Although the absolute values of f are very sensitive to the accuracy of the glassy data, the relative order shown here should remain valid. Figures 6 and 7 also indicate the desirability of information on systems in the range $T_g < 300°K$ and $> 450°K$.

III. Conclusions

The results on the diverse systems examined extend and strengthen previous conclusions. In the liquid state, the quantitative performance of the theory appears now sufficiently defined. Practically useful estimates of liquid densities can be obtained from a minimum of experimental information. The characteristic scaling parameters, in this work only V^* and T^*, which are determined from experiment, can provide more informative comparisons between different systems than the macroscopic quantities themselves. Moreover, they are a guide for the selection of additional structures for investigation. Here the pressure variable is important and future publications are to extend previous work[3,22] in this direction.

The extension into the glassy region by a combination of experiment and theory enables us to characterize different glasses in terms of the structural parameter y and its temperature derivative, or the frozen fraction f. As is illustrated by means of the methacrylate series, these quantities sensitively monitor structural differences. As has been pointed out earlier, these results have a bearing on the phenomenological treatment of the transition process in terms of frozen ordering parameters. Here again pressure studies are important.[6] Densities can be estimated from the correlations presented, once V^*, T^*, and T_g are known. Considerable fluctuations in the numerical values of f produce much smaller variations in specific volume, for example, 20 *vs.* 0.1%. Of course, the converse places a considerable strain on experimental accuracy.

While our objects of investigation have been organic polymer glasses, it will certainly be interesting to explore these quite general ideas for other types of glasses as well.

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Thermal Expansion and Differential Scanning Calorimetry Phenomena in the γ-Relaxation Region ($\approx$ 150°K) of Nylon 6,6, Nylon 11, and Ethylene-*co*-(Vinyl acetate)

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ABSTRACT: Linear thermal expansion coefficients, α', have been determined in the temperature range from liquid N_2 to T_g for Nylon 6,6 Nylon 11, and ethylene-*co*-(28 wt % vinyl acetate). α' shows a two- or possibly three-stage discontinuity well above experimental error for the two nylons but a less drastic increase for the copolymer. These events appear to be associated with the well-known mechanical γ relaxation at ~150°K for these three polymer systems. These increases in α' are much greater than for polystyrene which lacks a strong γ relaxation in an equal temperature span below its T_g. Increases in α ($= 3\alpha'$) well below T_g, which we associate with in-chain motion of $(-CH_2-)_n$ moieties (with $n \geq$ 3-5), are considered responsible for the fact that literature values of α_g just below T_g for these three polymers are higher than the normal α_g of 2×10^{-4} deg^{-1} reported for many polymers such as polystyrene. DSC scans on Nylon 6,6 and the copolymer show no unusual features in the γ region.

One of us recently noted[2a] that values of the glassy state coefficient of cubical expansion, α_g (measured just below the glass temperature, T_g), were considerably above the normal value of about 2×10^{-4} deg^{-1} for aliphatic nylons and ethylene–vinyl acetate (E-VAC) random copolymers. We proposed that these high values of α_g were associated with the $T < T_g$ or γ relaxation present in these polymers and copolymers and generally ascribed to motion of three to five in-chain methylene groups.[2b,3] We postulated the existence of discontinuities in thermal expansion at T_γ from this in-chain motion, in analogy with discontinuities in α found by Simha and his colleagues for side-chain motion in the alkyl methacrylate[4,5] and alkyl vinyl ether[6,7] families of polymers.

Since this postulate was crucial in our attempt[2a] to understand the glass transition and thermal expansion behavior of polyethylene, some experimental verification seemed desirable. The linear variable differential transformer technique, LVDT, used extensively by Simha and his collaborators[4-8] is ideally suited for the temperature range of most interest, namely, from liquid nitrogen to the glass temperature. It is also used down to liquid helium temperatures. Our materials were also examined in the latter range but these results will be reported elsewhere as part of a master's thesis by one of us.[9]

The aliphatic nylons and E-VAC copolymers can be written generically as containing the moiety, $-R-(CH_2)_n-R-$, with appropriate values of R. We[2a] assumed them to be ideal model compounds for studying the glass transition phenomena in polyethylene for two reasons. (1) They have relatively unambiguous glass transitions which decrease with n, in addition to a γ relaxation around 150°K whose temperature is approximately independent of n, al-

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[1] (a) Department of Macromolecular Science; (b) The Dow Chemical Co.

