Strengths of the Mechanical α-, β-, and γ-Relaxation Processes in Linear Polyethylene[†]

Richard H. Boyd

Department of Materials Science and Engineering and Department of Chemical Engineering, University of Utah, Salt Lake City, Utah 84112. *Received June 23, 1983*

ABSTRACT: The experimental anelastic relaxation behavior of linear polyethylene is analyzed phenomenologically. The (isochronal, torsion pendulum) dynamic shear modulus data of Illers on specimens covering a wide range of crystallinities were fit to an empirical equation that incorporates relaxed and unrelaxed moduli, a central relaxation time, and a width parameter (all temperature dependent) for each of the α, β, and γ processes. The fits achieved were good and allow discussion of the relaxation characteristics of each process. The variation of the unrelaxed and relaxed shear moduli with crystallinity shows that all three processes have amorphous-phase origin mechanically (although deeper connection with the crystal phase for the α process is discussed). A composite model that bounds the modulus of lamellar structures was used to analyze the crystallinity variation, and estimates of the unrelaxed and relaxed moduli of the amorphous phase, as it behaves in the semicrystalline environment, were determined for the α, β, and γ processes. The relaxed amorphous-phase shear modulus for the β process is ~100 MPa at 300 K, a value similar to the relaxed rubbery-phase modulus above (in temperature) the β glass–rubber relaxations in other semicrystalline polymers that have been analyzed. The β process is very broad in the frequency domain, even somewhat more so than in other semicrystalline polymers (which all have very broad β processes). The β process in LPE lacks overall prominence in isochronal scans relative to some other semicrystalline polymers because it is somewhat broader, its relaxation strength is reduced by the γ process being somewhat stronger, and the presence and proximity of the α process tend to obscure the modulus increment. Further, the *relative* prominence of the β process is insensitive to crystallinity variation because α, β, and γ *all* correlate as amorphous processes. However, the relaxational characteristics are quantifiable and similar to the amorphous-fraction glass–rubber relaxations in other semicrystalline polymers.

The relaxation properties of semicrystalline polymers are a subject of continuing interest. In polymers that crystallize very rapidly (and cannot easily be quenched to below the maximum in the crystallization rate vs. undercooling curve) to high degrees of crystallinity there tend to be at least three relaxation processes. These are labeled α, β, and γ in descending order with temperature isochronally.[1,2] The α process is commonly agreed to be connected to the presence of the crystalline phase.[1-9] The β process is often presumed to be the glass–rubber relaxation in the residual uncrystallized amorphous fraction.[6,10-13] The γ process is known to also involve the amorphous fraction,[6,14,15] although a partial origin in the crystal has been proposed.[6,14] Linear polyethylene (LPE), no doubt by virtue of its appealing structural simplicity and its technological importance, has engendered a large number of studies of both its crystallization and its relaxation behavior. It is therefore probably the most important member of this class of polymers. In linear polyethylene it can now be concluded that for practical purposes the γ relaxation is entirely of amorphous-phase origin.[16] Like other members of the class of easily crystallizable polymers, in LPE when the relaxation behavior is plotted isochronally vs. temperature in order to simultaneously display all the relaxation processes, the β process is not prominent in comparison with the α and γ processes. This has led several investigators[15,17] to question its existence in LPE and to therefore describe the more prominent γ process as the glass transition in the amorphous fraction. Although isochronal relaxation scans do indicate the presence of a β relaxation, the question could be a purely semantic one if the glass transition is defined as the most prominent amorphous-phase relaxation. However, conceptually the question goes deeper. In many crystalline polymers the equivalents of the β and γ relaxations are both prominent and easily observed and described. A hypothesis that rationalizes profound differences in behavior between the γ and β relaxations is that the β process involves longer range, generalized segmental chain motions via bond rotations akin to the glass–rubber relaxation in wholly amorphous polymers while the γ process involves shorter range, more localized motions in a matrix that is quiescent with respect to generalized segmental motion (akin to subglass relaxations in wholly amorphous polymers). It is therefore important to determine to what extent this language is appropriate to easily crystallizable polymers like LPE. It is known that in cases where the completely amorphous counterpart of a semicrystalline polymer is available for comparison (via quenching,[18-21] melting,[22] or copolymerization[23-26]), the β relaxation in the crystalline specimen is still present but is enormously broadened and somewhat displaced to higher temperature (isochronally) compared to the wholly amorphous ones. This is obviously the result of immobilization of the amorphous phase by the presence of the crystal phase. This immobilization not only has a dynamic character (broadening and displacement of relaxation times) but also results in a dramatic increase in the relaxed rubbery modulus of the amorphous phase.[26] It would be particularly interesting to be able to describe quantitatively, in LPE, the broadness and the relaxed modulus (i.e., the relaxation strength) of the β process. Then its behavior could be placed in context with other crystalline polymers.

It turns out to be quite possible to adequately analyze the mechanical relaxation behavior of LPE and thereby resolve the contributions of the various processes and assign relaxation strengths and relaxation parameters to the individual α, β, and γ relaxations. The present work reports the results of such as analysis. In addition, we have taken advantage of a recently proposed method[27] for representing the mechanical response of lamellar semicrystalline polymers in terms of their separate crystalline and amorphous phases in analyzing the specimen relaxation strengths in terms of phase origin.

Analysis of the Anelastic Relaxation Behavior of LPE

We begin with a discussion of the data available. Most of the appropriate data consists of isochronal scans through temperature of the dynamic shear (G^*) or tensile modulus

---

[†] Dedicated to Walter H. Stockmayer on the occasion of his 70th birthday.

0024-9297/84/2217-0903$01.50/0

(E^*). In the context of assigning phase origin, studies on specimens of widely varying crystallinity are important. Here there is available quite a bit of data concerning G' and G'' vs. temperature taken in the torsion pendulum (at ~1 Hz).[13–15,28–31] Indeed most of the discussions of the mechanical relaxations in LPE center on these isochronal plots from the torsion pendulum. There is no basic disagreement in the data among the major studies. In fact data on similar specimens agree rather well. A single study, that of Illers,[31] encompasses a wider range of crystallinity than the others and agrees with them in their range of crystallinities. Therefore we use Illers' data as representative of isochronal G^* behavior as a function of temperature and crystallinity. Only for the α process are there appropriate time- or frequency-domain data. Nakayasu, Markovitz, and Plazek[32] measured dynamic shear (J^*) and creep ($J(t)$) compliance on a single specimen and McCrum and Morris[33] measured $J(t)$ at essentially one crystallinity. We will use their data as a check on the relaxation parameters determined from the isochronal scans.

It seems not to be generally appreciated how much information can be extracted from isochronal scans, especially if a few simplifying assumptions are justified. In our case the analysis is fairly straightforward if it is assumed that the relaxation processes are symmetric (about log $\omega_{\max}$) in the frequency domain. In dielectric studies on the γ and β processes in crystalline polymers[5,22,25,34,35] this appears to be the case. More directly, this assumption leads to good fits of log G' and log G'' vs. temperature in crystalline polymers where the β process is well resolved, and some a priori knowledge of temperature dependence of relaxation time is available.[26]

As is well established in dielectric studies there is a great advantage in data representation in utilizing a parameterized empirical relaxation function. An equation embodying the symmetry in log ω conjectured that has been applied to both γ and β processes in crystalline polymers[26] is

$$G^* - G_R = (G_U - G_R)(i\omega\tau^0)^{\bar{\alpha}}/(1 + (i\omega\tau^0)^{\bar{\alpha}}) \qquad (1)$$

where τ^0 is a central relaxation time, $\bar{\alpha}$ is a width parameter, and G_U and G_R are unrelaxed and relaxed shear moduli, respectively. This equation is immediately recognizable as the generalization of the familiar dielectric Cole–Cole equation[36] to a relaxation process rather than a retardation one. In its utilization we allow for temperature variation by writing

$$\log G_U = \log G_U{}^0 + S_U(T - T_0) \qquad (2a)$$

$$\log G_R = \log G_R{}^0 + S_R(T - T_0) \qquad (2b)$$

$$\bar{\alpha} = \bar{\alpha}^0 + \bar{\alpha}'(T - T_0) \qquad (2c)$$

$$\log \tau^0 = A/(T - T_\infty) + B \qquad (2d)$$

where T_0 is an arbitrary reference temperature and S_U, S_R, and $\bar{\alpha}'$ are linear temperature coefficients.

