prepared state is close to swelling equilibrium. Larger ratios lead to significant syneresis and opalescence; smaller values favor polymerization of large coils, which consequently overlap each other. In this latter condition a wide range of center-of-mass motions can arise that are similar in nature, although limited in space, to translational diffusion in an un-cross-linked solution. The effect of these overlapping regions can be understood schematically as follows. In the regions of the coil where there is no overlap, the relaxation of the "breathing", or gel, modes is simply determined by the osmotic pressure gradient and the polymer–solvent friction coefficient, i.e., by the solvent viscosity. For the overlapping regions participating in the same breathing mode, however, relaxation proceeds via the separation and rearrangement of the two constituent coils, which, on account of the polymer–polymer friction, is a much slower process. Since these modes also contribute to the concentration fluctuations, they scatter light, giving rise to a nonexponential signal. In gels in a good solvent, the cross-linking removes such slow modes, provided the samples are sufficiently swollen; this condition seems to be difficult to attain in Θ gels.

In conclusion, for the semidilute range of the Θ gels investigated previously, and reanalyzed here, as well as for those described in this paper, the collective diffusion coefficient *D* is in accord with the predictions of simple scaling. The same conclusion also applies to the concentration dependence of the shear modulus *G*. Unlike Θ solutions,[1] there is no angular dependence of *D*, because the network is permanent. No effects were observed of contributions of entanglements to *G*; this is consistent with the fact that the polymer chains are too short for entanglements to occur.

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Segmental Mobility in the Equilibrium Liquid below the Glass Transition

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ABSTRACT: Volume and enthalpy recovery data from near the glass transition temperature are suggested to be useful for indicating segmental mobility below the glass transition temperature in the equilibrium liquid. The procedure makes use of a recent theory by Robertson, Simha, and Curro for the kinetics of aging of polymer glasses. The theory is fitted to recovery data at temperatures above the glass transition, and then the time–temperature shift parameter is adjusted to obtain a fit to recovery data at temperatures below the glass transition. Segmental mobility can be estimated for temperatures below that of the measurement of recovery through the use of the free volume distribution arising from thermal fluctuations. The procedure was applied to poly(vinyl acetate), for which the rapid decrease in mobility on cooling from temperatures above the glass transition was found to moderate below the glass transition. This is suggested to arise from the influence of motions associated with lower temperature mechanical and dielectric loss peaks.

Introduction

How does the segmental mobility of the equilibrium liquid depend on temperature below the glass transition temperature? The segmental mobility above the glass transition temperature has long been known. For polymer liquids as well as for many small-molecule liquids in the 100 °C or so temperature range just above the glass transition, the temperature dependence of the segmental mobility, whether expressed as a viscosity or the reciprocal of the relaxation time, is well described by an equation of the form[1-5]

$$\log a_T = -c_1 + c_1 c_2/(T - T_g + c_2) \qquad (1)$$

where a_T is the time–temperature shift parameter, c_1 and

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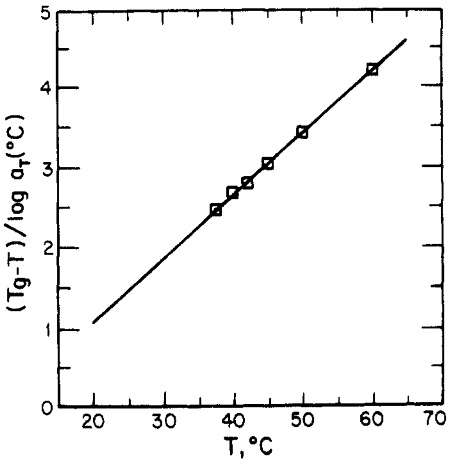

Figure 1. $(T_g - T)/\log a_T$ vs. temperature for poly(vinyl acetate). Data from Plazek[6] in the "softening region". The solid line is a linear least-squares fit to the data.

