Viscoelastic Properties of Amorphous Polymers. 2. Anomalous Temperature Dependence of the Steady-State Recoverable Compliance in Low Molecular Weight Polymers

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ABSTRACT: Previous study of the viscoelastic behavior of low molecular weight polystyrenes found that the steady-state recoverable compliance, $J_e°$, decreased markedly with temperature as the glass temperature, T_g, was approached from above. This anomalous viscoelastic property of polystyrene was explained by a model of coupled molecular motions. Application of the coupling model to low molecular weight polyisobutylene (PIB) leads to the prediction that the anomalous marked decrease of $J_e°$ will *not* be observed in PIB. This prediction made for the behavior of polyisobutylene was verified by new creep recovery measurements on a specimen of low molecular weight. The physical reasons for the observation of a breakdown of the Rouse model (modified for undiluted polymers) for low molecular weight polystyrene and the absence of it in polyisobutylene are given. The explanation, based on the coupling model, is illucidated by detailed comparisons between the viscoelastic properties of polystyrene and polyisobutylene.

Introduction

In the first[1] of a current series of papers (1) addressing critical issues of viscoelastic properties of amorphous polymers, we focused on the difference in the temperature dependences of the local segmental relaxation and the terminal dispersion of high molecular weight entangled linear polymers. Experimentally, it was found in entangled polystyrene (PS),[2] poly(vinyl acetate) (PVAc),[3] atatic polypropylene (a-PP),[4] and poly(cyclohexyl methacrylate) (PCHMA)[5] that the local segmental motion has a temperature dependence (as measured by the time-scale shift factor, $a_{T,\alpha}$) stronger than that of the terminal dispersion. The latter, $a_{T,w}$, is experimentally identical with that of the viscosity $a_{T,\eta}$. This feature of viscoelasticity has been explained by the coupling model which is applicable to both the crowded local segmental dynamics and to the entangled chain dynamics. Both viscoelastic mechanisms involve cooperative dynamics, albeit different in nature. They are characterized by two different coupling parameters n_α and n_η which are not arbitrary adjustable parameters but can be determined directly from the time/frequency dependences of the viscoelastic mechanisms obtained by various spectroscopies.[1] The two shift factors are related by the expression[1]

$$\log a_{T,\alpha}/\log a_{T,\eta} = (1 - n_\eta)/(1 - n_\alpha) \qquad (1)$$

There are many amorphous polymers including PS, PVAc, a-PP, and PCHMA (see also ref 6) in which n_α is significantly larger than n_η, and eq 1 was able to explain[7] quantitatively the experimental fact that $a_{T,\alpha}$ is much larger in magnitude than $a_{T,\eta}$. The emphasis in paper 1 is on polyisobutylene (PIB) which has the smallest n_α known for amorphous polymers to date, and its value is comparable to n_η, i.e. $n_\alpha \simeq n_\eta$. As a consequence of this, eq 1 predicts $\log a_{T,\alpha} \simeq \log a_{T,\eta}$ and thermorheological simplicity is preserved. New viscoelastic measurements presented in paper 1 have verified this prediction for PIB.

