copolymer theory is concerned.

The Relative Strengths of the T_g and T_γ (Amorphous) Transitions in Linear Polyethylene

As S-M observed[2] the strength of the 145°K relaxation, as measured by the difference in coefficients of expansion across it, namely, $\alpha_{168°\mathrm{K}} - \alpha_{113°\mathrm{K}} = 3.3 \times 10^{-4}$, is quite high for a secondary or $T < T_g$ relaxation. This is one of the reasons why they assigned 145°K as T_g. It is still less than the 7.6×10^{-4} we would calculate from eq 2 if T_g is 145°K. We commented earlier that α_g for the pure hydrocarbon, poly(octene-1), is 6.9×10^{-4}. Accepting the normal $\alpha(T < T_g)$ as 2.00×10^{-4} deg^{-1}, $\Delta\alpha(T < T_g)$ would be 4.9×10^{-4} deg^{-1}. We have shown elsewhere[18] that whereas eq 1 holds for diene polymers and copolymers, eq 2 fails if an appreciable amount of *trans*-polybutadiene is present. In fact, for pure trans, $\Delta\alpha T_g$ is 0.05. Calculating an α_l of 8.2×10^{-4} and subtracting 2.00×10^{-4} gives a $\Delta\alpha$ at $T < T_g$ of 6.2×10^{-4} deg^{-1}. In this case a prominent pair of $T < T_g$ mechanical relaxations has been found at 85 and 125°K by Morgan, Nielsen, and Buchdahl.[71] Thus, the $\Delta\alpha$ at $T < T_g$ of 3.3×10^{-4} observed by S-M is large, but not large enough, when compared with two other hydrocarbon systems, to classify as a $\Delta\alpha$ at T_g.

Aside from these numerical comparisons which strengthen our view that T_γ = 145°K, we might comment on the actual high strength of the T_γ relaxation in polyethylene. As suggested in our copolymer analyses associated with Figure 7, all amorphous phase $(CH_2)_n$ sequences of $n \geq 3$ appear to contribute to the T_γ relaxation. This may be a result of the unsubstituted nature of polyethylene which permits considerable freedom of motion about the chain axis. Morgan *et al.*[71] postulate a

---

(59) W. A. Lee and G. J. Knight, in "Polymer Handbook," J. Brandrup and E. H. Immergut, Ed., Interscience, New York, N. Y., 1966.

(60) L. A. Wood, *J. Poly. Sci.*, **28**, 319 (1958).

(61) K. I. DeVries and M. L. Williams, *Intern. J. Nondestructive Testing*, **2**, 363 (1971). For original data, see D. K. Bachman and K. I. DeVries, *J. Polym. Sci., Part A-1*, **7**, 2134 (1969).

(62) R. F. Boyer, *Polym. Prepr.*, **13**, 2, 1124 (1972).

(63) M. Goldstein, *J. Chem. Phys.*, **51**, 3728 (1969).

(64) S. Matsuoka and Y. Ishida, *J. Polym. Sci., Part C*, **14**, 247 (1966).

(65) A. A. Miller, *J. Poly. Sci., Part A-2*, **6**, 249 (1968).

(66) E. W. Fischer and F. Kloos, *J. Polym. Sci., Part B*, **8**, 685 (1970).

(67) T. Hara, *Rep. Progr. Polym. Phys. Jap.*, **14**, 323 (1971).

(68) E. A. DiMarzio and J. H. Gibbs, *J. Polym. Sci.*, **40**, 121 (1959).

(69) B. M. Grievson, *Polymer*, **1**, 499 (1960).

(70) J. A. Faucher and J. V. Koleske, *Polymer*, **9**, 44 (1968).

(71) R. J. Morgan, L. E. Nielsen, and R. Buchdahl, *J. Appl. Phys.*, **42**, 4653 (1971).

crankshaft as responsible for the two extremely strong $T < T_g$ relaxation in trans poly(butadiene-1,4). Presumably the Schatzky crankshaft[45] can operate in polyethylene and might also be very strong.

