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Viscoelastic Properties of Amorphous Polymers. 1. Different Temperature Dependences of Segmental Relaxation and Terminal Dispersion

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ABSTRACT: Two drastically different temperature dependences of the segmental relaxation and terminal dispersion previously observed in entangled polystyrene, poly(vinyl acetate), and polypropylene were explained before in the framework of the coupling model as due to the large difference between the segmental motion coupling parameter, n_α, and the entanglement coupling parameter, n_η, in these polymers, with n_α being significantly larger. The n_α for a polyisobutylene was found recently to be the smallest among amorphous polymers, and its value is comparable to that of n_η. As a consequence the coupling model requires that the temperature dependences for segmental relaxation (near the glassy level) and the terminal dispersion be similar. Viscoelastic measurements were carried out in a high molecular weight (entangled) polyisobutylene sample to verify this clear prediction. The experimental results presented here have borne out the theoretical expectations.

Introduction

In the past years creep measurements made on linear polymers using a torsional creep and recovery apparatus have revealed several anomalous properties in their viscoelastic spectra.[1-4] These anomalous properties have been found in many different polymers, appear to be general, and have been confirmed repeatedly throughout the years by others.[5-18] They can be considered as different manifestations of the surprising fact that in entangled linear polymers several viscoelastic mechanisms including the segmental motion responsible for the glass temperature T_g, the modified Rouse modes[19] contributing to the softening (glass to rubberlike) viscoelastic dispersion, and the terminal (rubberlike to steady-state) dispersion can all exhibit different time-scale shift factors.[1-3,6-8,10-18] In low molecular weight unentangled analogues[4,5,9,16-18,20,21] the different temperature dependences are observed together with drastic changes in the viscoelastic spectrum with temperature. The data indicate the loss of contributions from modified Rouse modes for undiluted and unentangled polymers with the longest retardation times. These are spectacular anomalies because they are not expected from traditional concepts in the viscoelasticity of amorphous polymers. They are also important because fundamental properties of the viscoelastic mechanisms are involved. In spite of their importance as basic issues, it is remarkable that except for applications of the coupling model[10,12,16,20,22] there has been no other serious attempt to explain them.

The coupling model has been applied before to explain extant experimental data from measurements made earlier on polystyrene (PS)[10] and poly(vinyl acetate) (PVAc)[10] and more recently on amorphous polypropylene (a-PP).[12] The anomalous viscoelastic properties observed in all three polymers are similar. The explanations offered by the coupling model are quantitative and are based on comparisons of the size of the coupling parameter of segmental motions n_α with those of other viscoelastic mechanisms. The three polymers mentioned above have comparable values of n_α, 0.64 for PS, 0.57 for PVAc, and 0.64 for a-PP. As a consequence the deviations from thermorheological simplicity expected from the coupling model for these three polymers are rather similar, as was observed experimentally. Good quantitative agreement between the predictions and the experimental data was obtained in each case.

Recently a comprehensive study of segmental relaxation over many amorphous polymers has uncovered a remarkable correlation between the time and temperature dependences of segmental motion in amorphous polymers.[23] The results of this study clearly indicate that there are amorphous polymers like polyisobutylene (PIB) that have significantly smaller values of n_α. The interesting relation of n_α to molecular structure will be the subject of a future publication. Measurements required to observe the viscoelastic anomalies found in PS, PVAc, and a-PP have not been performed on those polymers with low n_α. It was anticipated on the basis of the coupling model that PIB would exhibit very different viscoelastic properties than PS. In a series of papers of which this is the first, we shall discuss these predictions and present the shear creep and recovery measurements made in response to these predictions. This paper will focus on the difference between the temperature dependences of the segmental motions and the terminal dispersion of linear entangled amorphous polymers.[1-3,7,8,11,12,14,15,17-19] This difference was observed in PS, PVAc, and a-PP and previously explained by the coupling model.[10] We shall show that the coupling model predicts this difference should not be seen in the behavior of a high molecular weight linear PIB. New creep and creep recovery measurements have been carried out on a PIB sample to test the prediction.