Similtaneously fitting G' and G'' is fortunately rather demanding or discriminating of parameters. Relaxation *location* along the temperature axis (e.g., peak location) tends to fix A/B (eq 2d, T_∞ fixed). The apparent *width* of the relaxation along temperature responds to activation energy, $2.303RAT^2/(T - T_\infty)^2$, and to the frequency-domain width paramter, $\bar{\alpha}$. However, increasing the activation energy sharpens the G'' plots vs. T by decreasing the area under them[1] but leaves $G''_{\max}$ (at $\omega\tau^0 = 1$) unchanged. In contrast, increasing $\bar{\alpha}$ sharpens the plots but increases $G''_{\max}$ as well. Changes in log G' with temperature due to temperature dependence of G_R and G_U tend to be distinguishable from changes with T due to relaxation because of different effects on log G''. Finally, it is important to note the effect of temperature dependence of $\bar{\alpha}$ on the *shape* (symmetry) of the temperature plots. For an Arrhenius behavior of log τ^0, plots vs. log ω or $1/T$ (i.e., log ($\omega\tau$)) with other parameters temperature independent have the same shape and are therefore symmetric in $1/T$. A plot vs. T is skewed toward higher temperature. The effect of $\bar{\alpha}$ increasing with temperature is to counter this skewing or even reverse it, resulting in skewing of G'' toward low temperature in isochronal plots. We believe that it is the well-known tendency for relaxations to narrow with increasing temperature ($\bar{\alpha}$ increasing) in crystalline polymers that is largely responsible for the low-temperature-side skewing of the γ processes in these polymers. In addition to this skewness, however, there is sometimes an indication of some structure in the form of an inflection or shoulder on the low-temperature side of the γ peak. This appears to be a phenomenological effect due to a low-temperature cutting-off of the drop of the $\bar{\alpha}$ parameter with decreasing temperature. We have incorporated this effect into the fitting equations by altering eq 2c for the γ process only as

$$\bar{\alpha} = \bar{\alpha}^0 + [\bar{\alpha}'\Delta T + (\bar{\alpha}'^2\Delta T^2 + k)^{1/2}]/2 \qquad (2e)$$

where $\Delta T = T - T_0$ and T_0 in this instance is now a temperature selected to be on the low-temperature side of the γ peak to produce the proper shape. This equation provides for a transition between linear proportionality of $\bar{\alpha}$ with T at higher temperature ($\gg T_0$) and $\bar{\alpha} = \bar{\alpha}_0$ at low temperature ($\ll T_0$). The parameter k controls the sharpness of the transition. A value of $k = 0.001$ was selected as giving satisfactory behavior.

In fitting an individual specimen an initial set of parameters was determined by adjustment interactively against computer-generated plots. Then in a least-squares refinement, Newton–Raphson iteration was used to reduce the residuals of the calculated and experimental values. As an illustration of the application of eq 1 to previously well-characterized relaxations in semicrystalline polymers, we have fit it to the β subglass and the α_a glass–rubber relaxation in poly(ethylene terephthalate) (PET). The isochronal torsion pendulum data of Illers and Breuer[18] were used. The $\bar{\alpha}_0$ and A parameters for the β process were not unique in the least-squares adjustment, a consequence of the small relaxation strength of the β process in this polymer. Therefore we constrained $A(\beta)$ at 2800, the value found from dielectric measurements.[19] The least-squares-adjusted parameters found were log $G_U{}^0 = 0.23$, $S_U = -1.8 \times 10^{-4}$, log $G_R{}^0 = 0.04$, $S_R = -2.0 \times 10^{-4}$, $\bar{\alpha}_0 = 0.066$, $\bar{\alpha}' = 2.07 \times 10^{-3}$, $T_0 = 150$ K (in eq 2a,b,d,e,), $A = 2800$ (not adjusted), $B = -16.30$, and $T_\infty = 0$ (asumed Arrhenius behavior) for the β process and log $G_R = -0.51$, $S_R = -1.6 \times 10^{-3}$, $\bar{\alpha}^0 = 0.154$, $\bar{\alpha}' = -2.0 \times 10^{-4}$, $T_0 = 350$ K (in eq 2a–d), $A = 3233$, $B = -26.87$, and $T_\infty = 244$ K (taken from dielectric measurements and kept fixed) for the α_a process. Comparison of this parameterization of eq 1 with the experimental data is displayed in Figure 1. The fit is excellent, nearly to within experimental error. The converged values of A and B for the α_a process were very close to the dielectric values 3214 and −27.10 (and $T_\infty = 244$ K)[37].

In our work here on LPE we write G^* as the sum of three terms as in eq 1, one each for the α, β, and γ processes. As a trial value for the γ process we took log $\tau^0(\gamma) = 3270/T + B(\gamma)$. This is Arrhenius behavior ($T_\infty = 0$) and $A(\gamma) = 3270$ implies $H^*(\gamma) = 15$ kcal mol^{-1} (62.8 kJ mol^{-1}), a value typical of dielectric results for the process.[5] For the α process we took log $\tau^0(\alpha) = 6000/T + B(\gamma)$, Arrhenius behavior with $\Delta H^*(\alpha) = 27.5$ kcal mol^{-1} (115 kJ

Table I
Mechanical Relaxation Parameters for Linear Polyethylene γ Process[a]

sample	crystallinity	log $G_U{}^0$	$S_U \times 10^4$	log $G_R{}^0$	$S_R \times 10^4$	$\bar{\alpha}_0$	$\bar{\alpha}' \times 10^3$	A	B
1	0.48	0.54	−1.0	−0.06	−0.5	0.06	4.2	2413	−20.3
2	0.60	0.50	−1.0	0.00	−1.5	0.07	3.3	2749	−22.2
3	0.66	0.50	−1.0	0.09	−1.5	0.07	3.4	3062	−23.8
4	0.72	0.50	−1.0	0.14	−1.5	0.06	3.3	2994	−22.9
5	0.79	0.52	−1.0	0.22	−1.5	0.06	2.9	3916	−28.1
6	0.87	0.53	−1.0	0.29	−1.5	0.07	3.0	3565	−25.4
7	0.92	0.53	−1.0	0.39	−0.5	0.07	3.7	2737	−20.3
8	0.96	0.55	−1.0	0.41	−0.5	0.06	2.2	3000	−22.1

[a] Parameters for eq 2a,b,d,e; $T_0 = 120$ K, $T_\infty = 0$. Units of G are GPa.