But we must also explain why T_g(L) and T_g(U) are relatively weak. First, we would note that since the glass transition is divided into two parts (except for amorphous polyethylene), then either of the parts will seem small (compare Figure 1). But in a more general sense, a $T < T_g$ relaxation robs strength from the T_g transition. This shows up quite clearly in the diene polymer thermal expansion study.[62] One can also see it by comparing dynamic mechanical loss peaks in the alkyl methacrylate[15] and alkyl vinyl ether polymer series[16] in conjunction with the related thermal expansion data.

For the nylon family, Illers showed,[30] as stated earlier, that the strength of the glass transition, which we designate S_g, varies with n as

$$S_g = A + Bn^{-1} \tag{16}$$

where A and B are constants. The Kawaguchi S_g data[48] do not appear to be in complete agreement with the Iller's T_g results. The Kawaguchi strength data for the γ relaxation, S_γ, changes as

$$S_\gamma = C(n - 1) \tag{17}$$

where C is a constant. Actually, there must be some limiting value for S_γ as n increases but eq 17 is valid up to $n = 12$. The ratio S_g/S_γ is given by

$$S_g/S_\gamma = A/C(n - 1) + B/C(n^2 - n) \tag{18}$$

Equation 18 quantifies but does not prove that S_g becomes relatively weaker with n because of the increase in S_γ. For this we rely on a free volume argument. Cooling from the liquid state, the fractional free volume at T_g is 0.11 relative to extrapolated liquid line at 0°K.[10] This free volume at T_g will be less if there are prominent subgroup transitions. Hence the apparent strength of T_g as measured by $\Delta\alpha$ at T_g will be reduced in direct numerical magnitude by the strength(s) of one or more $\Delta\alpha$'s at $T < T_g$. This can be seen numerically by considering the data of Simha and his collaborators.[15-17] Alternately one can say that all motions which occur below T_g are still happening at T_g but are not causing mechanical loss at T_g. Only the new motions setting in at T_g at the frequency of the test method contribute to the T_g loss peak.

Summary and Conclusions

We collect in Table II the various thermal expansion quantities cited throughout this paper. As one compares the S-M and the Illers' values, in conjunction with the earlier criteria, eq 1-3, it appears reasonable to conclude four things. (1) The S-M thermal expansion data extrapolated to the amorphous state seem correct for the stated temperatures but are mislabeled so far as the glass transition values are concerned. (2) Thermal expansion data for the amorphous state appears to provide a powerful tool for understanding multiple transition phenomena in crystalline polymers. (3) The amorphous state $T_g = T_g$(L) of linear polyethylene is 195 ± 10°K in agreement with Illers[41] and Maurer[40] as well as earlier workers whose results have been collected.[1,2] (4) Semicrystalline polyethylene shows a double glass transition, T_g(L) and T_g(U).

We further conclude that the assumption of a double glass transition in semicrystalline polyethylene (χ = 0.5–0.8 and probably from 0.2 to 0.85) as shown in Figure 1 provides the most plausible means of reconciling the current literature controversy about the T_g of linear polyethylene.

We consider it equally plausible to assume that the same remarks hold for low density, branched polyethylene with moderate amounts of branching. We base this on multiple breaks in length–temperature plot by Dannis;[22] on the T_g(U) measured by Natta *et al.*[25] and Gubler and Kovacs;[26] on the Illers[41] copolymer and thermal expansion data previously discussed in detail and on the time effects noted by Chang.[27]

Polymethylene prepared from diazomethane presents conflicting results. Dannis,[22] using an uncharacterized specimen, finds a sharp break in length–temperature at 155°K but nothing at higher temperatures. Magill, Pollack, and Wyman,[72] using a well-characterized specimen of 40–50% crystallinity in the orthorhombic form, shows a definite break in a length–temperature plot at 247°K but nothing was seen down to liquid nitrogen temperature. These different behaviors probably result from the influence of different morphologies on the several amorphous states of polyethylene.

We have shown here, for the first time anywhere to our knowledge, an explicit connection between the glassy state coefficient of expansion, α_g, and the magnitude of the in-chain mechanical loss peak at T_γ for a family of nylons. By implication, the same $\alpha_g - \gamma$ relaxation relation holds for ethylene–vinyl acetate copolymers and for amorphous polyethylene. In a parallel, contemporaneous study[18] we suggest that α_g of butadiene polymers and copolymers is similarly influenced by in-chain $T < T_g$ relaxations of the crankshaft type. These three correlations of in-chain relaxations and thermal expansion complement the extensive study of Simha and his collaborators[15-17] about the role of sidechain $T < T_g$ relaxations in increasing α_g.