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Table I
Summary of Sample Histories

Sample No.	Material	Molding Conditions	Cooling in Dilatometer
1A	E-27.7VAC	30° above T_m, and quenched to room temperature	Normal slow cooling
1B	E-27.7VAC	30° above T_m, and quenched to room temperature	Quenched to 78°K
2	Nylon 6,6	30° above T_m, and quenched to room temperature[a]	Normal slow cooling
3A	Nylon 11	30° above T_g, and quenched to room temperature[b]	Normal slow cooling
3B	Nylon 11	30° above T_m, and quenched to room temperature[c]	Normal slow cooling

[a] This sample showed a typical crystalline nylon X-ray scan with sharp peaks at $2\theta = 21.8$ and $2\theta = 24.5°$. [b] This sample showed a single X-ray peak at $2\theta = 22.5°$ which apparently arises from a pseudohexagonal or smectic structure of the type discussed by Keller.[10] X-ray crystallinity was approximated as being in the range of 32-55%. [c] This sample showed X-ray diffraction peaks at $2\theta = 20.2$ and $2\theta = 24.5°$. [d] The different values of α' for samples 3A and 3B are believed consistent with differences in the X-ray patterns and not a result of some artifact such as anisotropy of the molding.

though breadth and area under the T_γ loss peaks increase with n.[2a] (2) Their properties should approach those of polyethylene as $n \rightarrow \infty$.

Materials Investigated[10]

The three polymers employed are as follows. (1) Elvax 260 is a commercial ethylene-vinyl acetate copolymer made by E. I. duPont de Nemours with a melt index in the range of 5-7 and a nominal vinyl acetate content of 27-29%. This material was in pellet form when received. The actual sample had a vinyl acetate content of 27.7% by infrared analysis. Crystallinity, as judged by an X-ray diffraction scan, was considered to be about 13%. (2) The Nylon 6,6 sample was a commercial polymer which was dried for 3 weeks in a vacuum oven at 75°. This material was also received in pellet form. The sample had an X-ray crystallinity of 38%. (3) The sample of Nylon 11 was obtained in the form of bars 15 × 5 × 0.3 cm which were previously compression molded from fibers. The sample was dried as with Nylon 6,6. It had an X-ray crystallinity of 32-55%, the uncertainty being caused by an overlap of the amorphous and crystalline peaks.

Experimental Methods

Sheets of all the samples were compression molded and samples were cut having the approximate dimensions of 1.5 × 0.5 × 0.01 in. The E-VAC and Nylon 6,6 were molded at 30° above their respective melting points. The Nylon 11 was molded in one case at 30° above its T_g and in a second case at 30° above T_m. The molded sheets were all quenched to room temperature.

The cut specimens were all treated in the following manner. The sample material is mounted in the sample grips with the use of a special jig which assures proper alignment. After the samples are clamped into the grips, the assembly is examined on an optical comparator to check sample alignment and length (±0.001 in.). When the sample has been properly mounted, it is connected to the LVDT by the support tubes and the whole assembly is inserted into the inner Dewar of the dilatometer. The system is then closed and evacuated for at least 6 hr. Helium gas is introduced into the sample chamber and its jacket prior to cooling. The system is cooled from room temperature to $\approx$85°K by filling the outer Dewar with liquid N_2. This is referred to as the normal slow cooling method. In one instance, an E-VAC specimen was quenched by direct contact with liquid N_2.

The system is held at that temperature for 2-3 hr to allow complete equilibrium of the supporting tubes. The system is then heated at a rate of 120 ± 2 sec per °K. The amplified LVDT signal is then recorded as a function of temperature. The length of the sample as a function of temperature is obtained after correction for the expansion of the apparatus. The linear thermal expansion coefficient, $\alpha' = 1/L(\partial L/\partial T)$, is then calculated by the moving arc method.[8] The error in α' is $\pm 1 \times 10^{-6}$ deg^{-1} or about the size of the dots in Figure 2. In several instances we quote a coefficient of cubical expansion, $\alpha = 3\alpha'$, which involves the implicit assumption that the samples are isotropic. We believe the specimens are relatively free from anisotropy.