Table II
Mechanical Relaxation Parameters for Linear Polyethylene β Process[a]

sample	log $G_R{}^0$	$S_R{}^- \times 10^4$	$S_R{}^+ \times 10^3$	$\bar{\alpha}_0$	$\bar{\alpha}' \times 10^3$	T_0	A	B	T_∞	T_g[b]
1	−0.30	−1.5	−3.3	0.17	1.3	250	335	−8.2	160	201
2	−0.22	−1.0	−4.8	0.15	1.0	260	375	−8.3	160	205
3	−0.17	−1.0	−4.6	0.14	1.1	270	408	−10.0	160	201
4	−0.07	−1.0	−3.7	0.15	1.2	270	462	−10.0	160	206
5	−0.00	−0.5	−4.8	0.18	1.3	290	428	−11.2	160	198
6	0.08	−3.0	−3.5	0.19	1.2	290	471	−11.2	160	202
7	0.20	−1.0	−4.4	0.13	0.9	290	400	−11.4	160	195
8	0.28	−1.0	−3.1	0.21	1.4	290	416	−9.7	160	203

[a] Parameters for eq 2a-d; $S_R{}^-$ is to be used below T_0, $S_R{}^+$ above. log $G_U{}^0$ and S_U are equal to corresponding log $G_R{}^0$ and S_R values for the γ process (Table I). A low-temperature cutoff on $\bar{\alpha}$ of 0.05 was used. [b] Defined here as the temperature at which log $\tau^0 = 0$.

mol^{-1}), a value consistent with both mechanical[32,33] and dielectric[5] studies. The mechanical α process is complex, showing evidence of two processes (α and α′, McCrum and Morris[33]; α_I and α_{II}, Nakayasu et al.[32]). Illers'[31] data extend only to temperatures embracing primarily the lower process. We have only attempted to fit this one (α or α_I) and have ignored the higher temperature one (α′ or α_{II}). It is evident that for the α process both the unrelaxed and relaxed moduli are fairly strongly temperature dependent. McCrum and Morris took both to have the same slope vs. temperature in analyzing their data and constructing a master creep curve. We follow them in making this assumption. However, the high slope S_U for log G_U for the α process cannot continue to low temperature and be consistent with the observed isochronal moduli, and therefore eq 2a is inadequate for the temperature dependence. We have incorporated this more complicated temperature dependence in the simplest way possible by using two slopes for $S_R(\beta)$ ($=S_U(\alpha)$), one, $S_R{}^+(\beta)$, above T_0 and another, $S_R{}^-(\beta)$, below T_0. McCrum and Morris had confidence in the premise that they had constructed a meaningful master creep curve and Nakayasu et al. had similar confidence in a master $J''(\omega)$ curve. This implies $\bar{\alpha}$ is temperature independent for the α process, and we have taken $\bar{\alpha}'$ (α) = 0.

In summary, we have the following parameters for adjustment for each specimen: "strong" parameters, log $G_U{}^0(\gamma)$, log $G_R{}^0(\alpha,\beta,\gamma)$, $B(\alpha,\beta,\gamma)$, $A(\alpha,\beta,\gamma)$, $T_\infty(\beta)$, and $\bar{\alpha}_0(\alpha,\beta,\gamma)$; "intermediate" parameters, $S_R{}^+(\beta) = S_U(\alpha) = S_R(\alpha)$ and $\bar{\alpha}'(\gamma,\beta)$; and "weak" parameters, $S_U(\gamma)$, $S_R(\gamma)$, and $S_R{}^-(\beta)$. The parameter $T_\infty(\beta)$ was effectively dropped from the list by keeping it fixed in the adjustments of other parameters but trying several values overall. The value of 160 K was settled on for all specimens. A value of this order is demanded by the data in order to attenuate the low-temperature side of the β-process G'' (or tan δ) curves. Otherwise the observed sharp high-temperature side of the γ-process G'' could not be accommodated. In the least-squares refinement all of the strong and intermediate parameters were varied except $A(\alpha)$ and $\bar{\alpha}_0(\alpha)$. The initial A value and the $\bar{\alpha}_0$ value from the interactive adjustment seemed to give quite good results and were not further adjusted. As was the case for PET, in LPE sample 8, the relaxation strength of the γ process was so small that the A and $\bar{\alpha}_0$ parameters were not unique, and A was constrained at 3000 in this one sample.

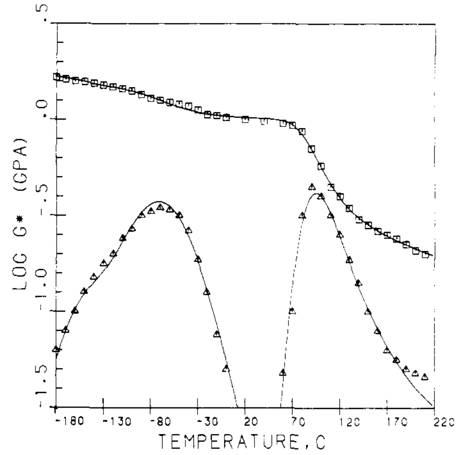

Figure 1. Cole–Cole equation fitting of the dynamic shear modulus of semicrystalline poly(ethylene terephthalate) (torsion pendulum, ~1 Hz). log G'' (lower curve) is displaced upward in plotting by 1.0. The points are representative of the experimental data of Illers and Breuer (ref 18, sample 9); the curves are calculated from eq 1 and 2a–e (see text for parameters used).

Data reported by Illers[31] on eight specimens covering the crystallinity range 48–96% were fit. The parameters determined are listed in Tables I–III. The fits for log G' and log G'' are displayed in Figures 2 and 3.

As a check on our parameterization we have calculated $J^*(\omega) = G^*(\omega)^{-1}$ for comparison with the data of Nakayasu, Markovitz, and Plazek[32] and $J(t)$ for comparison with the results of McCrum and Morris.[33] The sample studied by Nakayasu et al. had a density close to that of sample 5 of Tables I–III. Their data are compared in Figure 4 to curves calculated with the parameters of sample 5 but with B for the α process changed to −19.0 from −18.5. This corresponds to a small shift along the frequency axis. With

Table III
Mechanical Relaxation Parameters for Linear Polyethylene α Process[a]

sample	$\log G_R{}^0$	$S_R \times 10^3$	$\bar{\alpha}_0$	$\bar{\alpha}' \times 10^3$	T_0	A	B
1	−1.00	−3.3	0.36	0.0	250	6000	−19.3
2	−0.88	−4.8	0.40	0.0	260	6000	−18.5
3	−0.84	−4.6	0.40	0.0	270	6000	−18.4
4	−0.70	−3.7	0.40	0.0	270	6000	−18.5
5	−0.60	−4.8	0.40	0.0	290	6000	−18.5
6	−0.45	−3.5	0.40	0.0	290	6000	−18.7
7	−0.12	−4.4	0.40	0.0	290	6000	−18.5
8	−0.07	−3.1	0.40	0.0	290	6000	−18.7

[a] Parameters for eq 2a-d; $\log G_U{}^0$ and S_U are equal to corresponding $G_R{}^0$ and S_R values for the β process (Table II); $T_\infty = 0$.

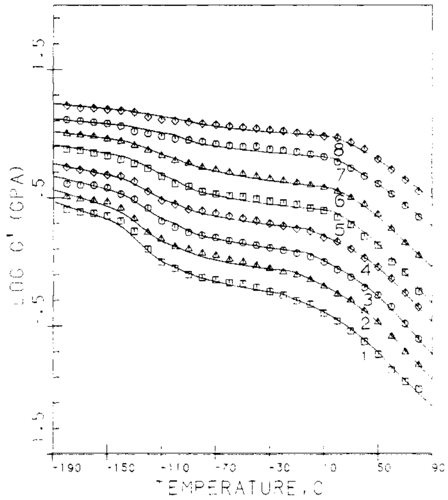

Figure 2. Dynamic storage shear modulus of linear polyethylene (torsion pendulum, ~1 Hz). Points are representative of the data of Illers (ref 31). The curves are calculated from eq 1 and 2a–e (generalized to three processes). The parameters are from Tables I–III. The numbering of the curves corresponds to the sample numbers in the tables. For clarity of plotting, each ordinate (log G') has been displaced upward by $0.1(N - 1)$, where N is the sample number.