The difference between $a_{T,\alpha}$ and $a_{T,\eta}$ is expected from eq 1 to be more dramatic in low molecular weight unentangled polymers[8] because there is no entanglement coupling therein and $n_\eta = 0$. For amorphous polymers such as PS and PPMS, which have larger n_α, $a_{T,\alpha}$ is much larger than $a_{T,\eta}$. Therefore the relaxation time, τ_α*, of the local segmental motion will increase more rapidly than the relaxation times, τ_p's, of the Rouse chain normal modes $p = 1, ..., N$ (modified by Ferry for undiluted polymer[9]) as T approaches the glass temperature T_g from above. Henceforth whenever the Rouse model is mentioned in this work, we mean the Rouse model modified for undiluted polymers. The rapid encroachment in time scale of τ_α* into τ_p's causes a breakdown of the Rouse model because in the Rouse model the temperature dependences of τ_α* and the τ_p's should be the same and be governed by the same monomeric friction coefficient. Previously, we have shown, as a consequence of encroachment in time scale of the local segmental motion toward the Rouse modes, some of the long wavelength normal modes may not survive.[8] The survival probability of the pth mode is a rapidly decreasing function of decreasing p and increasing ratio of the relaxation times, τ_α^*/τ_N, where τ_N is τ_p for $p = N$ and N is the number of submolecules that make up the chain. Hence, on a decrease in temperature the long wavelength normal modes cannot survive, and these viscoelastic mechanisms are lost, resulting in a rapid drop of the recoverable compliance, J_e. This anomalous but marked decrease of J_e with decreasing temperature and the loss of retardation mechanisms were first observed experimentally in a low molecular weight PS.[10] This loss is confirmed by the dynamic viscoelastic measurements on PS of Gray et al.,[11] by the recoverable compliance measurements on poly(propylene glycol) of Cochrane et al.[12] and by the dielectric relaxation measurements on poly(propylene glycol)[13,14] and polyisoprene[15] of Schlosser and Schönhals.

Among amorphous polymers studied so far, PIB has the smallest coupling parameter[1,6] (approximately equal to 0.45) for local segmental relaxation, n_α. This distinctive property of PIB is thought to originate from its symmetric and compact monomeric molecular structure which minimizes intermolecular coupling and hence requires a small n_α. From eq 1 small n_α means the two shift factors, $a_{T,\alpha}$

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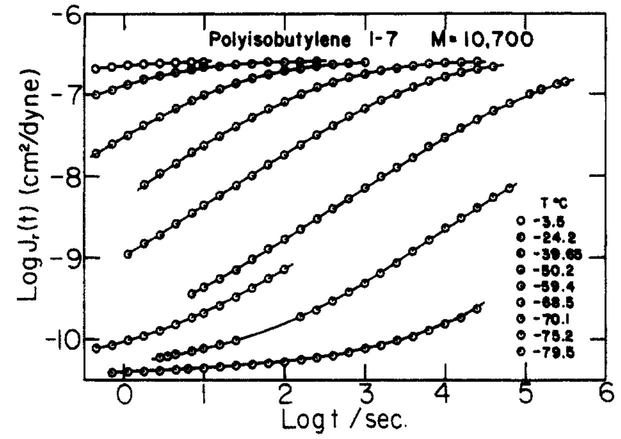

Figure 1. Recoverable creep compliance curves, $J_r(t)$, for polyisobutylene I-7 presented logarithmically at nine temperatures between −80 and −3 °C, as indicated, as a function of logarithmic time.

and $a_{T,\eta}$ are not very different. Encroachment of the local segmental relaxation time toward the Rouse relaxation times in PIB is not as severe as in PS which has a much larger n_α. Under the same experimental conditions we can conclude that the temperature dependence of J_e, which was observed in PS, should be much reduced in PIB. This prediction has led us to carry out extensive measurements of shear creep and creep recoverable compliance on a low molecular weight PIB sample as a function of temperature near and above its glass temperature. The data obtained for PIB are compared below with a corresponding data set of a PS sample with molecular weight such that at high temperatures it has the same steady-state compliance.

Experimental Section

The creep, $J(t)$, and recoverable creep compliance, $J_r(t)$, measurements were carried out in a frictionless magnetic bearing torsional creep apparatus at constant temperature. The design and operation of the apparatus have been described earlier.[16] Viscosity was obtained from creep measurements in the region where the viscous deformation contribution, t/η, dominates the response. The polyisobutylene sample I-7 was generously provided by Roger Porter. It is one of a series of fractions that were prepared at the Chevron Corp. by means of careful column elution chromotography. The fractions obtained were believed to be extremely narrow; M_w/M_n <1.05. I-7 was reported to have a molecular weight of 10 700. The glass temperature, T_g = −76.4 °C, was determined by monitoring the sample's length in the creep apparatus while it was cooled 0.3 °C/min. The recoverable creep compliance was measured at nine temperatures from −79.5 to −3.5 °C and is presented in Figure 1. Sample geometrical factors generally are believed to be accurate to within 5%. Changes in the derivatives d log $J_e(t)$/d log t should be precise to well within 1% except in the far terminal region where instrumental systematic errors begin to dominate the results.