Table I summarizes the different samples with their thermal histories plus comments about the X-ray scans on the two nylons.

Experimental Results

Figure 1 shows the linear coefficient of thermal expansion, α', for Elvax 260. Reding *et al.*[3] report a 1-Hz mechanical loss peak for this nominal composition at about 140°K as indicated by the vertical arrow. They ascribe this γ loss peak to sequences of 3-5 CH_2 units in the copolymer. There is no discontinuity in α' between 90°K and the start of T_g at about 200°K. Nevertheless, α' essentially doubles in this temperature interval which is a far greater increase than one would anticipate in the absence of a transition. According to Zakin *et al.*[8] α' for atactic polystyrene increases from 0.57 to 0.67 × 10^{-4} deg^{-1} in this same temperature interval, even though polystyrene has a mild mechanical relaxation peak at about 150°K,[11,12] Hammer[13] has observed (see his Figure 2) that an ethylene-*co*-(40 wt % vinyl acetate) sample exhibits an extremely broad dynamic mechanical loss peak extending from about 230°K to well below 90°K. Presumably the large variety of structures (sequence lengths of methylene units) present in such a mostly amorphous random copolymer gives rise to an extremely broad γ relaxation in contrast with the sharp discontinuity in thermal expansion and the relatively narrow dynamic loss peak reported[14] for linear polyethylene fractions with crystallinities in excess of 50%.

However, the important point for the thesis we have advanced[2a] is that α_g (the coefficient of cubical expansion just below T_g) is $3 \times 0.925 \times 10^{-4}$ or 2.78×10^{-4} deg^{-1}. Correction for the slight amount of crystallinity will raise this to about 3×10^{-4} deg^{-1}. Thermal expansion data by Illers (reported in Figure 2 of ref 2a) indicates an extrapolated α_g of 3.9×10^{-4} deg^{-1} for this composition. In either case, α_g is well above the normal value of 2×10^{-4} deg^{-1} found for poly(vinyl acetate) (Figure 2 of ref 2a) and, more generally, for polymers without prominent subgroup transitions.[15] Moreover, the value of α_g below

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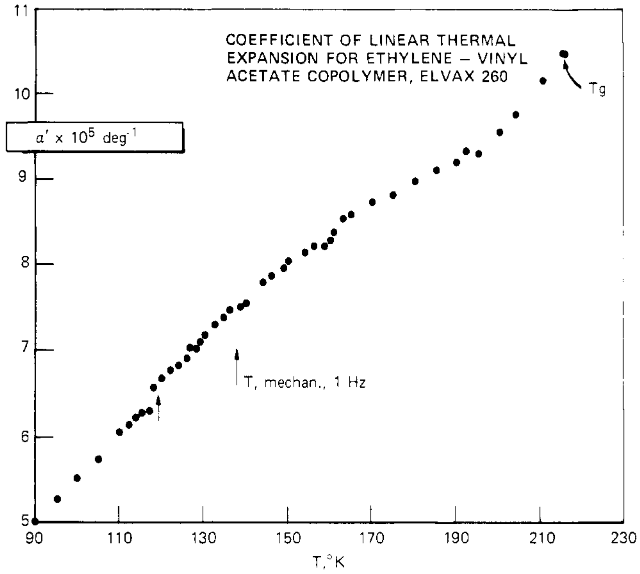

Figure 1. Coefficient of linear thermal expansion for sample 1A. The vertical arrow indicates the estimated location of a dynamical mechanical loss peak on a sample of this composition.