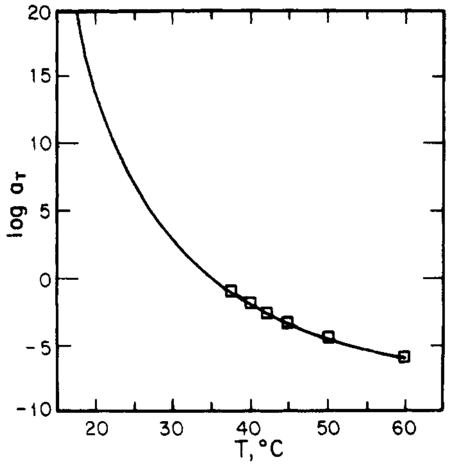

Figure 2. Time-temperature shift parameter, a_T, for poly(vinyl acetate) vs. temperature. Data from Plazek[6] in the "softening region". The solid line is from the least-squares fit in Figure 1.

c_2 are the WLF (Williams-Landel-Ferry) constants, T_g is the glass transition temperature, and T is the temperature. The quality of fit of eq 1 to the time-temperature shift parameters is demonstrated by the plot of $(T_g - T)/\log a_T$ vs. temperature in Figure 1 using data recently reported by Plazek for the "softening region" of poly(vinyl acetate).[6] The straight-line fit to the data in Figure 1 appears very good, good enough that an extrapolation below the glass transition temperature at 35 °C, if not down to the intercept with the abscissa at $T_g - c_2 = 6.26$ °C, seems warranted. (A least-squares fit of the straight line to this data yields $c_1 = 12.81$ from the slope of the line and $c_2 = 28.74$ °C from the intercept with $T_g = 35$ °C.) The corresponding time-temperature shift parameter extrapolated below the glass transition temperature is shown in Figure 2.

Several studies suggest, however, that the segmental mobility of the equilibrium liquid may deviate from the WLF behavior below the glass transition temperature. (Relaxation studies of the nonequilibrium glass below the glass transition, such as those summarized by Rusch[7] for poly(methyl methacrylate) and polystyrene, show deviation from WLF behavior. But these studies of the glass do not necessarily reflect the properties of the equilibrium structure. This difference was emphasized recently also by Hunston, Carter, and Rushford[8] in connection with epoxy resins.) In an early study of the equilibrium liquid below the glass transition, Kovacs, Stratton, and Ferry[9] measured the mechanical relaxation behavior of poly(vinyl acetate) specimens that had been aged or recovered below the glass transition. Their measurements, made over the temperature range of 31.25-39.2 °C, yielded a time-temperature shift parameter that could be described by eq 1 with $c_1 = 19.30$, $c_2 = 42.5$ °C, and $T_g = 35$ °C.

For comparing the different WLF constants, a convenient parameter is the slope at T_g of $\log a_T$ with temperature, which equals $-c_1/c_2$. The constants derived by Kovacs, Stratton, and Ferry yield the slope -0.45. The WLF constants often used for poly(vinyl acetate), which were obtained by Ferry, Williams, and Landel[10-12] from the temperature range of 45-90 °C, yield the slope of only -0.33. This would suggest that the time-temperature shift parameter a_T increases more rapidly with decrease in temperature below T_g than predicted by the WLF equation that describes behavior above T_g. On the other hand, the WLF constants derived by Plazek[6] for the softening region, 37.5-60 °C, yield the slope -0.44, which is effectively the same as that obtained by Kovacs et al.

A problem with these comparisons, however, is that the poly(vinyl acetate) employed in these studies was not the same. To overcome this problem, Lagasse and Letton[13] used the same poly(vinyl acetate) in their study of the mechanical relaxation in torsion over the temperature range 28-72 °C. The specimens used below the glass transition were again fully recovered, as was checked by remeasuring them after further days of aging. Lagasse and Letton found that the WLF constants that fit the time-temperature shift relationship above 40 °C did not fit it below, especially the points at 28, 32, and 35 °C. (T_g for this material was assumed to be 43 °C.) In this case, the shift parameter below T_g was smaller than that predicted by the WLF equation fitted above T_g.

Another reason for thinking that the segmental mobility may deviate from the WLF equation below the glass transition is that deviations above the glass transition have been found. For example, because of the onset of a new transition, Plazek[6] found that the WLF equation that described the time-temperature shift parameter in poly(vinyl acetate) over the softening range, 37.5-60 °C, could not describe it over the "terminal region", 75-155 °C.