Results

The shear creep recovery curves are shown in Figure 1. The response displayed represents the glassy behavior at temperatures near T_g, extends to contribution from the Rouse modes which are believed to dominate above log $J_r(t)$ of −9.5, and attains steady-state behavior at the highest temperatures. No rubbery plateau is present because the molecular weight is barely above the molecular weight per entangled unit M_e = 7600 (or 8900).[9] This *viscoelastic* property indicates that $n_\eta \simeq 0$ for the low molecular weight polymer studied here. The molecular entanglement network is not developed until $M > 10M_e$. This conclusion is consistent with the dynamic moduli measurements of PIB melts by Fetters et al.[17] in the terminal and plateau zones for a molecular weight of 2.7 × 10⁴ which shows that it has just entered into the entangled regime. Inspection of Figure 1 shows that there is little decrease in the steady-state compliance, $J_e°$, with a decrease in temperature. This behavior is quite different from the strong decrease in $J_e°$ with a decrease in temperature, as observed in a polystyrene sample PS A-61 with molecular weight 16 400 (see Figure 2 of ref 10). It is appropriate to compare the viscoelastic behavior of PIB I-7 with PS A-61 because the maximum value of $J_e°$ attained in PS A-61 at the highest temperature of 119.4 °C is about the same as the temperature-independent value of $J_e°$ in PIB I-7. The PS A-61 chains have 315 backbone carbon atoms, and PIB I-7 has 382. All the features in the behavior of PIB mentioned above become exceptionally clear after the recovery curves of PIB are superimposed by reducing the time scale at each temperature to T_0 = 68.4 °C. Plots of the recoverable compliance curves of both polymer specimens against the logarithm of the reduced time, t/a_T, are displayed in Figure 2. Here a_T is the shift factor used to bring the recovery curves at temperature T to superimpose on the recovery curve at the reference temperature, T_0. No significant depature from successful superposition can be discerned. Since η and $J_e°$ are steady-state parameters that together determine the final form of the terminal zone of viscoelastic response, their product $\eta J_e°$ is an average retardation time for approach to steady-state creep. The ratio $\eta(T)J_e°(T)/\eta(T_0)J_e°(T_0)$ is the time-scale reduction factor of the terminal creep zone that can be obtained from the experimental data. Its temperature dependence is compared with that of a_T in Figure 3 for PIB I-7. Figure 3, where the difference $\log[\eta(T)J_e°(T)/\eta(T_0)J_e°(T_0)] - \log a_T$ is plotted against $T - T_g$, shows that in PIB I-7 the two shift factors have almost the same temperature dependence. There are small though noticeable departures at temperatures near T_g, indicating that the local segmental relaxation time has a slightly stronger temperature dependence than the terminal zone relaxation time.