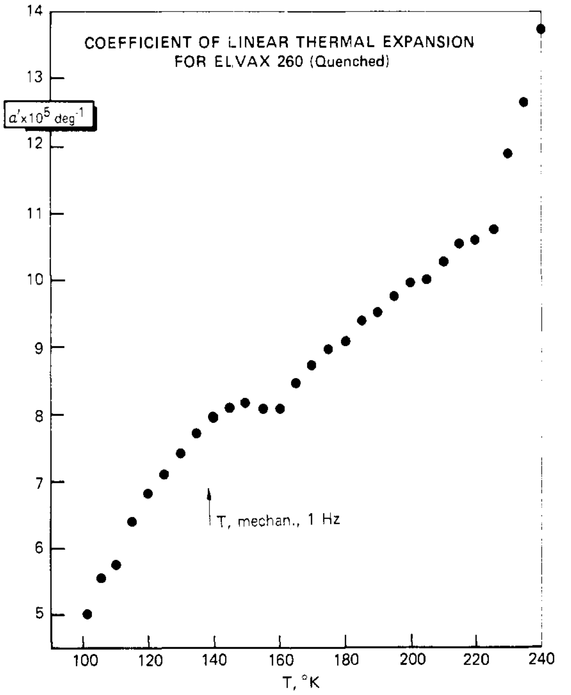

Figure 2. Coefficient of linear thermal expansion for sample 1B. The vertical arrow indicates the estimated location of a dynamic mechanical peak.

the γ region (at 90°K) is 1.5×10^{-4} deg^{-1}, a reasonable value. Amorphous PE has an α of 2×10^{-4} deg^{-1} at 113°K.[14]

Figure 2 is a plot of α' for this same copolymer except on a sample quenched from room temperature to 78°K and then heated. The α' of this run is almost identical with the previous one except for a plateau around 150 to 160°K.

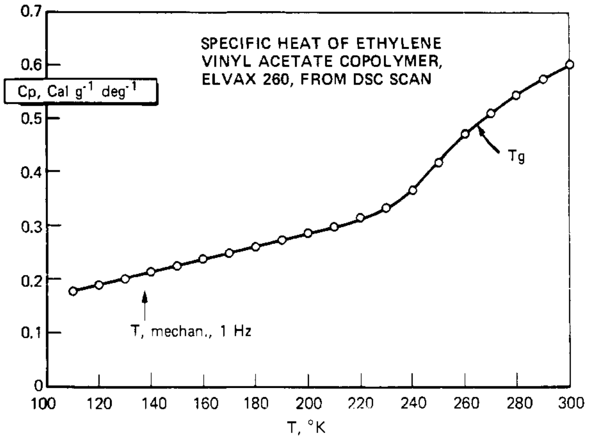

Figure 3. Specific heat calculated from DSC scan on pellets of an ethylene–27.7% vinyl acetate copolymer.'

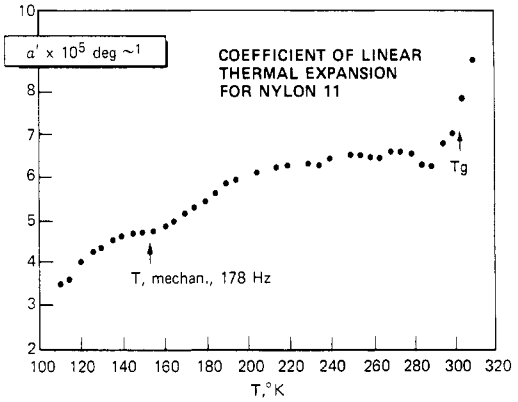

Figure 4. Linear thermal expansion, α', of Nylon 11, sample 3A. There is some evidence for a two-step γ process with mid-points at about 120°K and 180°K. The apparent scatter or instability in α' from 200°K to 260°K may result from H_2O-amide linkage interaction. The vertical arrow shows the location of a dynamic mechanical loss peak.

Figure 3 is a specific heat-temperature scan on as-received pellets of this same copolymer. Values of C_p were calculated by Gray[16] from a DSC scan made on a Perkin-Elmer Model DSC-2. Consistent with the thermal expansion data, there is no evidence of a discontinuity at a secondary transition. The start of the glass transition is higher than in Figure 1, as expected with a scanning rate of about 40°/min, compared with an "equilibrium" thermal expansion run.