The general statement that $\alpha_g > 2 \times 10^{-4}$ deg^{-1} whenever a prominent $T < T_g$ mechanical relaxation is present is obviously an important advance in understanding multiple relaxation phenomena.

Our conclusion that a T_γ relaxation occurs in ethylene copolymers for $n \geq 3$ in -(CH$_2$)$_n$- extends and confirms the earlier observation of Reding *et al.*[44] than n should be at least 3–5 as do corresponding data for nylon[48-50] and for a special series of olefin polymers.[73]

We have extended the electron spin resonance probe study of Rabold[54] to provide an even more convincing correlation between T_g and the temperature at which the line width drops to 50 G. This plot (Figure 9) clearly places the T_g of polyethylene at T_g(L). We offer a tentative explanation as to why T_γ and T_g(U) of Figure 1 are not clearly seen.

We have discussed other evidence for our conclusion that T_g = 195 ± 10°K, as well as evidence favoring the S-M conclusion, T_g = 145°K.

We comment on the relative strengths of the three amorphous transitions in PE in terms of molecular motions and free volume theory.

Finally, reference was made to another contemporaneous study[6] in which is collected literature evidence suggesting that a double glass transition occurs in many crystalline hydrocarbon polymers, notably polypropylene, poly(butene-1), poly(pentene-1), poly(4-methylpentene-1), *Hevea* rubber, gutta-percha, and polystyrene. This greatly strengthens the conclusion first reached on polyethylene as shown in Figure 1.

Our total study on the three amorphous transitions in polyethylene thus involve not only the present manu-

---

(72) J. H. Magil, S. S. Pollack, and D. P. Wymann, *J. Polym. Sci., Part A-2*, **3**, 3781 (1965).

(73) J. R. Martin and J. K. Gillham, *J. Appl. Poly. Sci.*, **16**, 2091 (1972).

TABLE II
Summary and Comparison of Thermal Expansion Properties of Amorphous Polyethylene[a]

	Stehling and Mandelkern[2]	This Report S-M Values	 Illers' Values	Av[b]	Range[b]
$\alpha_g \times 10^{-4}$ deg^{-1}	2.01	5.31	4.70[c]		
$\alpha_l \times 10^{-4}$ deg^{-1}	5.31	7.5–7.8[g]	8.9	$0.164/T_g$	
$\Delta\alpha \times 10^{-4}$ deg^{-1}	3.30	2.19	4.2	$0.113/T_g$	
T_g °K	145	193	196		
$\alpha_l T_g$	0.076	0.148	0.174	0.164	0.122–0.205
$\Delta\alpha T_g$	0.047	0.042	0.082	0.113	0.081–0.14
$\Delta\alpha' \times 10^{-4}$ deg^{-1}		5.64[d]	6.9[d]		
$\Delta\alpha' T_g$		0.109	0.135	0.113	0.081–0.14
T_g/T_M	0.37	0.48	0.48[e]	0.680[f]	0.50–0.89[f]

[a] The S-M samples are mostly fractions of linear polyethylene whereas the Illers copolymers of ethylene-vinyl acetate are made by the high-pressure process. [b] Simha-Boyer.[10] [c] Defined as value just below T_g but above a secondary γ process. [d] Defined after the manner of Simha and Boyer[10] who recommended going below a $T < T_g$ loss process to obtain the correct $\Delta\alpha$ to use in calculating $\Delta\alpha T_g$. [e] T_M assumed as 410°K. [f] Average and range for 20 hydrocarbon polymers (aliphatic and aromatic) reported by Lee and Knight (W. A. Lee and G. J. Knight, *Polym. J.*, **2**, 73 (1970)) 85% of all polymers are in the range of 0.5–0.8 with a maximum number around 0.66. The extremes for all polymers are about 0.24 and 0.97 (see Lee and Knight in footnote *f*). [g] From dashed line in Figure 4.

script, which coordinates all points of view, but one each on dynamic mechanical loss,[62] specific heats and hole theory,[35] and double glass transitions in semicrystalline polymers[6] and four on thermal expansion.[14,18,19,74] The last of these elaborates and extends some of the ideas contained herein. It also touches briefly on the philosophy behind the lengthy controversy concerning the glass temperature of polyethylene.