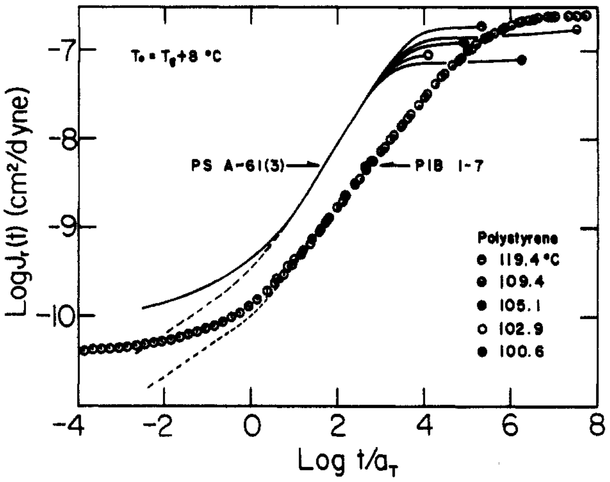

Figure 2. Double logarithmic plot of the recoverable compliance, $J_r(t)$, as a function of reduced time, t/a_T, for PIB I-7 and PS A-61 (3). Temperatures where data points for I-7 were obtained are indicated. The reference temperatures for reduction T_0 are T_g +8 °C for both specimens. The dashed lines are log $[J_r(t) - J_g]$, where J_g is the glassy compliance. For polystyrene, the five levels of steady-state compliance in descending order correspond to temperatures of 119.4, 109.4, 105.1, 102.9, and 100.6 °C, respectively.

In Figure 2 we have plotted the reduced recovery curves of PS A-61 using T_0 = 100 °C as the reference temperature. The reference temperature is approximately related to the glass temperature by $T_0 = T_g$ + 8 °C for both PIB-I7

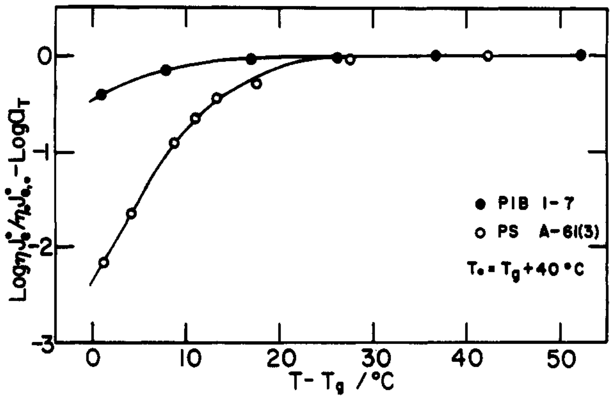

Figure 3. Logarithmic difference of the terminal, $\eta J_e^\circ/\eta_o J_e^\circ$, and softening zone, a_T, temperature shift factors as a function of the temperature difference, $T - T_g$, for PIB I-7 and PS A-61 (3). The reference temperatures T_o are T_g + 40 °C.

and PS-A61. The reduced recoverable compliance curves are obtained by reducing the time scale at each temperature as t/a_T to superimpose the transition portions of the recovery curves. Although temperature reduction fails for the recoverable compliance response of PS A-61, the product ηJ_e° characterizes the terminal zone. We compare the temperature dependences of a_T and $\eta(T)J_e^\circ(T)/\eta(T_o)J_e^\circ(T_o)$ of PS A-61 also in Figure 3. In contrast to PIB I-7, these two shift factors for PS A-61 have very different temperature dependences. Particularly near T_g, the differences are large, indicating that in PS A-61 the temperature dependence of the local segmental relaxation time is considerably stronger than that of the terminal creep. As discussed in the Introduction, the fact that the local segmental relaxation time, τ_α^*, has a stronger temperature dependence than the terminal zone retardation time is expected from eq 1 because $n_\alpha > 0$ and $n_\eta = 0$ in low molecular weight unentangled polymers. PS A-61 also has no entanglement network because its M_e is 17 000. Also the fact that the temperature dependence of τ_α^* in PIB I-7 is only slightly stronger while in PS A-61 it is considerably stronger than the terminal zone retardation time follows as a consequence of the n_α of PIB being significantly smaller than that of PS (0.45 as compared with 0.65). The viscoelastic behavior of PS A-61 is thus very different from PIB I-7. The recovery curves cannot be superimposed onto each other by temperature-dependent horizontal shifts. The pattern of divergence of the reduced curves at long reduced times is clear from Figure 2. This breakdown in time–temperature superposition is observed as a monotonic decrease of J_e° as temperature is decreased in steps from 119.4 °C.