Figure 4 is the plot of linear thermal expansion for Nylon 11, sample 3A, showing the start of the glass transition at about 300°K. Champetier and Pied[17] report the dilatometric T_g for Nylon 11 (of unstated crystallinity) as 319°K. There is some evidence in Figure 4 for a transition around 180°K, which is below the well-known mechanical loss β peak arising from the interaction of water molecules with amide linkages.[18] The mechanical γ peak reported by Kawaguchi[19] is 153°K at 178 Hz. The step at 180°K could be part of the γ relaxation. The sharp drop in α' between 100 and 140°K could well be the equilibrium γ relaxation although the value of $3 \times 0.3 = 0.9 \times 10^{-4}$ deg^{-1} at 100°K seems abnormally low for the glassy state below a secondary relaxation. However, poly(methyl methacrylate) shows an α of about this same magnitude at 100°K.[5] The value of $\alpha_g = 3 \times 6.5 \times 10^{-5} = 1.95 \times 10^{-4}$ deg^{-1} is relatively low, although correction for crystallinity would increase this to the expected level.

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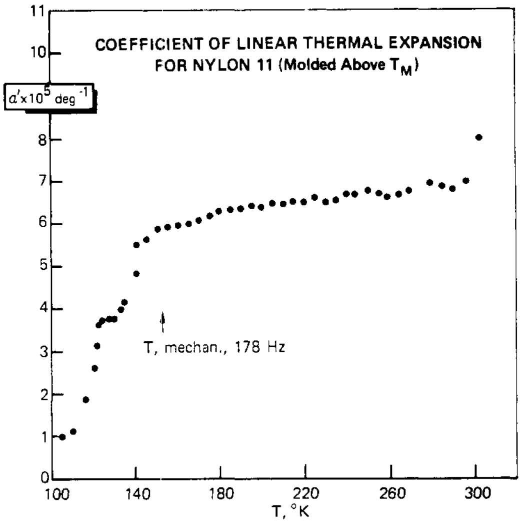

Figure 5. Linear thermal expansion, α' for Nylon 11, sample 3B, showing the well-resolved two-step γ relaxation. The vertical arrow shows the location of a dynamic mechanical loss peak.

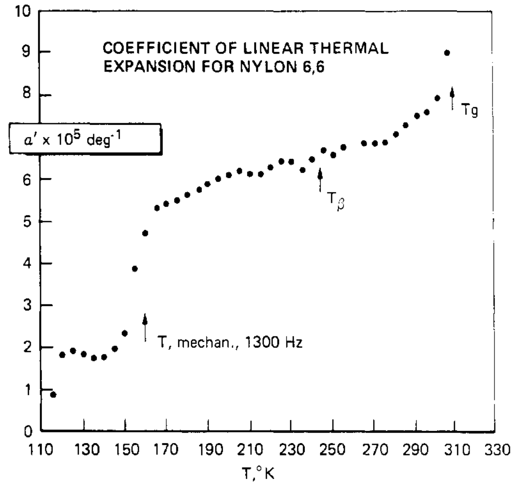

Figure 6. Linear thermal expansion, α' for Nylon 6,6, sample 2 with a double step at about 120 and 160°K. The vertical arrow indicates a dynamic mechanical loss peak. T_β is probably the H_2O-amide linkage interaction.

Figure 5 is a plot of α' again for Nylon 11 but with sample 3B which has well-developed crystallinity. The two-step nature of the γ relaxation is now quite evident. There is some evidence in the Kawaguchi[19] loss data for a low-temperature shoulder on the T_γ peak of Nylon 11.

Figure 6 is a plot of α' for Nylon 6,6 whose T_g is reported to be about 330°K[20] but variable with moisture content. A dynamic mechanical γ loss peak has been reported by Woodward *et al.*[21] at 160°K (1300 Hz). The very abrupt discontinuity in α' between 150 and 170°K is consistent with such a mechanical γ peak. The β peak is essentially missing, which is to be expected because of the low moisture content.[18,21,22]

The α_g is around 2.1-2.4 × 10^{-4} deg^{-1}. This will increase with increasing amorphous content. Stehling and Mandelkern[14] showed (their Figure 3) that α is relatively independent of crystallinity in the truly glassy state below any transition, but increases linearly with amorphous content above an amorphous phase transition. Assuming α at 110°K of 0.6 × 10^{-4} deg^{-1} characteristic of the crystalline state, and α_g at the start of T_g is 2.25 × 10^{-4} for 48% crystallinity, one can make a crude linear extrapolation to α_g (amorphous) of about 4 × 10^{-4} deg^{-1}. A commercial Nylon 6,6 of unstated crystallinity was reported to have an α_g of 2.73 × 10^{-4} deg^{-1}.[23] Ecochard[24] reported mean values of α for 66, 6, 610, and a 66/6 copolymer of 2.4, 3.15, 3.20, and 3.5 × 10^{-4} deg^{-1}, all on samples of unstated crystallinity in the range of 0-30°.