Expectation for PIB

For "thermorheological simple behavior" there is only one friction factor ζ_0 for all viscoelastic mechanisms from the glassy level to the terminal flow region.[17-19] Hence, all contributions to any viscoelastic function from the various mechanisms will shift by the same amount on a log time/frequency axis when the temperature is changed. Viscoelastic mechanisms of a polymer extend over many decades of time or frequency scale at any temperature. Instruments used in the measurement of viscoelastic

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behavior have finite time/frequency windows, and they usually cannot monitor two different but widely separated groups of viscoelastic mechanisms at a single temperature. This makes it difficult to check for thermorheological simplicity. If this simplicity obtains, measurements made at different temperatures will yield an extended reduced curve of response when the curve segments are shifted along the logarithmic time/frequency scale to superpose onto the curve measured at an arbitrary chosen reference temperature T_0. It is possible to obtain apparently successful but fallacious superposition particularly if the time/frequency window is narrow. Using a torsional creep and recovery apparatus with a window of about 5 decades of time (1 s to 1 day) it was possible to see that the vinyl polymers PS and PVAc were not thermorheologically simple.[1-4] The softening dispersion has a different temperature dependence of the time-scale shift factors ($a_{T,\mathrm{s}}$ or $a_{T,\alpha}$) from that of the terminal dispersion ($a_{T,\mathrm{w}}$) which is experimentally identical with that of the viscosity $a_{T,\eta}$. However even with the same apparatus no significant departure from successful superposition in a-PP[11] was observed, though it was seen that $a_{T,\alpha}$ has a different temperature dependence from that of the viscosity $a_{T,\eta}$. In fact the last conclusion was arrived at for a-PP and a fortiori for PS and PVAc[24] by a separate series of viscosity measurements made following the attainment of steady-state flow at a higher temperature. With the constant torque maintained, the temperature was changed and equilibrated at a number of temperatures down to the lowest temperatures which overlap the range where $a_{T,\alpha}$ was determined. With the help of very high viscosity data taken by the procedure described it has been possible to show significantly smaller values of $a_{T,\eta}$ than those obtained from the segmental orientation. This remarkable viscoelastic property of these vinyl amorphous polymers has been confirmed by other workers in many other polymers and appears to be general.[7,8,12,14,15]

A quantitative explanation of the difference in the temperature dependences of the segmental relaxation and the terminal dispersion was given 6 years ago by us.[10] The details can be found in refs 10, 12, and 14. Hence, only the essentials will be summarized. For entangled monodisperse linear polymer melts, the *entanglement* coupling between the chains is described in the coupling model by a coupling parameter n_η. From the shape of the terminal dispersion[22,25] we have determined its value to lie within the bounds of