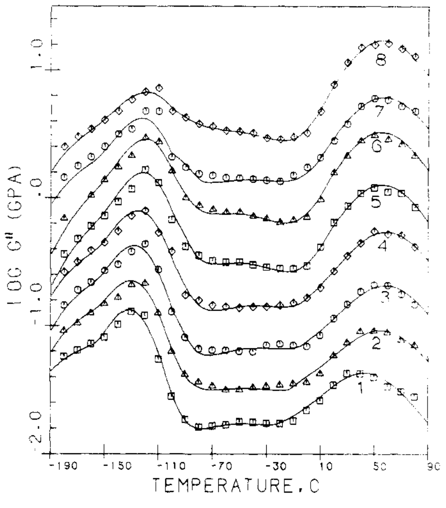

Figure 3. Dynamic loss shear modulus of linear polyethylene. Same details as Figure 2 but upward shift of ordinates (log G'') is $0.3(N - 1)$.

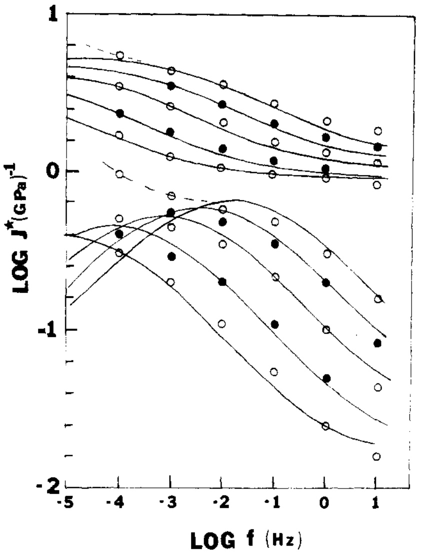

Figure 4. Dynamic compliance of linear polyethylene in the α-relaxation region. Isothermal scans at five temperatures (2.3, 15.5, 29.0, 40.4, and 50.5 °C) vs. frequency. Points are representative of the data of Nakayasu, Markovitz, and Plazek.[32] The curves are calculated from eq 1 and 2a–e using the parameters of Tables I–III for sample 5 (which is close in density to the sample of ref 32), but with $B(\alpha) = -19.0$. Dashed curves show onset of the α_{II} process at the highest temperature.

this adjustment the agreement between the experimental dynamic data (covering 5 decades of frequency and temperatures covering the α_I region) and the curves with parameters determined from the isochronal torsion pendulum scans is quite satisfactory.

The creep compliance $J(t)$ was calculated via[38]

$$J(t) = \int_{-\infty}^{\infty} L(\ln \tau)(1 - e^{-t/\tau})\, \mathrm{d} \ln \tau + J_U \qquad (3)$$

where $L(\ln \tau)$ is the spectrum of logarithmic retardation times. The latter was found analytically in terms of the parameters of eq 1 (extended to three relaxation processes) from[38]

$$L(\ln \tau) = \frac{1}{2\pi j}[J^*(e^{j\pi}/\tau) - J^*(e^{-j\pi}/\tau)] \qquad (4)$$

as

$$L(\ln \tau) = 1/\pi(b_1 + b_2 + b_3)/[(G_e + a_1 + a_2 + a_3)^2 + (b_1 + b_2 + b_3)^2] \qquad (5)$$

where $a_i = {}^1/_2(G_U - G_R)_i[\cos \bar{\alpha}_i\pi + \exp(\bar{\alpha}_i \ln s_i)]/[\cosh(\bar{\alpha}_i \ln s_i) + \cos \bar{\alpha}_i\pi]$, $b_i = {}^1/_2(G_U - G_R)_i \sin \bar{\alpha}_i\pi/(\cosh(\bar{\alpha}_i \ln s_i) + \cos \bar{\alpha}_i\pi)$; the subscripts i = 1–3 refer to the three relaxation processes γ, β, and α, G_e is the relaxed modulus after all three processes ($=G_R(\alpha)$), and $s_i = \tau_i{}^0/\tau$. The integration of eq 3 was carried out numerically. The resulting creep curves at 20 °C for samples 5 and 6 of Table I–III are compared with the master creep curve of McCrum and Morris[29] (also at 20 °C) in Figure 5. These samples have densities bracketing that of the sample of McCrum and Morris. The agreement is quite good up to the point where the higher temperature α' process begins to contribute to the creep compliance in McCrum and Morris' work. As we stated, Illers' data does not permit including it in our analysis. The agreement is especially impressive because the master creep curve construction by McCrum and Morris required major vertical shifts as well as hori-

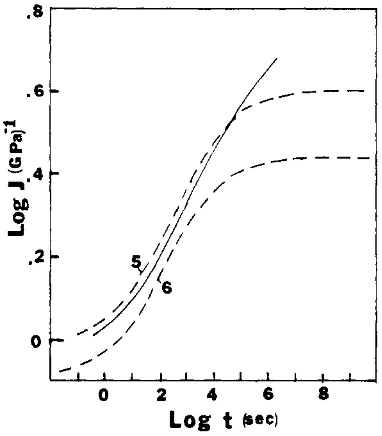

Figure 5. Creep curve $J(t)$ of linear polyethylene at 20 °C (α-relaxation region). Solid curve is master creep curve constructed by McCrum and Morris from their experimental data.[33] Dashed curves are calculated from eq 3 and 4 of text using parameters of Tables I–III for samples 5 and 6 (which bracket the density of the sample of ref 33).

zontal ones. This is due to the relatively strong temperature dependence of J_U and J_R for the α process.

Variation of Relaxation Strength with Crystallinity

The morphological assignment of the relaxation processes to the amorphous or crystalline phases by assessment of the variation of observed relaxation strengths with crystallinity has been discussed previously.[14,16] In our own discussions variation of the storage modulus G' at various temperatures (rather than limiting relaxed and unrelaxed moduli) with crystallinity was considered.[16] However, it was clearly apparent that the γ process must have its origin in the amorphous fraction. It was also concluded that the softening accompanying the α process was in the amorphous phase. No resolution of the relaxation strength into a contribution from the β process was attempted. Now that we have what we believe are reliable values of specimen relaxation strengths for all three processes, we can attempt phase assignment for all three in a unified manner. In Figure 6 we plot the experimentally determined unrelaxed and relaxed specimen moduli vs. crystallinity. It is immediately apparent from these plots that $G_R(\gamma)$ and $G_R(\beta)$ both converge at high crystallinity on the unrelaxed modulus G_{U2} for the crystal phase, showing that both the γ and β processes have amorphous-phase origin. The same conclusion appears reasonable for the α process as well ($G_R(\alpha)$). It obviously has strong amorphous-component character to it. But because of the lower values of $G_R(\alpha)$, convergence to G_{U2} at 100% crystallinity indicating exclusive amorphous-phase origin is not as certain. We defer to application of theoretically based expressions for crystallinity variation of modulus for more guidance on this point. A further point of considerable interest in the context of application of equations for modulus variation with crystallinity is determination of the effective modulus of the amorphous phase as it behaves in the semicrystalline environment. In making these assessments, we require a "mixing equation" for combining the separate phase moduli into specimen modulus. Various approaches to mixing equations have been discussed before.[16] In the work here we take advantage of a recent treatment of the mechanical response of semicrystalline polymers that have locally lamellar morphology.[27] The method results in bounds on the specimen moduli. These bounds are much tighter than the crude Reuss (volume fraction additivity of phase compliances) lower bound and Voigt (volume fraction additivity of phase moduli) upper bound. The treatment also explicitly incorporates the extreme mechanical anisotropy of polymer crystals. Input for calculation of the bounds is the elastic constant matrix of the crystal, the shear modulus, and Poisson's ratio of the (isotropic) amorphous phase and the volume fraction crystallinity. Because it is apparent from Figure 6 that the γ and β processes are amorphous phase in origin and to see if the relaxed α-process modulus can be represented as an entirely amorphous one, we suppose that the crystal elastic constants show no relaxation processes and use numerical values reported before.[27] Approximating Poisson's ratio by 0.33, the only free parameter then is the shear modulus of the amorphous phase, G_1. The curves in Figure 6 are calculated ones from the *lower* bound lamellar morphology equations[27] that use for each curve a single crystallinity-independent value of G_1. The fit of these curves is seen to be very good, including that for the relaxed α-process shear modulus.