As discussed in the Introduction, we have traced the origin of the decrease of J_e° in PS with decreasing temperature to the stronger temperature dependence of the shift factor of the local segmental motion compared with that of the modified Rouse modes. These experimental facts on the breakdown of thermorheological simplicity have been explained by the coupling model.[8] The new set of data in PIB exhibits entirely different properties. The viscoelastic data are approximately thermorheologically simple, and there is an absence of any anomalous temperature decrease of J_e°. We have alluded, above, to the fact that the dramatic difference in behavior between PS A-61 and PIB I-7 is also expected because of the difference in their n_α. In the remaining sections we shall discuss in detail these aspects of the viscoelastic properties of unentangled polymers.

Temperature Dependence of J_e

The thermorheologically complex behavior of low molecular weight polystyrene was noted[10] and confirmed[11] by creep recovery and dynamic mechanical measurements. At temperatures that are far above T_g, the steady-state compliance, J_e° defined by the limit of $J_r(t)$ as t tends to infinity, assumed a fairly constant value which is close to the Rouse model predicted value[9] of $J_e = 0.40(M/\rho RT)$, where M is the molecular weight, ρ is the density, R is the gas constant, and T is the temperature. As T was decreased to approach T_g, a marked decrease of J_e was observed. In a small temperature range near T_g, J_e decreased by 30-fold, contrary to the predicted small increase of J_e according to of the Rouse model. The retardation spectrum,[2] $L(\log \tau)$ calculated from the relation $J_r(t) = J_g + \int_{-\infty}^{\infty} L(1 - e^{-t/\tau})d(\ln \tau)$ with the $J_r(t)$ data at different temperatures revealed that the Rouse modes with the longest retardation times were successively lost as T was decreased. In spite of the unexpected manner in which the Rouse model was shown to fail in PS and the implications this feature should have in polymer physics,[9] there has been only one theoretical attempt,[8,14,18] to explain it. This anomaly occurs not only in low molecular weight PS but also in poly(methylphenylsiloxane) (PMPS[19]), poly(propylene glycol) (PPG[12,13]), and *cis*-polyisoprene (PI[15]). Hence it is a general phenomena that invites theoretical understanding. Alternative compatible explanations of the marked decrease in J_e as the temperature of measurement approaches T_g from above will be presented here. These new explanations offered here are based on the same physical picture used previously. It is a consequence of the result given by eq 1 in the special case, $n_\eta = 0$, for unentangled polymers. Thus all explanations given before[8] and to be given here are consistent with each other. They differ only in the path to the conclusion. The earlier explanation given in ref 8 still stands. It will not be reviewed further here.

(a) Method Based on Breakdown of the Rouse Model. Let us review definitions and conclusions of the bead-spring model of Rouse suitably modified for undiluted polymers.[9] The Rouse model is based on Gaussian submolecules. Each submolecule contains q monomer units. The root-mean-squared end-to-end length of a submolecule is $\sigma = \mathbf{a}\sqrt{q}$, where $\mathbf{a}$ is the basic step length which generally is of the order of several times the length of a single chain bond. The flexible polymer molecule is represented as a chain of N Gaussian submolecules. The root-mean-squared end-to-end distance of the entire molecule is

$$\langle R^2 \rangle^{1/2} = \sigma\sqrt{N} = \mathbf{a}\sqrt{P} \tag{2}$$

where P is the degree of polymerization. The friction coefficient f_0 represents the frictional force per unit velocity encountered by a submolecule junction as it moves through the medium consisting of other polymer molecules. The stress relaxation function from the Rouse theory is

$$G(t) = (\rho RT/M)\sum_{p=1}^{N} \exp(-t/\tau_p) \tag{3}$$

where the relaxation times are approximately given by

$$\tau_p = \sigma^2 N^2 f_o/6\pi^2 p^2 kT \tag{4}$$

It is assumed that f_o is proportional to q, i.e.

$$f_o = q\zeta_o \tag{5}$$

where ζ_o is the monomeric friction coefficient. With this assumption, eq 4 for τ_p is equivalent to

$$\tau_p = \mathbf{a}^2P^2\zeta_o/6\pi^2p^2kT \qquad (6)$$

which has the desirable property that the values of τ_p depend only on ζ_o and $\mathbf{a}$ but not on any properties of the artificial submolecule. The temperature shift of the Rouse relaxation time spectrum is governed by the temperature dependence of ζ_o.