The value of α at 110°K, namely, 0.6 × 10^{-4} deg^{-1} seems abnormally low for the glassy state but duplicate runs gave identical values. For example, polyethylene of 50% crystallinity has an α of 1.8 × 10^{-4} deg^{-1} at 113°K.[8] The much higher polarity of nylon, and hence greater intermolecular forces, could well be responsible for the reduced coefficient of thermal expansion.

A DSC scan on this specimen of Nylon 6,6 shows nothing unusual in the T_γ region. We had anticipated finding a distinct endotherm at about 150°K in view of the sharpness of the $\Delta\alpha$ in this region. However, such was not the case. Illers[16] found that a ΔC_p occurring at T_γ in linear PE is missing in branched PE. A ΔC_p was also missing in Nylons 6 and 8 in the T_γ region (his DSC scan was from −170 to −100°).

Discussion of Results

Several points might be emphasized concerning the nylon data. (1) The λ relaxation is associated with the $-(CH_2)_n-$ portion of the polymer chain because it increases in intensity with increasing n.[11,19,21] (2) It is an amorphous transition since it increases in intensity with quenching[11] and with copolymerization.[21] (3) It is normally considered to be a single process by dynamic mechanical tests. However, the high resolving power of the thermal expansion method, reported here for the first time, clearly shows evidence of a two or even a three step process for Nylon 6,6 and Nylon 11 in all three runs (Figures 4-6). We will label the higher of these $T_{\rm I}$, the lower as $T_{\rm II}$, consistent with Illers[25] for PE.

$T_{\rm II}$ is very nearly the same for all three runs: 118°K for Nylon 6,6; 116°K and 124°K for the two Nylon 11 samples. One of the Nylon 11 samples, 3A, shows evidence for a third step around 180°K which is barely visible in Nylon 11, 3B.

Illers has shown that the γ-relaxation process in linear PE[26] and in branched PE[25] can be resolved into a higher temperature $\gamma_{\rm I}$ and a lower temperature $\gamma_{\rm II}$ process differing in temperature by about 25-30°, with an E_a of about 7 kcal for $\gamma_{\rm II}$ and about 15 kcal for $\gamma_{\rm I}$. He concludes that $\gamma_{\rm II}$ may be associated with short sequences of 3-4 CH_2 groups, whereas the $\gamma_{\rm I}$ process is associated with somewhat longer sequences in disordered regions.

Illers suggested that since E_a for 6-, 6,6-, 8-, and 6,12-polyamides was 9-11 kcal and since there was no ΔC_P in the γ region, then the γ process in polyamides might be similar to the $\gamma_{\rm II}$ process in polyethylene. If long and short CH_2 sequences are involved, as Illers suggests, it is understandable that Nylon 11 in Figure 5 could show the two-step γ process more clearly than does Nylon 6,6. Dynamic mechanical plus thermal treatment techniques developed by Illers for PE might well reveal the double peak in nylons, especially in those with the longer CH_2 sequences. There is some evidence that Kawaguchi's γ peak for Nylon 11 can be resolved into two peaks.

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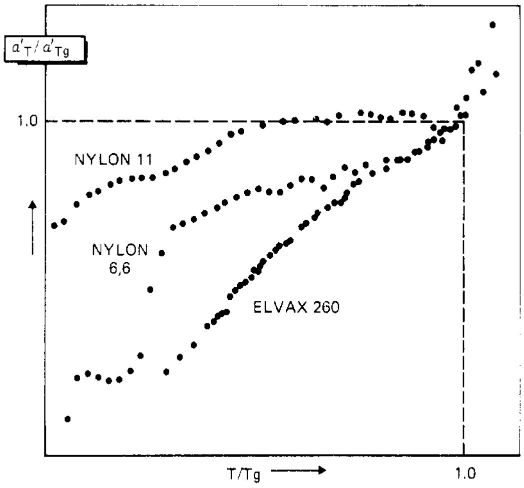

Figure 7. Reduced linear thermal expansion, α'/α'_g *vs.* T/T_g for E-VAC (sample 1A), Nylon 6,6 and Nylon 11 (sample 3A) showing the marked difference in behavior through the γ region.