$$0.40 \leq n_\eta \leq 0.45 \tag{1}$$

The value of n_η is independent of the molecular structure of the polymer because entanglement involves a length scale much larger then the size of the monomer unit. The local segmental relaxation involves *crowding* coupling between the relaxing monomeric units. Its crowding coupling parameter, n_α, depends on the intermolecular couplings between the monomers and in turn on the molecular structure of the monomer. Strong intermolecular coupling and hence large n_α are expected for polymers with polar side groups such as PVC or inflexible side groups involving carbon double bonds such as 1,2-polybutadiene (e.g., poly(vinylethylene) (PVE)). Moderate intermolecular coupling and intermediate n_α is expected for vinyl polymers with reasonably flexible side groups such as PS, PVAc, PMA, and a-PP. Weak intermolecular coupling and small n_α will occur in "symmetric" and "smooth" polymers such as polyisobutylene (PIB). Further detailed discussion of the correlation between n_α and monomer molecular structure is outside the scope of this work. The crowding coupling parameter n_α has been determined from the experimental data for many amorphous polymers.[23] They in fact exhibit the expected trend with molecular structure. For example, $n_\alpha = 0.77$ for PVC,[26] 0.73 for PVE,[27] 0.63 for PS,[10] 0.57 for PVAc,[10] and about 0.45 for PIB.[23] The crowding coupling parameters, n_α, for different polymers were determined from experimental data in several ways. One way is to fit stress relaxation modulus data arising from segmental motion by the function $G(t) = (G_\mathrm{g} - G_\mathrm{e}) \exp[-(t/\tau^*)^{1-n_\alpha}] + G_\mathrm{e}$, where G_g is the glassy modulus and G_e is the equilibrium modulus for segmental motion. Another way is to fit shear creep compliance data by the corresponding expression $J(t) = J_\mathrm{g} + (J_\mathrm{e}^\mathrm{s} - J_\mathrm{g})[1 - \exp(-(t/\tau^*)^{1-n_\alpha})]$, where J_g is the glassy compliance and J_e^s is the long time limit of the contribution of the segmental motions to the compliance. Dynamic modulus $G^*(\omega)$ and compliance $J^*(\omega)$ data were used whenever available to determine n_α by fitting the shape of the loss modulus or compliance spectra with the corresponding viscoelastic functions obtainable from the Fourier transforms of the expression for $G(t)$ and $J(t)$ given above. Photon correlation spectroscopic data if available also provide a direct measure of n_α through the autocorrelation function, which is directly measured. Dielectric relaxation data offer additional information for the value of n_α, although we must be aware of the fact that in some polymers dielectric relaxation is not identical with mechanical relaxation.[28] The values of n_α for most amorphous polymers have been determined with confidence. The value of n_α for PIB is less certain because a monomer of PIB has a very small dipole moment and reliable dielectric relaxation data that can be interpreted with certainty are not available. Mechanical relaxation and compliance data of PIB are complicated by the difficulty of isolating the contribution of the local segmental motion from those of the various sub-Rouse modes that become prominent. Photon correlation spectroscopy data[29] of PIB give an estimate that $0.50 > n_\alpha > 0.45$. The value of 0.45 for n_α is consistent with that deduced by linear extrapolation of the correlation of the temperature sensitivity, d log a_T/d(T_g/T) where a_T is the temperature shift factor of segmental relaxation, determined at T_g with n_α established by the collection of other amorphous polymers (see Figure 2 of ref 23) and with that obtained from the anomalous momentum transfer dependence of the local chain motion observed by quasi-elastic neutron scattering.[30]

In the coupling model there is one underlying average friction coefficient $\zeta_0(T)$ for all viscoelastic mechanisms. This, indeed, would be the friction coefficient that governs the temperature dependence of the entire viscoelastic spectrum if none of the viscoelastic mechanisms involves cooperative dynamics caused by coupling between the relaxing units. However, we know at least this is not true for the local segmental motion (due to crowding couplings) and the terminal dispersion (due to entanglement coupling) if the polymer is entangled. One consequence[8,10,14] of the coupled nature of the relaxation is that the shift factor $a_{T,\eta}$ for the viscosity is no longer $[\zeta_0(T)/\zeta_0(T_0)]$ where $\zeta_0(T_0)$ is the friction coefficient at the chosen reference temperature T_0 but is given by the coupling model as (see eq 23 of ref 10)

$$a_{T,\eta} = [\zeta_0(T)/\zeta_0(T_0)]^{1/(1-n_\eta)} \tag{2}$$

Similarly, the shift factor $a_{T,\alpha}$ for the local segmental motion is given by the expression

$$a_{T,\alpha} = [\zeta_0(T)/\zeta_0(T_0)]^{1/(1-n_\alpha)} \tag{3}$$

(see eq 26 of ref 10).

The two shift factors are related by the expression

$$\frac{\log a_{T,\alpha}}{\log a_{T,\eta}} = \frac{1-n_\eta}{1-n_\alpha} \tag{4}$$

(see eq 29 of ref 10). With n_η given by eq 1 for all polymers and n_α individually known for many amorphous polymers, eq 4 provides not only an explanation of two temperature dependences whenever $n_\alpha > n_\eta$ but also a quantitative test of the coupling model by comparing it with the experimental data. Values of n_α given earlier for PS, PVAc, and a-PP are significantly larger than n_η. Equation 4 predicts the shift factor $a_{T,\alpha}$ varies more rapidly with temperature than $a_{T,\eta}$, rendering the viscoelastic spectrum thermorheological complex as observed in these polymers. Moreover, quantitative tests of eq 4 are satisfactory for all three polymers (see Figures 3–7 of ref 10 and Figure 3 of ref 12).