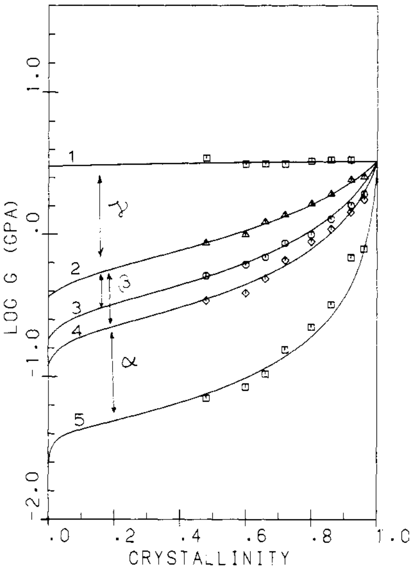

Figure 6. Relaxation strengths vs. crystallinity (V_2) in linear polyethylene. Plot 1 is the unrelaxed shear modulus for the γ process (at 175 K), $G_U(\gamma)$. Plot 2 is the relaxed shear modulus for the γ process $G_R(\gamma)$ = the unrelaxed shear modulus for the β process, $G_U(\beta)$ (175 K). Plot 3 is the relaxed shear modulus for the β process $G_R(\beta)$ (at 175 K). Plot 4 is the same quantity as plot 3 but at 300 K = unrelaxed shear modulus for the α process, $G_U(\alpha)$. Plot 5 is the relaxed shear modulus for the α process (300 K). The points are for the eight samples of Tables I–III. The curves are calculated ones using the lower bound equations for the lamellar morphology of ref 27. Amorphous-phase modulus (G_1) values used are indicated by left-hand ordinates for each curve.

The application of the upper lamellar bounds results in poor fits. This is because of the extreme crystal mechanical anisotropy. The modulus in the c-axis direction (~300 GPa) is many times higher than in the transverse directions (~5–10 GPa). The lower bound estimate of the 100% crystalline isotropic aggregate is dominated by the transverse values whereas the upper bound estimate is dominated by the fiber modulus. Thus there is a wide divergence of the bounds at 100% crystallinity. Fortunately this divergence takes place vs. crystallinity only at quite high crystallinity values where the upper bound swings sharply upward. Experimentally it seems clear that this upswing in specimen modulus as 100% crystallinity is approached does not take place and that the lower bound estimate is close to the correct value. Furthermore, it is found that the lower bound equation gives a much better representation of variation of specimen modulus

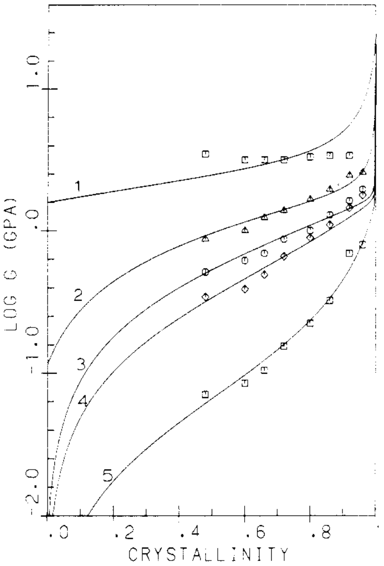

Figure 7. Limiting moduli vs. crystallinity. Same details as Figure 6 except that the curves are calculated ones for behavior intermediate between lamellar lower and upper bounds ($\xi = 100$ in eq 6). log G_1 values (left-hand ordinates) used for curves 3, 4, and 5 are −2.3, −2.7, and −3.6, respectively.

over wide crystallinity ranges with a single crystallinity-independent value of the amorphous-phase modulus than does the upper bound equation. We conclude either that the specimens change from lower toward upper bound behavior with accompanying amorphous modulus changes as crystallinity decreases or that the lower bound behavior is inherently closer to the truth. As an illustration of these effects we plot in Figure 7 the variation in modulus for a system that is intermediate between lower and upper bound in behavior over all of the crystallinity range and has a fixed amorphous-phase modulus. If the specimen shear modulus predicted by the lamellar upper bounds is denoted G_{upper} and that from the lower bound as G_{lower}, intermediate behavior can be represented by a Halpin–Tsai-like[39] equation where

$$G = (1 + \xi G_{\text{upper}})/(\xi + 1/G_{\text{lower}}) \qquad (6)$$

and ξ is a parameter specifying the degree of approach to either bound ($\xi \to 0$, $G \to G_{\text{lower}}$; $\xi \to \infty$, $G \to G_{\text{upper}}$). In Figure 7 the curves shown are calculated for ξ fixed at 100 and G_1 fixed at each temperature. The fits, especially for curves 1–4, are not as good as for $\xi = 0$ lower bound behavior (Figure 6). For $\xi > 100$ the fits are progressively worse.

Discussion of the Relaxation Behavior of Linear Polyethylene

It is of interest to place the mechanical relaxation strengths and relaxation parameters of linear polyethylene in context with those in other semicrystalline polymers, and this we attempt in the ensuing discussion.

Dynamic Relaxation Parameters. A "loss map" for one of the samples analyzed here is shown in Figure 8 where log τ_0 is plotted vs. $1/T$ for the three processes. Also shown are the corresponding values[5] for the dielectric α and γ processes in a specimen of similar density (and containing a few carbonyl groups). No dielectric parameters for the β process were reported.[5] In figure 9 comparison is made with the β- and γ-process values for poly(hexamethylene adipate) ("6–6 polyester")[25,26] and poly(hexamethylene sebacate) ("6–10 polyester").[40] These linear aliphatic semicrystalline polymers have well-quantified β and γ processes in similar temperature ranges as LPE. Also shown for comparison as polymers with the glass–rubber relaxation in a similar range are (amorphous) poly(propylene oxide)[41] and (semicrystalline) poly(ethylene oxide).[34,42]

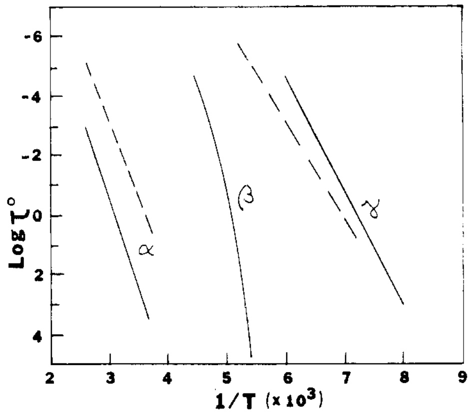

Figure 8. Loss map for linear polyethylene, sample 5 (Tables I–III). log τ_0 vs. $1/T$ for the α, β, and γ processes. The dashed curves for the α and γ processes are dielectric results for a (C=O dipole decorated) sample of similar density (ref 5, sample 94-1A).