Bell and Murayama[27] have shown that the unresolved peak in Nylon 6,6 is enhanced by quenching and destroyed by annealing. From this they conclude that it arises from CH_2 groups in chain folds. This does not appear consistent with enhancement of the γ peak by copolymerization.[21]

The apparent relaxation at 180°K in Nylons 6,6 and 11, and perhaps also in quenched Elvax 260 might result from motion of CH_2 groups coupled with motion of polar amide or acetate groups. Curtis[28] has suggested dielectric evidence that polar groups may participate in the γ relaxation of nylon.

Figure 7 is a composite double reduced plot of $\alpha'_{Tg}/\alpha'_{Tg}$ *vs.* T/T_g for specimens 1A, 2, and 3A in order to emphasize the great differences in thermal expansion behavior between the three polymer systems just discussed, all having a strong T_γ relaxation around 150°K. It appears from Figure 7 together with Figure 5, that the $T < T_g$ expansion behavior is sharper near T_γ, the smaller the number of CH_2 units and/or the greater the crystallinity. On this same scale and method of plotting, atactic polystyrene would always be above the plot for Nylon 11, with a slight downward slope to the left and no sharp, distinguishing features.

Concluding Remarks

In summary, coefficients of thermal expansion increase at varying degrees of abruptness on going through the γ-relaxation region of our three "model" materials, which presumably results from one or more types of in-chain motion involving short sequences of methylene groups.

These new experimental results appear to strengthen the conclusion reached previously[2a] that the coefficient of cubical expansion found by Stehling and Mandelkern at 168°K of 5.31×10^{-4} deg^{-1} is not an α_l (just above a T_g of 145°K as claimed by them) but is an α_g (just below a T_g of 195°K as claimed by one of us), enhanced over the normal value of 2×10^{-4} deg^{-1} by the very strong γ relaxation at 145°K in polyethylene.

The thermal expansion and DSC results reported here, especially in conjunction with the recent work of Illers,[25] raises some question as to how well the CH_2 sequences in nylons and ethylene copolymers are exact models for a linear PE chain.

The absence of a ΔC_p corresponding to the $\Delta\alpha$ in the T_γ region of the two nylons and the E-VAC copolymer, in apparent conflict with the Ehrenfest relationships, is consistent with prior observations on other polymer systems.[29-32] Quach and Simha[32] have estimated that for an observed $\Delta\alpha$ of 0.3×10^{-4} deg^{-1} at $T < T_g$ in polystrene, the calculated ΔC_p would be in the range of 10^{-2}–10^{-3} cal g^{-1} deg^{-1}. The circles in Figure 3 have a diameter of about 10^{-2} and hence any possible ΔC_p could escape notice.

Throughout this manuscript we have used such terms as "normal," "expected," "abnormally low," etc., in connection with numerical values of α' or α. Such terms resulted from detailed consideration of precision thermal expansion behavior of a variety of polar and nonpolar polymers and copolymers in the temperature range from either liquid He or liquid N_2 to T_g.[2a,4-8,14] Simha, Roe, and Nanda[33] have developed an equation of state approach for thermal expansion in the glass. When tested experimentally in the cryogenic range, it was found that deviations from the master curve were prominent only if a strong $T < T_g$ mechanical relaxation was present.

Acknowledgments. We are indebted to Professor Robert Simha for helpful advice and to Professor Phillip Geil (both of Case Western Reserve Univ.) for assistance in estimating X-ray crystallinities, to Dr. Allan Gray and Richard L. Fyans (Perkin Elmer Corp.) for obtaining the two DSC scans, and to Dr. K.-H. Illers of BASF for supplying a manuscript prior to publication. We also acknowledge partial support of this project by the National Science Foundation under Grant GK-20653.

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