The experimental approach of using recovered glasses has been limited to a relatively narrow temperature range below the glass transition. We attempt to show in this paper that it may be possible to look further below the glass transition by using data from the recovery process itself.

Prediction of the Recovery Kinetics

Equation 1 and the constants derived from Plazek's data for the softening region of poly(vinyl acetate) were used with the theory of Robertson, Simha, and Curro[14] for the kinetics of recovery or physical aging to compute the volume recovery of poly(vinyl acetate) following temperature steps (indicated as being from T_0 to T_1) in the vicinity of the glass transition temperature, 35 °C. The results of the calculation are shown in Figure 3 along with the experimental data obtained by Kovacs.[15] (To be able to show the calculated lines better, only about one-third of Kovac's data points are shown; the data were selected in a nonbiased way by choosing points that were at least a minimum distance away from points previously chosen.) Plotted along the ordinate is the effective relaxation time, τ_{eff}, which is related to the instantaneous volume V by

$$\tau_{\text{eff}}^{-1} = -(\mathrm{d}V/\mathrm{d}t)(V - V_1)^{-1} \qquad (2)$$

where V_1 denotes the equilibrium volume at the temper-

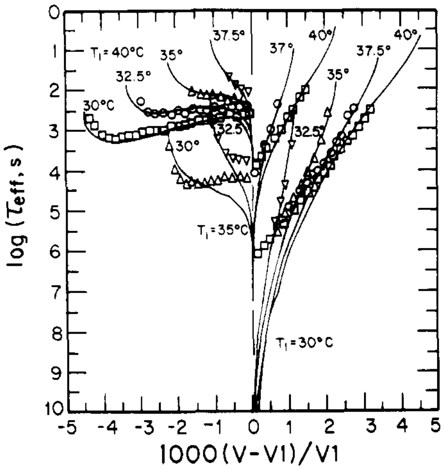

Figure 3. Effective relaxation times for volume recovery of poly(vinyl acetate) vs. deviation from equilibrium. Data from Kovacs.[15] Solid lines computed by using the time–temperature shift parameter in Figure 2.

ature T_1. Plotted along the abscissa is the relative deviation of the volume from equilibrium. The initial temperatures (T_0) for these experiments were 30, 32.5, 35, 37.5, and 40 °C. The final temperatures (T_1) were 30, 35, and 40 °C. All combinations of these initial and final temperatures were used for both the calculations and experiments in Figure 3. The upsteps (to 35 and 40 °C) are on the left side of Figure 3, and the downsteps (to 30 and 35 °C) are on the right.

Various assumptions are involved in these calculations, as discussed previously.[14] The major fitting parameters, besides the WLF parameters c_1 and c_2 and the Simha–Somcynsky characteristic parameters that describe the thermodynamic behavior of poly(vinyl acetate), p^*, V^*, and T^*, are the following: N_s, the number of segments (monomer units) needed to define the free volume or, at least, to define changes in free volume; z, the number of these regions, each containing N_s segments, that participate in changes in free volume; and R, a rate parameter that converts the equations from, basically, the macroscopic formulation to microscopic processes. The values used for N_s and z were those used previously (26 and 13, respectively). To obtain R, the calculated curves as a whole were shifted along the ordinate in Figure 3 to give the best fit to the experimental data (which gave $R = 0.0022$).

The fit in Figure 3 of the calculated curves to the data is remarkably good for all curves at early times, where the difference between V and V_1 is greatest. This fit, using the WLF parameters from Plazek's data in the softening region of poly(vinyl acetate), is much better than the fit obtained earlier,[14] where the WLF parameters derived from the work of Ferry, Williams, and Landel[10–12] were used. For the upper left set of four curves (for T_1 = 40 °C), the fit between the calculated curves and Kovacs' data is generally good over the entire range of V–V_1, except near $V = V_1$, where the data themselves lose accuracy. For the middle set of four curves (for T_1 = 35 °C), the fit is less satisfactory for the two curves on the left, a lack of fit noted earlier,[14] though the two on the right still fit the data fairly well. But the fit to the data of the lower right set of curves (for T_1 = 30 °C), with the possible exception of the curve for the step from 32.5 to 30 °C, is not good beyond early times. The theory predicts very long recovery times that are not exhibited by the experiments.