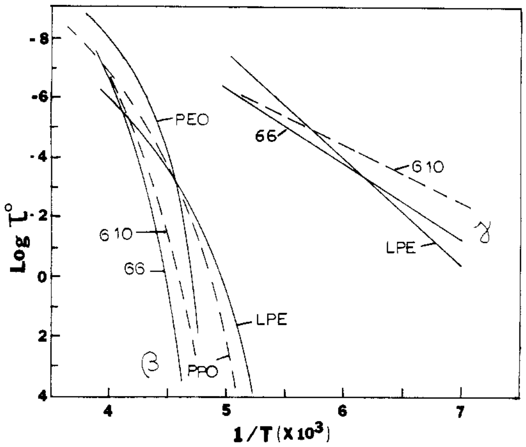

Figure 9. log τ_0 vs. $1/T$ for linear polyethylene, sample 6 (LPE), γ and β processes compared with some other polymers. (PEO = poly(ethylene oxide), PPO = poly(propylene oxide), 6–10 = poly(hexamethylene sebacate), 6–6 = poly(hexamethylene adipate); τ_0 assumed = $1/\omega_{\max}$ for PEO and PPO).

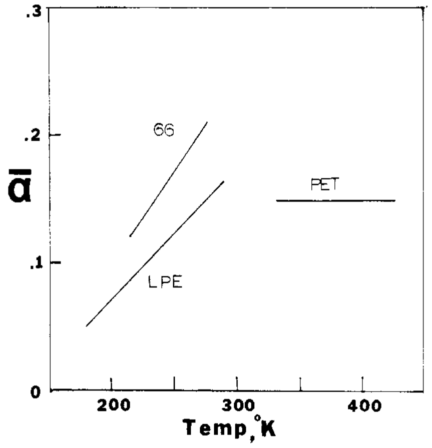

Figure 10. β process width parameter ($\bar{\alpha}$) vs. temperature for linear polyethylene, sample 5. Also shown are width parameters for the glass–rubber relaxation in semicrystalline PET and 6–6 aliphatic polyester.

The width in the frequency domain ($\bar{\alpha}$ parameter) of the β process in LPE sample 5 is compared with the widths of the glass–rubber relaxations in 6–6 polyester and PET in Figure 10. The $\bar{\alpha}$ parameter for 6–6 polyester is from

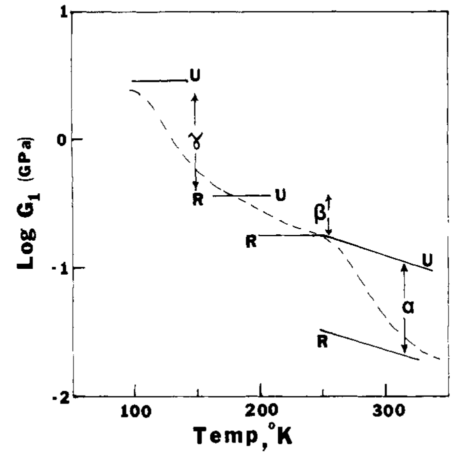

Figure 11. Amorphous-phase modulus in linear polyethylene. Unrelaxed and relaxed values for the γ, β, and α processes. Upper bound estimates from the lamellar lower bound fits in Figure 6. Dashed curves are schematic of isochronal relaxation vs. temperature.

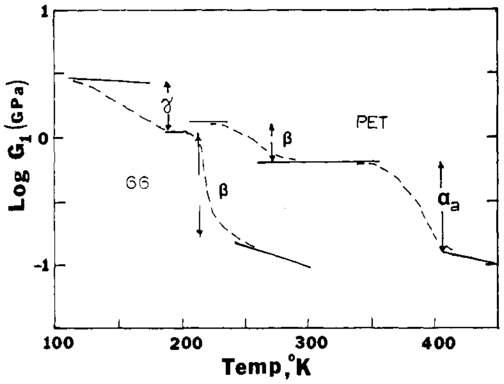

Figure 12. Amorphous-phase modulus in 6–6 aliphatic polyester and PET. Unrelaxed and relaxed values for the γ and β processes (or the equivalent β and α_a processes). These are also estimates from lamellar lower bound equations.

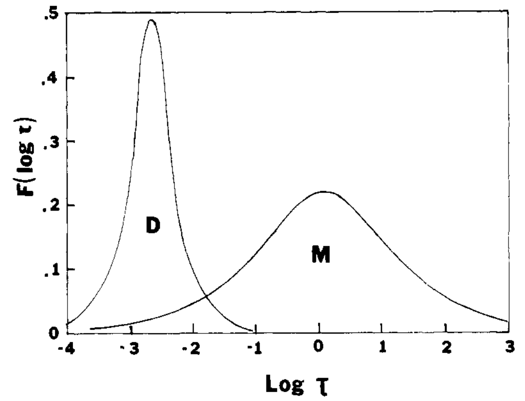

Figure 13. Comparison (at 50 °C) of the dielectric (D) and mechanical (M) relaxation time distributions for the α process in linear polyethylene (sample 5, Table III; sample 94-1A, ref 5).

ref 26 and for PET is that used for the fit in Figure 1. It may be seen that the relaxations are extremely broad in all of them and that LPE is the broadest of the three.

Relaxation Strengths. The strengths of the α, β, and γ processes are conveniently discussed via the behavior of the amorphous-phase modulus. In Figure 11 the unrelaxed and relaxed amorphous-phase shear moduli, G_1, for the three processes are shown. These are the lower bound equation values used in Figure 6 and therefore are upper bound estimates to G_1. In Figure 12 a similar plot is shown for 6–6 polyester and for PET. For the former[27] the G_1 values are from a wide crystallinity variation (effected through copolymerization) fit similar in vein to Figure 6. However, for PET is represents G_1 behavior in the 40–50% crystallinity range only. From Figures 11 and 12 it may be seen that the relaxed amorphous-phase shear modulus estimates are similar in all three polymers, being in the neighborhood of 100 MPa and decreasing fairly strongly with increasing temperature. Aside from LPE having an observable α relaxation process, the major difference between LPE and the other two polymers is the strength of the γ relaxation, the process being stronger in LPE. The lower relaxed value of G_1 for the γ relaxation in LPE leads to a compression of the strength of the β since the relaxed value for the latter is similar to that of the other polymers.

Nature of the α Process. It is important to comment on the assignment of the mechanical α process as involving softening of the *amorphous* fraction. This assignment has been made before[16,43,44] and the present work is a step in quantifying it more carefully. There is also incontrovertible evidence from mechanical,[3,4] dielectric,[5] and NMR[45,46] studies that the α relaxation involves and requires the crystalline phase. The resolution of this apparent inconsistency has been commented on before.[2,16] However, it needs reiteration here. It is apparent from Figure 11 that the immobilization of the amorphous phase by the crystal phase above the β process in temperature (relaxed G_1, β process ~100 MPa) is indeed severe. The constraints imposed by the connections to and even the prescence of the crystals drastically limit the configurations available to amorphous segments, and hence the relaxed amorphous-phase modulus is very high. The basic molecular mechanism underlying the α process is known to be a rotational, translational motion or step of the chains along the *c* axis in the crystal by half a unit cell.[9] These elementary motions are immediately active and detectable in the dielectric and NMR methods. However, the elementary steps do not immediately lead to the change in shape of the crystal that would be required from mechanical activity assignable to the crystal phase. However, accumulation of a number of these steps and hence acquisition of *c*-axis mobility does lead to redistribution of constraints on amorphous segments attached to the crystals and allows further deformation of the amorphous fraction. The dielectric relaxation times for the α process as seen in Figure 8 are shorter than the mechanical ones at the same temperature. The dielectric process, monitoring as it does the elementary steps directly, is nearly single relaxation time whereas the mechanical process requiring accumulation of steps is broader (but with relaxation times having the same activation energy). In Figure 13 the spectrum of dielectric relaxation times is compared to the spectrum of mechanical relaxation times at the same temperature for specimens of similar density. It may be seen that the idea that the dielectrically measured elementary process relaxation times lie at the onset (shortest relaxation times) of the mechanical process is a reasonable one. We can only speculate, but perhaps the higher temperature yet α' or α_{II} process results from enough accumulation of elementary steps to result in change of shape of the crystal and hence in mechanical activity directly assignable to the crystal fraction.