It must be borne in mind that eq 6 is valid only if ζ_o appearing on the right-hand side is actually the friction coefficient of the monomer contained in a step length $\mathbf{a}$. It must also govern the temperature dependence of the relaxation time, $\tau_{\mathbf{a}}^*$, of the local motion which involves these monomers. This condition cannot be fulfilled in real polymers for reasons to be discussed.

A collection of experimental data[10-15,18,19] of undiluted unentangled amorphous polymers has shown that the shift factor, $a_{T,\alpha}$, for the local segmental motion has a much stronger temperature dependence than either that of the Rouse modes, $a_{T,R}$ or of the shear viscosity, $a_{T,\eta}$. This large difference in the two temperature dependences is also expected from eq 1 of the coupling model for the special case of $n_\eta = 0$ which becomes

$$\log a_{T,\alpha}/\log a_{T,\mathrm{R}} = 1/(1 - n_\alpha) \qquad (7)$$

Unlike the case of fully entangled polymers, J_e° may vary with temperature and the shift factors $a_{T,R}$ and $a_{T,\eta}$ may not be identical. We choose to use $a_{T,R}$ in eq 7 because the Rouse relaxation times spectrum is more fundamental than the viscosity. Equation 7 was obtained from the coupling model as a consequence of the cooperative nature of the local segmental motions. In this approach,[1,6-8,14,18,20] all molecular motions have the same friction coefficient $\zeta_o(T)$ before intermolecular cooperativity is taken into consideration. At this stage, all modes have constant relaxation rates which is $W_{o\alpha} = \tau_{o\alpha}^{-1} \propto 1/\zeta_o(T)$ for the local segmental motions, $W_{o\mathbf{a}} = \tau_{o\mathbf{a}}^{-1} \propto 1/\zeta_o(T)$ for the motion of the monomers included in the step length $\mathbf{a}$, and $W_{op} = \tau_p^{-1} \propto 1/\zeta_o(T)$ for the Rouse modes. Due to dense packing of monomers, the local segmental motion as well as the motion of monomers within step length $\mathbf{a}$ are intermolecularly cooperative in nature. According to the coupling model intermolecular cooperativity slows down the individual relaxation rate W_{oA}, on the average, to $W_{oA}(\omega_c t)^{-n_A}$, where the reciprocal of ω_c is the onset time and n_A is the coupling parameter. Here A is either α or $\mathbf{a}$. We distinguish all quantities for α from the corresponding ones for $\mathbf{a}$ because the modified Rouse model for undiluted polymers[9] so far has not explicitly related the local segmental motion to the motion of the monomers in a step length $\mathbf{a}$. It is not necessary that they have to be identical. Until this point is clarified in the modified Rouse model, the possibility of the two being different remains and is allowed for in our formulation here. This slowed down relaxation rate leads to a stretched exponential relaxation function

$$\phi_A(t) = \exp -(t/\tau_A^*)^{1-n_A} \qquad 0 \le n_A < 1 \qquad (8)$$

where the effective relaxation time, τ_A^* is related to τ_{oA} by

$$\tau_A^* = [(1 - n_A)\omega_c^{n_A}\tau_{oA}]^{1/(1-n_A)} \propto [\zeta_o(T)]^{1/(1-n_A)} \qquad (9)$$

Even if the local segmental motion and the similar motion of monomers in a step length are different, both motions involve local length scales. We thus expect the two coupling parameters n_α and $n_{\mathbf{a}}$ to bear a relation to each other. We expect the correlations involving the local segmental motion found earlier[6] will continue to hold for the motion of monomers in a step length.