The very long recovery times predicted for the temperature step to 30 °C arise from the rapidly rising values of the time–temperature shift parameter a_T below the glass transition temperature at 35 °C (Figure 2). This is exacerbated by the distribution of free volume due to thermal fluctuations assumed by the theory. The distribution at 30 °C for the fractional free volume contained in 26-segment size regions, which was the size of the regions assumed in the calculation, is shown in Figure 4. (The distribution shown is that for 16 discrete amounts of free volume indicated by the squares. The ordinate refers to the probability of each of these discrete amounts.) Corresponding to each local free volume is a local relaxation time. The local relaxation time is assumed equal to that given by the time–temperature shift equation, in which the local free volume is simply substituted for the average free volume. That is, the range of local free volumes occurring at a given temperature is analogous to the range of average free volumes occurring over a range of temperatures. Hence, the time–temperature shift parameter for a range of temperatures can be sampled by a recovery experiment at a single temperature. It turns out that the calculated recovery at a single temperature is influenced by the time–temperature shift parameter nearly 10 °C below it. (Plazek[16] has recently attempted to describe the time–temperature shift parameter over both the softening and terminal regions of poly(vinyl acetate) by a single equation. The equation employs fractional powers for the temperature dependence. When used in the Robertson–Simha–Curro theory, however, this equation yields an even poorer fit to Kovacs' recovery data than that given in Figure 3.)

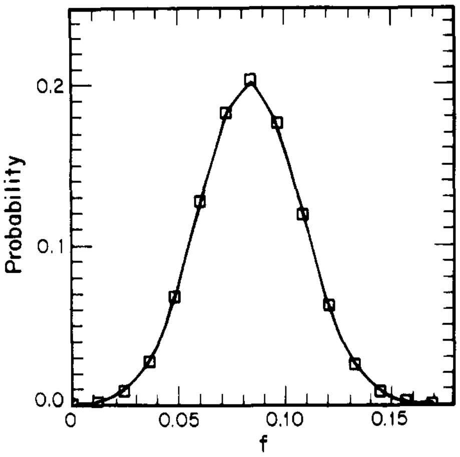

Figure 4. Distribution of free volume for regions containing 26 monomers.

Recovery Data and Sub-T_g Mobility

Since the above theory fits Kovacs' recovery data over much of the range for most curves in Figure 3, let us assume that the theory and free volume distribution are correct, but that the extrapolated time–temperature shift parameter shown in Figure 2 is not. A possible reason that the extrapolated shift parameter fails to describe recovery at low temperatures is that it fails to account for the segmental mobility associated with lower temperature loss peaks. Most amorphous polymers have dynamical mechanical or dielectric loss peaks below the glass transition. These loss peaks occur when the rate of the motion associated with them slows (or rises) to the rate of the detecting experiment. The temperatures at which these loss peaks occur, even in the equilibrium liquid, are usually noticeably different from that of the glass transition. This suggests that the motions associated with these loss peaks probably are not represented in the equation describing the fludity of the liquid above the glass transition. (Nor is it likely that these motions are a significant part of the fluidity of the liquid.) Yet, at least the first loss peak below the glass transition has been associated with structural recovery.[17-19] These loss peaks have been found to decrease in magnitude as recovery progresses.