Since writing the above, we became aware of a study by Lowell and McCrum[75] showing a close parallel between the γ process and the diffusion of normal butane in polyethylene. This analysis argues strongly that the γ process is very similar to the Schatzki[45] crankshaft and involves the place-exchange motion of at most four carbon atoms in the amorphous phase of polyethylene.

Acknowledgments. This material was presented at The Midland (Michigan) Macromolecular Institute on June 29; at the Chemistry Department of The Lomonossov Moscow State University of July 12; and at the Leningrad Institute for Macromolecular Compounds on July 17, 1972. It benefited from lengthy discussion comments in all three cases. Dr. K.-H. Illers supplied unpublished data and a manuscript in press. He also commented in detail on this and on an earlier version and furnished additional references. The assistance of Dr. Alfrey in deriving and interpreting eq 9–14 and of Dr. Rabold for unpublished data and interpretation on esr are appreciated. Various changes have been made because of comments by the reviewers. T. Alfrey and J. K. Rieke, Dow Chemical Co., have read the manuscript critically.

Appendix

List of Symbols

A, B, C = constants
α = coefficient of cubical expansion, $(1/V)\,(\mathrm{d}V/\mathrm{d}T)_\mathrm{p}$
α_l = value of α immediately above T_g
α_g = value of α immediately below T_g
$\Delta\alpha = \alpha_l - \alpha_g$
β = temperature coefficient of specific volume, $\mathrm{d}V/\mathrm{d}T = \alpha V_\mathrm{sp}$
β_l = value of β immediately above T_g
β_g = value of β immediately below T_g
$\Delta\beta = \beta_l - \beta_g$
β relaxation = for polyethylene, a relaxation at 240°K = our T_g (U)
C_p = specific heat
ΔC_p = change in specific heat at a transition
χ = fractional crystallinity
δ = dynamic mechanical loss angle
f = mole fraction of ethylene in copolymer
G' = real part of dynamic mechanical loss modulus
G'' = imaginary part of dynamic mechanical loss modulus $= G' \tan\delta$
γ = common designation for 150°K dynamic mechanical relaxation process in polyethylene, ethylene copolymers, and nylons
κ = coefficient of compressibility $(1/V)(\mathrm{d}V/\mathrm{d}P)_T$
n = number of methylene units in a sequence $(CH_2)_n$ (eq 8)
N = number of ethylene units in a sequence $-(CH_2CH_2)_N-$ (eq 7)
$\bar{N}_\mathrm{N}$ = number-average value of N in ethylene copolymer (eq 9)
$\bar{N}_\mathrm{W}$ = weight-average value of N in ethylene copolymer (eq 10)
P = pressure
r_1, r_2 = copolymer reactivity ratios
S_g = strength of glass relaxation (eq 16)
S_γ = strength of γ relaxation (eq 17)
S-M = Stehling and Mandelkern[2]
tan δ = tan of mechanical loss angle and one measure of strength of a relaxation at a specific temperature.
T_g = glass transition temperature in amorphous polymers and copolymers
T_g(L) = lower glass transition temperature in semicrystalline polymers (Figure 1)
T_g(U) = upper glass transition temperature in semscrystalline polymers (Figure 1)
$T_{\Delta W = 50}$ = temperature at which line of esr signal has a width of 50 G (Figure 9)
V = specific volume cm^3 g^{-1}
V_g = specific volume at T_g
$W(N)$ = weight fraction of ethylene in sequences of length N for an ethylene-vinyl acetate copolymer of $r_1 = r_2 = 1$ (eq 11)
$W(N \geq 2, 3, 4, \ldots, N)$ = same for sequence lengths greater than indicated number (eq 14)

---

(74) R. F. Boyer, Swinburne Award Lecture, Plastics & Polymers (London), Feb, 1973.

(75) P. N. Lowell and N. G. McCrum, *J. Polym. Sci., Part B*, **9**, 477 (1971).