Prominence of the β Relaxation in LPE. Since there has been a great deal of discussion concerning the ease of detection of the β relaxation, it is worthwhile to recapitulate the reasons why the relaxation experimentally is not very prominent. First of all let it be reiterated that it is clearly present; the experiments all show that.[13,15,28-31] The question is why is it not more prominent in terms of loss peak heights or modulus increments compared to the γ

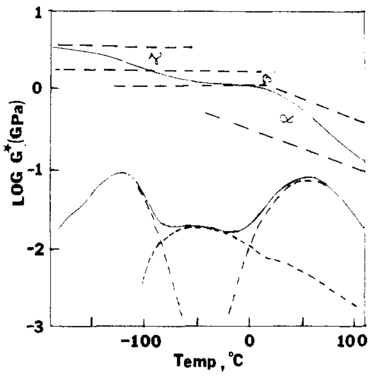

Figure 14. Resolution of the mechanical response of linear polyethylene (sample 5) into the component α, β, and γ processes. Superposed on the log G' curve are the unrelaxed and relaxed moduli $G_U(\gamma)$, $G_R(\gamma) = G_U(\beta)$, $G_R(\beta) = G_U(\alpha)$, and $G_R(\alpha)$ (Tables I-III). Superposed on log G'' are the individual contributions of the α, β, and γ processes.

and α processes. The analysis of the present work shows this to be the result of several factors operating in concert. First, the process is broad in the frequency domain. All crystalline polymers have very broad amorphous-phase glass-rubber relaxations but in LPE the β relaxation is somewhat more broad yet. Second, although the relaxed β-process modulus appears to be comparable to that of other crystalline polymers that have been investigated, the unrelaxed value is fairly low due to the γ process being rather strong. Thus the relaxation strength is reduced somewhat. Third, the proximity to the α process in isochronal scans tends to hide the modulus increment and also distort the loss peaks a bit. Finally we observe that many of the comments on the presence of the β process center on the effect of producing an extensive amorphous fraction via thermal treatment (i.e., quenching of ultrahigh molecular weight materials). Actually as shown in Figure 6 the observed relaxation strength *does* correlate quite well with crystallinity. The *relative* prominence of the α, β, and γ peak heights does not change much because *all three* correlate with crystallinity as amorphous processes. In Figure 14 we superpose several curves that help visualize the contributions of the various processes. On the G' curve are superposed the unrelaxed and relaxed moduli for the three processes. On the G'' curve are superposed the contributions of the individual α, β, and γ processes. The slight inflection on the high-temperature side of the β G'' curve is an artifact due to the discontinuity of the slopes of the relaxed β-process modulus at 290 K (Table III). This would no doubt disappear if a smoother representation of $G_R(\beta)$ with temperature were invoked. It is interesting to note that the maximum in $G''(\beta)$ is displaced to about 10 °C higher in temperature than the condition $\omega\tau = 1$ (appropriate for $\bar{\alpha}$ independent of temperature) would imply. The temperature dependence of $\bar{\alpha}$ is sufficient to result in noticeable displacement upwards.

Glass Temperature of Linear Polyethylene. In the semicrystalline polymers where experimental access to the completely amorphous condition can be made, it is clear the β (or α_a relaxation, the notation depending on the presence or absence of a crystalline-phase-dependent α relaxation) process in the semicrystalline specimens is the glass-rubber relaxation in the remaining amorphous fraction. It is much broader and the relaxed modulus is displaced dramatically upward but it is nevertheless directly traceable to a glass-rubber relaxation that occurs when the material is in the completely amorphous condition. In addition, another relaxation process occurs at lower temperatures in these polymers whether in the semicrystalline or completely amorphous state (and is largely or completely resident in the amorphous fraction when semicrystalline). Thus the γ (or β if no crystalline α is present) relaxation is best described as a subglass relaxation. The relative lack of sensitivity to morphological factors[5,14,18,19,25,26] (presence or absence of crystalline fraction) and the activation parameters[5,19,25,34] suggest that the γ relaxation has its origin in relatively localized molecular motions. On the basis of the results of the analysis of the present work we see no reason whatsoever to exclude linear polyethylene from this general picture. Describing its β relaxation as a glass-rubber relaxation is certainly conceptually attractive and sound, providing several caveats are appreciated. The term rubber is used advisedly since, although segmental motion has started, immobilization by the crystal phase keeps the relaxed amorphous-phase modulus very high in all semicrystalline polymers. If a crystalline α process is present, further relaxation of the amorphous fraction accompanies that process. To designate the γ process as the glass transition in LPE is justifiable only if one wishes to describe the more prominent amorphous-phase relaxation as the glass transition (and exclude the stronger α relaxation on the grounds above that it represents completion of softening). However, this unnecessarily places LPE out of context with respect to other semicrystalline polymers and with respect to mechanistic origins, and we do not recommend it. Finally, if one wished to assign T_g as a temperature at which the β process central relaxation time ($\tau_\beta{}^0$ in eq 2d) reaches some suitably large value, then the parameters of Table II give values in the neighborhood of −70 °C (for $\tau_\beta{}^0 = 1$ s). This in turn leads to a broad relaxation peak in the range −60 to −30 °C in 1-Hz isochronal temperature scans. It is to be emphasized that this figure pertains to the amorphous fraction as it behaves in crystalline specimens and not to a free unconstrained amorphous state. The latter material has been the subject of a number of investigations involving ultraquenching techniques[47-52] and appears to have a glass temperature significantly lower than that in the semicrystalline composite.

Acknowledgment. The author is indebted to the National Science Foundation, Division of Materials research, Polymers Program (Grant DMR 18326), for financial support of this work.

Registry No. Polyethylene (homopolymer), 9002-88-4.

References and Notes

(1) McCrum, N. G.; Read, B. E.; Williams, G. "Anelastic and Dielectric Effects in Polymeric Solids"; Wiley: New York, 1967.
(2) McCrum, N. G. In "Molecular Basis of Transitions and Relaxations"; Meier, D. J., Ed.; Michigan Molecular Institute: Midland, MI, 1978; Monograph No. 4.
(3) Eby, R. K. *J. Acoust. Soc. Am.* **1964**, *36*, 1485.
(4) Boyd, R. H.; Biliyar, K. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1973**, *14*, 329.
(5) Ashcraft, C. R.; Boyd, R. H. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 2153.
(6) Hoffman, J. D.; Williams, G.; Passaglia, E. *J. Polym. Sci., Part C* **1966**, *14*, 173.
(7) Tuijnman, C. A. F. *Polymer* **1963**, *4*, 259, 315.
(8) Booij, H. C. *J. Polym. Sci., Part C* **1967**, *16*, 1761.
(9) Mansfield, M.; Boyd, R. H. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1227.
(10) Boyer, R. F. *Macromolecules* **1973**, *6*, 288.
(11) Gaur, U.; Wunderlich, B. *Macromolecules* **1980**, *13*, 445.
(12) Davis, G. T.; Eby, R. K. *J. Appl. Phys.* **1973**, *44*, 4274.
(13) Illers, K. H. *Kolloid Z. Z. Polym.* **1969**, *231*, 622.
(14) Gray, R. W.; McCrum, N. G. *J. Polym. Sci., Part A-2* **1969**, *8*, 1329.
(15) Stehling, F. C.; Mandelkern, L. *Macromolecules* **1970**, *3*, 242.
(16) Boyd, R. H. *Polym. Eng. Sci.* **1979**, *19* 1015.
(17) Beatty, C. L.; Karasz, F. E. *J. Macromol. Sci., Rev. Macromol. Chem.* **1979**, *C17*, 37.