Poly(vinyl acetate) has a transition, the β-transition, roughly 100 K below the glass transition,[20] and others may occur at lower temperatures. Although the β-transition occurs 100 K below the glass transition in the nonequilibrium glass, it would be expected to occur at a temperature closer to that of the glass transition in the equilibrium liquid just because the free volume changes much more rapidly with temperature in the equilibrium liquid than it does in the glass. As an estimate, the β-relaxation can be assumed to occur at a particular value of the Simha–Somcynsky free volume. At 208 K, the Simha–Somcynsky free volume of the common nonequilibrium poly(vinyl acetate) glass, which forms at 308 K, is estimated to be 6.97%. The extrapolated equilibrium liquid has this free volume at approximately 290 K or 18 K below the glass transition temperature. Thus, the β-relaxation is estimated to occur at roughly 17 °C in the equilibrium liquid rather than at −65 °C, as in the glass. Although purely thermal effects have not been considered explicitly here, some account of them has been taken because the Simha–Somcynsky free volume of the nonequilibrium glass changes with change in temperature below the glass transition.

Let us assume that the time–temperature shift parameter b_T associated with the β-relaxation has the same form in the equilibrium liquid as that for the glass transition given in eq 1 and write it as

$$\log b_T = -C_1 + C_1C_2/(T - T_g + C_2) \qquad (3)$$

where the glass transition temperature T_g is again used as the reference temperature. This is not the form usually associated with the β-transition. McCrum, Read, and Williams,[21] for example, note that the temperature dependence of the β-transition is Arrhenius in the glass. But in the equilibrium liquid, where the structure changes with change in temperature as it does above the glass transition, the β-transition motions probably show the same temperature dependence as the glass transition motions.

In the liquid near the glass transition, the motions associated with the glass and the β-transitions both contribute to the overall mobility. Let us assume that they are additive and write the overall mobility, or the reciprocal of the relaxation time, as

$$\begin{aligned} \tau^{-1} &= (\tau_g a_T)^{-1} + (\tau_b b_T)^{-1} \\ &= (\tau_g A_T)^{-1} \qquad (4) \end{aligned}$$

where τ_b is the relaxation time of the β-relaxation at T_g, and A_T is the time–temperature shift parameter that includes both types of motion. (Note that because of their definition, both a_T and b_T equal 1.0 at T_g.) The form chosen for eq 4 allows the β-transition related motions to dominate at low temperatures and yet to disappear at high temperatures.

Let us try to deduce the values for C_1 and C_2 in eq 3 and τ_b in eq 4 by improving the fit between the calculated and experimental recovery rates for the temperature step from 40 to 30 °C. An adequate fit to the volume recovery data of Kovacs for the temperature step from 40 to 30 °C seems to require that the computed relaxation curve in Figure 3 pivot about the point A, as indicated in Figure 5, so that it passes through the vicinity of C rather than B. (B and C refer to a recovery that is 90–95% complete. As with the other experiments, a fit between experiment and theory is not expected as equilibrium is approached further.)

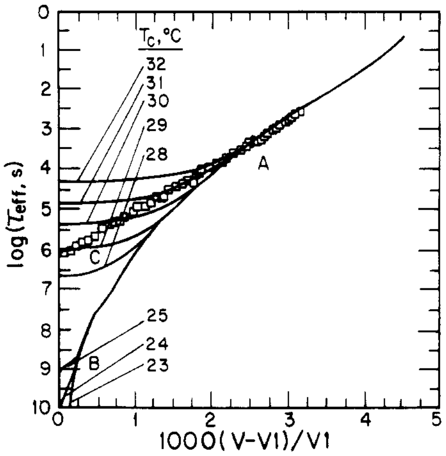

Figure 5. Effective relaxation times for the volume recovery of poly(vinyl acetate) for the temperature step from 40 to 30 °C. Data from Kovacs.[15] Solid lines computed with trial segmental mobility function.

For an initial survey of acceptable values for C_1, C_2, and τ_b, various constant values in lieu of $(\tau_b b_T)$ can be tried in eq 4. These values will be denoted by T_c, which is the temperature at which these values equal $\tau_g a_T$. The results of holding $\tau_b b_T$ constant, equal to the values of $\tau_g a_T$ at 32, 31, 30, 29, 28, 25, 24, and 23 °C, are shown by the solid curves in Figure 5.