PIB provides another critical test of the explanation offered by the coupling model. The crowding coupling parameter n_α of PIB has the value of about 0.45. It is the smallest among the currently known amorphous polymers and is comparable to the value of n_η for all linear polymers as given by eq 1. Following from eq 4, an immediate consequence of the comparable sizes of n_α and n_η is that for PIB the two shift factors $a_{T,\alpha}$ and $a_{T,\eta}$ are nearly the same. Therefore, eq 4 predicts that, in contrast to the vinyl polymers investigated before, PIB should be thermorheologically simple. The measurements to be reported here were made on a sample of high molecular weight PIB to test this prediction.

Experimental Procedures

Torsional creep and recovery measurements were carried out with a magnetic-bearing apparatus[1-4] with a PIB specimen with a narrow molecular weight distribution and a weight-average molecular weight of 78 500. This PIB (E-19) was obtained through the kindness of Roger Porter. It was chromatographically fractionated at the Chevron Corp. about 20 years ago. It has subsequently been kept in a freezer to avoid degradation. Its heterogeneity ratio M_w/M_n is believed to be less than 1.05. Preliminary creep measurements were made by *N.* Raghupathi at the University of Pittsburgh in 1971, but during the remeasurement it was discovered that the lower temperatures were in error.

When viscosities are above 10^{10} P, inordinately long times are required to reach steady state. Before steady state is attained in the terminal zone of response of a viscoelastic liquid, the accumulating deformation observed during creep is composed of both recoverable and permanent deformation. An extrapolation procedure proposed by Ninomiya[31] can be used to estimate the viscosity at times that are within 1, perhaps 2, decades away from achieving the limiting amount of orientation per unit of applied creep stress, which constitutes steady state. An alternative technique to achieve steady state in a short time was suggested by Leaderman et al.[32] A relatively high temperature of creep is chosen where steady state is achieved in a matter of minutes. While maintaining the constant applied stress in the sample, the temperature is lowered to that desired. Thus the orientation and steady state is maintained and the constant velocity measured yields the viscosity.

$$\lim_{t\to\infty} \frac{\mathrm{d}J(t)}{\mathrm{d}t} = \frac{1}{\eta}$$

A unique creep recovery can be measured at the chosen temperature by setting the stress on the sample to zero. The viscosities obtained at −26.5 °C and below were obtained in the preceding manner.

Results and Discussion

The recoverable creep compliance, $J_r(t)$, curves are shown in Figure 1. Curves are presented for 10 temperatures from −76.7 to +62.9 °C. The $J_r(t)$ curves are shifted along the time scale by the temperature-dependent shift factor a_T to superpose at the chosen reference temperature of −72.6 °C. In this manner, measurements made at different temperatures yield an extended reduced curve of response. It can be seen in Figure 2 that such a reduction is successful from the glassy state to the terminal zone. This success in high molecular weight PIB should be contrasted with the failures in high molecular weight PS,[1,18,33] PVAc,[3,18] and a-PP.[11] The set of shift factors a_T obtained from the temperature reduction of the log $J_r(t)$ vs log t curves in Figure 1 are plotted in Figure 3. The $J_r(t)$ curves measured, as well as the associated shift factors a_T (see Table I) obtained, at lower temperatures are related to the local segmental motions and the softening dispersion. On the other hand, the same quantities determined at higher temperature are related to terminal dispersion recovery data. The terminal dispersion fits well to a stretched exponential form of $J_r(t) = J_N + (J_e{}^\circ - J_N)[1 - \exp[-(t/\tau_\eta{}^*)^{1-n_\eta}]]$ with $n_\eta = 0.45$, $J_N \simeq 5.6 \times 10^{-7}$ cm^2/dyn, and $J_e{}^\circ = 1.78 \times 10^{-6}$ cm^2/dyn. In this manner we have determined the entanglement coupling parameter n_η for PIB. Its value is consistent with the bounds defined by inequalities in eq 1 established by analysis of the terminal dispersions of various monodisperse entangled linear polymers other than PIB. As mentioned before, unlike the situations in other polymers, in PIB the sub-Rouse modes make prominent but separate contributions to $J_r(t)$ down to the low compliance portion of the softening dispersion. It is difficult to isolate unambiguously the