(18) Illers, K. H.; Breuer, H. *J. Colloid Sci.* **1963**, *18*, 1.
(19) Ishida, Y.; Yamafuji, K.; Ito, H.; Takayanagi, M. *Kolloid Z. Z. Polym.* **1962**, *184*, 97.
(20) McCrum, N. G. *J. Polym. Sci.* **1962**, *60*, 53.
(21) Scott, A. H.; Scheiber, D. J.; Curtis, A. J.; Lauritzen, J. I.; Hoffman, J. D. *J. Res. Natl. Bur. Stand., Sect. A* **1962**, *66A*, 269.
(22) Boyd, R. H.; Porter, C. H. *J. Polym. Sci., Part A-2* **1972**, *10*, 647.
(23) Schmieder, K.; Wolf, K. *Kolloid Z.* **1953**, *134*, 149.
(24) Phillips, P. J.; Emerson, F. A.; MacKnight, W. J. *Macromolecules* **1970**, *3*, 771.
(25) Boyd, R. H.; Aylwin, P. A. *Polymer* **1984**, *25*, 330.
(26) Boyd, R. H.; Aylwin, P. A. *Polymer* **1984**, *25*, 340.
(27) Boyd, R. H. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 493.
(28) Pechhold, W.; Eisele, U.; Knauss, G. *Kolloid Z. Z. Polym.* **1964**, *196*, 27.
(29) Crissman, J. M.; Passaglia, E. *J. Res. Natl. Bur. Stand., Sect. A* **1966**, *70A*, 225.
(30) Cooper, J. W.; McCrum, N. G. In "Advances in Polymer Science and Engineering"; Pae, K. D., Morrow, D. R., Chen, Y., Ed.; Plenum Press: New York, 1972; p 225.
(31) Illers, K. H. *Kolloid Z. Z. Polym.* **1973**, *251*, 394.
(32) Nakayasu, H.; Markovitz, H.; Plazek, D. J. *Trans. Soc. Rheol.* **1961**, *5*, 261.
(33) McCrum, N. G.; Morris, E. L. *Proc. R. Soc. London, Ser. A* **1966**, *292*, 506.
(34) Porter, C. H.; Boyd, R. H. *Macromolecules* **1971**, *4*, 589.
(35) Boyd, R. H. *J. Chem. Phys.* **1959**, *30*, 1276.
(36) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1941**, *9*, 341.
(37) Saito, S. *Kolloid Z. Z. Polym.* **1963**, *189*, 116.
(38) Ferry, J. D. "Viscoelastic Properties of Polymers", 2nd ed.; Wiley: New York, 1970.
(39) Tsai, S. W.; Halpin, J. C.; Pagano, N. J. "Composite Materials Workshop"; Technomic: Stamford, CT, 1968.
(40) Boyd, R. H.; Hasan, A. A. *Polymer* **1984**, *25*, 347.
(41) Yano, S.; Rahalkar, R. R.; Hunter, S. P.; Wang, C. H.; Boyd, R. H. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1877.
(42) Connor, T. M.; Read, B. E.; Williams, G. *J. Appl. Chem.* **1964**, *14*, 74.
(43) Buckley, C. P.; McCrum, N. G. *J. Mater. Sci.* **1973**, *8*, 928.
(44) Davies, G. R.; Owen, A. J.; Ward, I. M.; Gupta, V. B. *J. Macromol. Sci., Phys.* **1972**, *B6*, 215.
(45) Olf, H. G.; Peterlin, A. *J. Polym. Sci., Polym. Phys. Ed.* **1970**, *8*, 753, 771, 791.
(46) Opella, S. J.; Waugh, J. S. *J. Chem. Phys.* **1977**, *66*, 4919.
(47) Hendra, P. J.; Jobic, H. P.; Holland-Moritz, K. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 365.
(48) Boyer, R. F.; Snyder, R. G. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 315.
(49) Lam, R.; Geil, P. H. *Polym. Bull.* **1978**, *1*, 127; *J. Macromol. Sci., Phys.* **1981**, *B20*, 37.
(50) Jones, J. B.; Barenberg, S.; Geil, P. H. *Polymer* **1979**, *20*, 903.
(51) Cutler, D. J.; Glotin, M.; Hendra, P. J.; Jobic, H.; Holland-Mortiz, K.; Cudby, M. E. A.; Willis, H. A. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 907.
(52) Jones, J. B.; Barenberg, S.; Geil, P. H. *J. Macromol. Sci., Phys.* **1978**, *B15*, 329.

Free Volume and the Kinetics of Aging of Polymer Glasses

Richard E. Robertson[*]

Research Staff, Ford Motor Company, Dearborn, Michigan 48121

Robert Simha[†]

Department of Macromolecular Science, Case Western Reserve University,
Cleveland, Ohio 44106

John G. Curro[‡]

Sandia National Laboratories, Albuquerque, New Mexico 87185.

Received July 6, 1983

ABSTRACT: A model for predicting the kinetics of the physical aging of polymer glasses is further developed and is applied to the volume recovery of poly(vinyl acetate). The model is based on the stochastic model previously described by Robertson. It makes use of the free volume or hole fraction arising from the cell model developed by Simha and Somcynsky for equations of state of polymer liquids. The volume recovery predictions computed for poly(vinyl acetate) are compared with the data of Kovacs. Some of the apparent divergence noted by Kovacs between the effective retardation times on approach to equilibrium at a common temperature from different temperatures is explained.

Introduction

Physical aging can affect the properties of plastics and fiber composites years after manufacture. For this reason, many attempts have been made to describe as well as to understand the kinetics of the aging process. Several models exist that can describe many or even most of the characteristics of physical aging. Those most frequently applied to aging problems are related[1] and are the models of Kovacs[2,3] and of Moynihan.[4-6] These models are phenomenological and attempt only to describe formally the kinetics of aging. Two other models attempt to explain the kinetics as well. One if that of Curro, Lagasse, and Simha,[7] which is based on a hole diffusion process. The other is the stochastic model originally suggested by Robertson.[8-11]

In this report, the stochastic model will be explored further. First, we wish to derive the stochastic model for volume relaxation using the free volume suggested by Simha and Somcynsky's cell model for polymer liquids.[12] The free volume suggested by this model is the hole fraction that results from the minimization of the configurational Helmholtz free energy with respect to the hole fraction. The use of this definition of free volume and the resulting temperature coefficient has been shown to yield very satisfactory predictions of the time–temperature shift parameters during the aging of poly(methyl methacrylate) and poly(vinyl acetate) following a downward step in temperature.[13,14] Second, we wish to apply the stochastic model to the volume relaxation of poly(vinyl acetate) and to compare the computed results with the experimental data of Kovacs.[15]

Theory

Equation of State and Free Volume. To model the time-dependent volume contraction and dilatation following changes in temperature, we need the equilibrium volumes at the respective temperatures, the hole fractions or free volumes, and the fluctuations in free volume. These

---

[†] Supported by NSF Grant DMR-80-12232, Polymers Program.
[‡] Supported by U.S. DOE DE-AC04-76 DP00789.

0024-9297/84/2217-0911$01.50/0