None of the curves in Figure 5 are themselves a good fit to the data, but they can help to assign values to $\tau_b b_T$ vs. temperatures to obtain a good fit. As mentioned by Robertson, Simha, and Curro,[14] recovery of the equilibrium state following a temperature step occurs first among the segments with the highest free volume and then works its way down the free volume distribution to the segments with the lowest free volume. Thus each stage of the recovery can be associated roughly with a particular free volume, and each free volume can be associated with the temperature at which it is the global average in the equilibrium liquid. The correspondence between extent of recovery (the value of $(V - V_1)/V_1$) and temperature is made in Figure 5 by assigning the temperature T_c to the extent of recovery at which the curve associated with T_c deviates significantly from the curve associated with T_c = 23 °C, which is nearly the same as the curve based on only the glass transition motions (where $\tau_b b_T \approx 0$). In the region just beyond A in Figure 5, the best fit occurs if the computed recovery follows the curve denoted by T_c = 31 °C. Thus, $\tau_b b_T$ should equal $\tau_g a_T$ around 31 °C. But just beyond C in Figure 5, where the degree of recovery corresponds to 25 °C, $\tau_b b_T$ should be such that the sum in eq 4 yields a computed recovery curve near the curve in Figure 5 denoted by T_c = 29 °C. This suggests that at 25 °C, $\tau_b b_T$ should equal what $\tau_g a_T$ alone does around 29 °C. A somewhat better fit betwen theory and experiment is obtained, however, if at 25 °C, $\tau_b b_T$ equals what $\tau_g a_T$ alone does around 28 rather than 29 °C.

The above procedure is fairly fast and gives a good first approximation to the time–temperature shift parameter, but to obtain the shift parameter that gives the best fit between theory and experiment, some further adjusting may be needed. The functions $(\tau_b b_T)^{-1}$ and $(\tau_g a_T)^{-1}$ are shown schematically in Figure 6 vs. temperature. Because the ordinate in Figure 6 is logarithmic, the sum in eq 4 is essentially identical with $(\tau_b b_T)^{-1}$ for $T - T_g < -7$ °C and with $(\tau_g a_T)^{-1}$ for $T - T_g > -1$ °C.

A third equation is needed to define C_1, C_2, and τ_b. For this, $(\tau_b b_T)^{-1}$ is assumed small at temperatures above T_g,

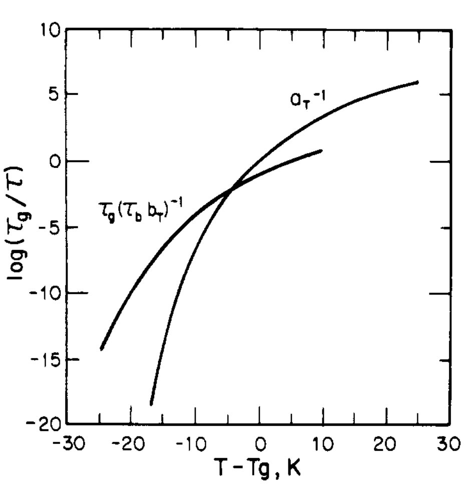

Figure 6. Segmental mobility, expressed as τ^{-1}, relative to that at the glass transition from the motions associated with the glass and β-transitions.

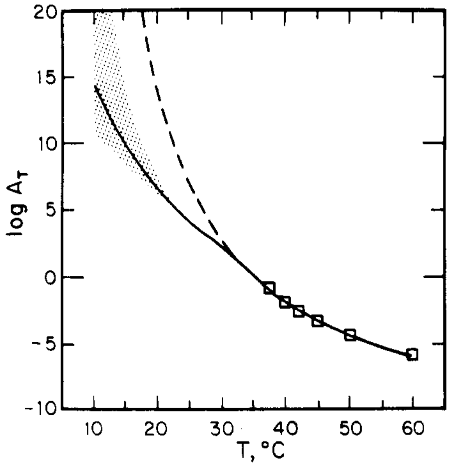

Figure 7. Time–temperature shift parameter for poly(vinyl acetate). The solid line is from eq 4 and the conditions in eq 5 with the further assumption that log $(\tau_b/\tau_g) = 1.0$. The shaded region indicates the range of shift parameters without the latter assumption. The dashed line is the WLF shift parameter derived from Plazek's data[6] alone.