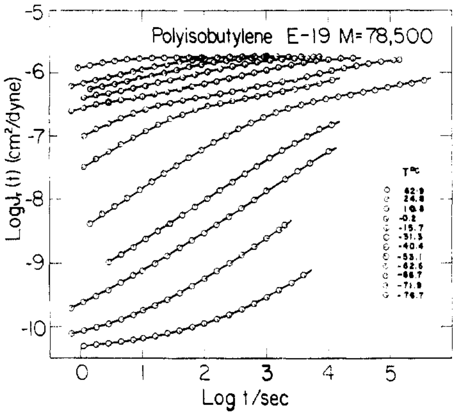

Figure 1. Logarithmic plot of the recoverable creep compliance curves for polyisobutylene E-19 with a M_w = 78 500 measured at 12 temperatures between −76.7 and +62.9 °C as a function of the logarithmic time.

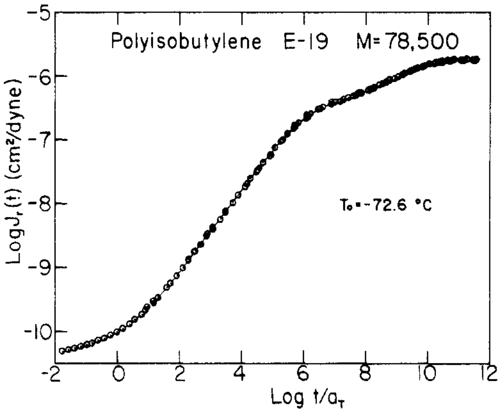

Figure 2. Data of PIB E-19 from Figure 1 plotted against the logarithm of the reduced time scale where the chosen reference temperature T_0 is −72.6 °C. T_0 is believed to be the T_g for a rate cooling of 0.2 °C/min. The temperature key is given in Figure 1.

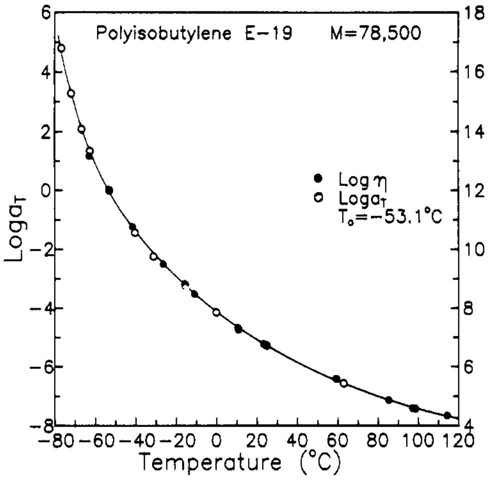

Figure 3. Comparison of the logarithm of the viscosity, η, and the temperature shift factors, a_T, obtained in the reduction of the recoverable compliance curves for PIB E-19. T_0 for the a_T values was chosen as −53.1 °C. log η and log a_T values are given in Table I.

Table I
Temperature Dependences

temp (°C)	log η (P)	temp (°C)	log a_T
114.3	4.35	62.9	−6.57
98.6	4.58	24.8	−5.28
97.0	4.596	10.8	−4.73
85.2	4.87	−0.2	−4.15
59.4	5.59	−15.7	−3.20
59.0	5.59	−31.3	−2.25
24.8	6.743	−40.4	−1.44
23.1	6.78	−53.1	0.00
10.5	7.332	−62.6	1.35
−11.0	8.475	−66.7	2.09
−15.7	8.748	−71.9	3.27
−26.5	9.496	−76.7	4.80
−41.6	10.76		
−53.1	11.986		
−63.0	13.17		

contribution of the local segmental motion from the experimental data of $J_r(t)$. For this reason, we have not attempted to determine the local segmental coupling parameter, n_α, by fitting the data of $J_r(t)$ above the glassy compliance, J_g. We rely on other experimental methods[23,29,30] for the determination of the value of n_α which is about 0.45. On comparing the values of n_η and n_α so determined for PIB, we conclude they are almost identical.