For Rouse modes, the only intermolecular coupling possible is through entanglement between chains. In this paper which confines the interest to low molecular weight polymers that are unentangled, there is no intermolecular cooperativity to be considered for the Rouse modes. Thus, the Rouse modes are unmodified. Equations 3–6 remain *formally* valid although, in view of eq 9, ζ_o in eq 6 cannot be identified with the friction coefficient of either τ_α^* or $\tau_{\mathbf{a}}^*$.

From eq 7 and a similar relation for $\tau_{\mathbf{a}}^*$,

$$\log a_{T,\mathbf{a}}/\log a_{T,R} = 1/(1 - n_{\mathbf{a}}) \qquad (10)$$

it is clear that the shift factor $a_{T,\alpha}$ of the local segmental motion as well as $a_{T,\mathbf{a}}$ for step $\mathbf{a}$ are much larger than $a_{T,R}$ of the Rouse modes. Hence, as T is decreased, the separation between τ_α^* or $\tau_{\mathbf{a}}^*$ and the Rouse relaxation time τ_p spectrum decreases. This tendency of τ_α^* and $\tau_{\mathbf{a}}^*$ to encroach into the domain of the Rouse relaxation times is the basic physics causing the breakdown of the Rouse theory in real polymers. Recent low-frequency dielectric spectroscopic measurements down to 10^{-5} Hz by Schlosser and Schönhals[13-15] in low molecular weights PPG and PI have observed and resolved two dielectric loss peaks contributed by the local segmental motion and the Rouse normal modes. This set of data clearly shows that $a_{T,\alpha}$ is much more temperature sensitive than $a_{T,R}$ and directly verifies the encroachment of τ_α^* into the Rouse relaxation time spectrum, confirming earlier findings. The friction coefficient, ζ_A, of either the local segmental motion or of the local motion of monomers in the step length a defined by

$$\tau_A^*(T)/\tau_A^*(T_o) = \zeta_A(T)/\zeta_A(T_o) \qquad (11)$$

is not ζ_o. Instead, from eq 9 we find it is only related to ζ_o by the relation

$$\zeta_A(T) = \zeta_A(T_o)\ [\zeta_o(T)/\zeta_o(T_o)]^{1/(1-n_A)} \qquad (12)$$

As stated before, although eqs 3–6 for the Rouse modes remain formally correct, we must bear in mind that the friction factor, ζ_o, appearing therein is not compatible with ζ_A of the local motions, but relating to each other by eq 12. This will present a problem when the relaxation time, τ_A^* has encroached into the neighborhood of the Rouse relaxation time spectrum. At this instance there are two possible choices for the friction factor of motion of monomers in a step length. One choice is ζ_o, offered by the Rouse model is indicated in eqs 5 and 6. The other choice is $\zeta_{\mathbf{a}}^*$ which is a consequence of the cooperative nature of the local motion of a few monomers in a step length of a dense packed polymer system.

One way to resolve this dilemma is to redefine the monomeric friction factor in the Rouse model as $\zeta_{\mathbf{a}}(T)$. The relation of the friction coefficient of a submolecule junction, f_o to $\zeta_{\mathbf{a}}(T)$ is

$$f_o = \tilde{q}\ \zeta_{\mathbf{a}}(T) \qquad (13)$$

where the *effective* number of monomers in a submolecule, $\tilde{q}$, is given by

$$\tilde{q} = [\zeta_o(T)/\zeta_{\mathbf{a}}(T)]q = (\zeta_o(T_o)/\zeta_{\mathbf{a}}(T_o))[\zeta_o(T_o)/\zeta_o(T)]^{n_{\mathbf{a}}/(1-n_{\mathbf{a}})}q \qquad (14)$$