where the mobility is well described by eq 1. The three conditions are, then

$$\text{(a) } \tau_b b_T = \tau_g a_T, \text{ at } 31\ ^\circ\text{C}$$

$$\text{(b) } \tau_b b_T \text{ at } 25\ ^\circ\text{C} = \tau_g a_T \text{ at } 28\ ^\circ\text{C}$$

$$\text{(c) } \tau_b b_T \gg \tau_g a_T, \text{ for } T > T_g \qquad (5)$$

Because of the first two conditions, the inequality in the last condition becomes $0.83 < \log(\tau_b/\tau_g) < 2.07$. This range can be narrowed further, reducing the upper limit to 1.18, by requiring that $C_2 > c_2$, i.e., by requiring that the mobility from the β-relaxation does not go to zero at a higher temperature than that from the glass transition.

Assuming $\log(\tau_b/\tau_g) = 1.0$, the conditions in eq 5 yield $C_1 = 11.24$ and $C_2 = 45.96$ °C. Over the temperature range from 60 °C down to 23 °C or lower, the time–temperature shift parameter for poly(vinyl acetate), denoted by A_T, is therefore suggested to vary with temperature as shown by the solid line in Figure 7. The WLF equation, eq 1, is shown as a dashed curve. The possible range of shift parameters allowed by the conditions in eq 5 is shown by the shading.

The time–temperature shift parameter indicated by the solid line in Figure 7 can be used to compute the volume recovery of poly(vinyl acetate) in the vicinity of the glass transition. The relaxation times computed, using values used previously[14] for all the other parameters, are shown in Figure 8. The fit to Kovacs' data is seen to be quite satisfactory. Using any of the other shift parameters falling within the shaded area in Figure 7 yields the same fit as in Figure 8 to Kovacs' data.

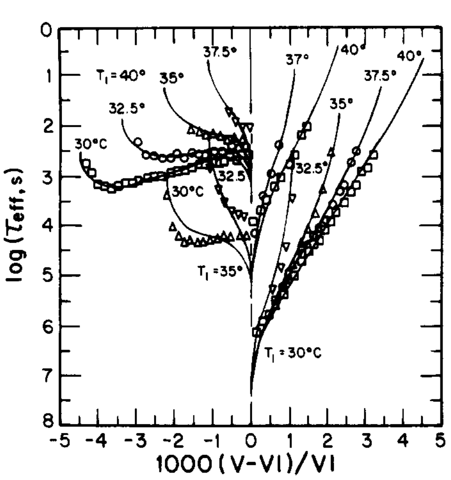

Figure 8. Effective relaxation times for volume recovery of poly(vinyl acetate) vs. deviation from equilibrium. Data from Kovacs.[15] Solid lines computed by using the time–temperature shift parameter indicated by the solid line in Figure 7.

Concluding Remarks

The above derivation of the low-temperature segmental mobility in the liquid depends on the correctness of the Robertson–Simha–Curro theory and the free volume distribution suggested.[14] Yet, as has been mentioned, the very good fit to the data at early times and at temperatures above T_g lends confidence to the theory and distribution.

This analysis was able to indicate segmental mobility at temperatures below those at which the measurements were made because of the distribution of free volume, of which Figure 4 is an example. For poly(vinyl acetate), the distribution suggested has allowed us to probe as much as 7 or 8 °C below the lowest temperature of measurement.

The deviation of the segmental mobility from the extrapolated WLF equation is suggested to be due to segmental motions associated with the first relaxation below the glass transition, the β-relaxation in poly(vinyl acetate). The loss peak for these motions, occurring where the motions slow to the measuring frequency, was estimated to occur in the extrapolated liquid at roughly 17 °C, or 18 °C below the glass transition. Presumably, lower temperature transitions should be considered near and below this temperature. The location of the β-loss peak was not specifically used in defining the composite shift parameter in Figure 7, mainly because knowing the location of the loss peak still does not determine the magnitude of the associated mobility. Nonetheless, it can be seen from Figures 6 or 7 that the shift parameter deduced for the β-motions is consistent with the estimate for the β-loss peak location in the equilibrium liquid.