The viscosity at various temperatures obtained in some cases by a series of separate determinations down to −63.0 °C near T_g are also plotted in Figure 3. The temperature dependence of the viscosity is nearly the same as that of a_T obtained from $J_r(t)$ measurements. We emphasize that the viscosity and the shift factor of local segmental motion were obtained in a common temperature range which includes temperatures close to T_g.

This behavior in PIB is to be contrasted with that in PS, PVAc, and a-PP which displayed two *different* shift factors $a_{T,\eta}$ and $a_{T,s}$ for η and $J_r(t)$, respectively, in the temperature range approximately defined by

$$T_g < T < T_g + 20\ °\mathrm{C} \qquad (5)$$

The differences between the temperature dependences of $a_{T,s}$ and $a_{T,\eta}$ in PS, PVAc, and a-PP are substantial, with $a_{T,s}$ having a much stronger temperature dependence near T_g. This behavior is illustrated in Figure 4 for three PS samples with different molecular weights. The striking difference in the temperature dependences of viscoelastic mechanisms between PIB and the other polymers becomes evident when Figures 3 and 4 are compared.

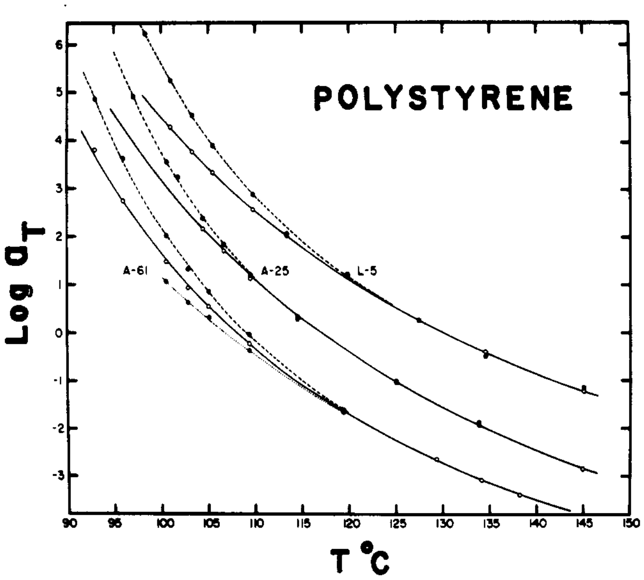

Figure 4. Logarithm of the temperature shift factors presented as a function of temperature for the anionically polymerized polystyrenes with narrow molecular weight distributions: (○ on solid lines) obtained from viscosity measurements; (● on dashed lines) obtained from recoverable compliance measurements in the softening dispersion; (● on the dotted line) $a_T = \eta J_e°/\eta_0 J_{e0}°$. The samples studied were L-5 with $M_v = 1.22 \times 10^5$, A-25 with $M_v = 4.7 \times 10^4$, and A-61 with $M_v = 4.7 \times 10^4$.

Near T_g, the $J_r(t)$ curves obtained in our torsional creep apparatus are related to the local segmental motion, and $a_{T,s}$ can be identified with $a_{T,\alpha}$ introduced earlier in eq 3. The substantial differences between $a_{T,s}$ and $a_{T,\eta}$ observed in PS, PVAc, and a-PP have been explained[10,12,14,15] in each case by eq 4, which comes as a prediction from the coupling model. In these three polymers the coupling parameters n_α are known and they all are significantly larger than n_η. The differences between $a_{T,s}$ and $a_{T,\eta}$ as predicted from eq 4 are in good agreement with the experimental data.[1-8,11-15] On the other hand, for PIB it is clear by inspection of Figure 3 that the two shift factors $a_{T,s}$ and $a_{T,\eta}$ of PIB are almost the same. This is also predicted by the coupling model through eq 4 together with the fact that n_α for PIB has approximately the same value as n_η. Experimentally, the absence of two distinct temperature dependences of the shift factors in PIB is remarkable because the highest viscosity reached in the present work is 1.5×10^{13} P, which is about 1 order of magnitude higher than that reached in PS[24] and a-PP.[11] As mentioned earlier, the prediction of this result was made before the experimental measurements reported here were carried out. The data indeed have verified the prediction. This is the main thrust of this paper.

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