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Effect of Absorbed Chemicals on the Local Mode Relaxation in Aliphatic Hydrocarbon Polymers

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ABSTRACT: Samples of low-density polyethylene, ethylene/propylene rubber, and 66 nylon were allowed to absorb various amounts of low molecular weight compounds, and their dynamic mechanical properties were measured. In several cases, the strength of the local mode relaxation was reduced, and the glass transition was shifted to markedly lower temperatures.

Introduction

In an earlier study,[1] it was found that the presence of up to 6.8% of various chemicals did not affect the temperature or strength of the γ-relaxation in poly(tetrafluoroethylene) (PTFE). Other relaxations which occur in the amorphous regions at higher temperatures were affected by the presence of absorbed chemicals. It was concluded that the γ-relaxation, which has been associated with the motion of short chain segments, in the amorphous regions[2] is entirely intramolecular.

The behavior of the γ-relaxation in PTFE is in sharp contrast with the effect of water or methanol on the γ-relaxation in 66 nylon.[3] In nylon, the γ-relaxation is reduced in strength and is shifted to slightly lower temperatures.[4] Water and methanol are antiplasticizers for nylon and increase its modulus at temperatures below the α-relaxation.[3] Dielectric studies[5] showed that absorbed water narrowed the γ-relaxation of nylon in the frequency domain, causing it eventually to approach the Debye model for a single relaxation time. It was concluded that at low temperatures water forms mechanically stable bridges between amide groups in adjacent chains, thus increasing the modulus and restricting the γ-relaxation to the motion of isolated polymethylene sequences between amide groups. Of course, the remaining dielectric activity indicates involvement of at least a few amide groups.

In view of the contrasting effects of absorbed chemicals on the local mode relaxations in PTFE and nylon, it was decided to investigate similar phenomena in polymers of ethylene and to study the effect of additional chemicals on nylon.

Experimental Section

Compression-molded bars of a low-density polyethylene (LDPE) having a density of 0.919 g/cm^3 after a standard cooling cycle were immersed in various solvents until the weight no longer increased. Other specimens were placed in closed jars with fixed amounts of solvents and equilibrated for times longer than those required to reach saturation. Similar experiments were performed on specimens of cured ethylene/propylene rubber (EPDM) having an ethylene/propylene mole ratio of 3.9. While this material was largely amorphous, it had an endothermal DSC peak at 54 °C, with a latent heat of 6.3 cal/g, corresponding to about 9% polyethylene-type crystallinity. Nylon studies were done on the oriented tape which had been used in earlier work.[3]

All samples were tested on the Du Pont 982 dynamic mechanical analyzer (DMA) coupled to the 1090 thermal analyzer.

Polymers of Ethylene

Initially, samples of low-density polyethylene were saturated with toluene, *n*-hexane, and isooctane, respectively. The dependence of the loss modulus on temperature is shown in Figure 1. The γ-relaxation at −115 °C was unaffected by the presence of 8.4% isooctane but largely suppressed in samples which had absorbed 14.9% toluene or 16.6% *n*-hexane. In all three cases, the β-relaxation was shifted to markedly lower temperatures.

Samples of LDPE were then allowed to absorb various amounts of toluene from 3.4% up to saturation. As shown in Figure 2, increasing levels of toluene progressively reduced the maximum in the loss modulus for the γ-relaxation with little change in temperature. The temperature of the β-relaxation shifted to lower temperatures as the amount of absorbed toluene was increased. A similar series with isooctane also showed a shift in the β-relaxation but no significant change in the γ-relaxation.

Because cross-linked ethylene/propylene rubber (EPDM) is highly amorphous, it is possible to study higher levels of absorbed toluene. The plots of loss modulus in Figure 3 show that as in LDPE, toluene lowered the peak height for the γ-relaxation and shifted the β-relaxation to lower temperatures. The pattern seems to change somewhat beyond 8% toluene.

Actually, the data for LDPE and EPDM fit together quite well. The maxima in loss modulus for the γ-relaxation follow the same relationship (Figure 4). The peak height decreases up to 8–10% toluene (dry basis) and then

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