On combining eqs 4, 13, and 14, we obtain the correct expression for the Rouse relaxation times,

$$\tau_p = \mathbf{a}^2P^2\zeta_a(T)(\zeta_0(T_0)/\zeta_a(T_0))[\zeta_0(T_0)/\zeta_0(T)]^{n_a/(1-n_a)}/6\pi p^2kT \quad (15)$$

for real polymers. This can be rewritten as

$$\tau_p = \mathbf{a}^2\tilde{P}^2\zeta_a(T)/6\pi^2p^2kT \quad (16)$$

where $\tilde{P}$ is given by

$$\tilde{P}^2 = P^2(\zeta_0(T_0)/\zeta_a(T_0))[\zeta_0(T_0)/\zeta_0(T)]^{n_a/(1-n_a)} \quad (17)$$

Now eq 15 or equivalently eqs 16 and 17 for the Rouse model, in contrast to eq 6, has been made consistent with the local segmental motion in real polymers at temperatures where the relaxation time $\tau_A{}^*$ of the local motion has encroached into the Rouse spectrum. It has retained the desirable property that the values of τ_p depend only on ζ_a and a, but not on any properties of the artificial submolecule because the actual friction coefficient, $\zeta_a(T)$ appears on the right-hand side. In eqs 16 and 17 $\tilde{P}$ is appropriately interpreted as the *effective* degree of polymerization. As temperature decreases, the reduction factor $[\zeta_0(T_0)/\zeta_0(T)]^{n_a/(1-n_a)}$ decreases rapidly in polymers which have large n_α or n_a. Equation 17 shows that as T decreases the effective degree of polymerization, $\tilde{P}$ is drastically reduced. Since molecular weight is proportional to the degree of polymerization, it follows that the *effective* molecular weight $\tilde{M}$ and hence the recoverable compliance, $J_e{}^\circ$ which is related to $\tilde{M}$ by [9]

$$J_e{}^\circ = 0.40\tilde{M}/\rho RT \quad (18)$$

will decrease with decreasing temperature accordingly as

$$J_e{}^\circ = 0.40M(\zeta_0(T_0)/\zeta_a(T_0))[\zeta_0(T_0)/\zeta_0(T)]^{n_a/2(1-n_a)}/\rho RT \quad (19)$$

The exponent

$$h = n_a/2(1 - n_a) \quad (20)$$

determines in part how rapidly $J_e{}^\circ$ decreases. The coupling parameter, n_a is expected to scale with n_α of the local segmental motion. Comparing two polymers, the polymer which has a larger n_α will have also a larger n_a. Polystyrene has a n_α (0.65) much larger than that of PIB (0.45). We expect the same relation holds between their respective n_a's. Hence the exponent h for PS is larger than that for PIB.

Let us compare the temperature dependence of $J_e{}^\circ$ for PS which has a larger h with that for PIB which has a smaller h. Samples of the two polymers are chosen with the condition that they have approximately the same $J_e{}^\circ$ at temperatures far above the respective glass temperatures. According to eq 19 the temperature dependence of $J_e{}^\circ$ will be quite different in these two samples. The decrease of $J_e{}^\circ$ in PIB will be significantly less than that in PS. For the same ratio $\zeta_0(T_0)/\zeta_0(T)$ for both polymers, the decrease of log $J_e{}^\circ$ in PIB is smaller than that in PS because h_{PIB} is smaller than h_{PS} by a factor of 0.44. The exponent h is not the only factor determining the decrease of $J_e{}^\circ$. For example, the ratio $\zeta_0(T_0)/\zeta_0(T)$ will vary from polymer to polymer. For these polymers of comparable chain length we also note that the temperatures at each of which $J_e{}^\circ$ can be reached within the experimental time window for PS is much closer to the T_g of PS than the corresponding temperatures in the case of PIB is to the T_g of PIB. By inspection of Figure 2 in ref 10, these temperatures for PS A-61 lie within the range $96.0 \le T \le 119.4$ °C which corresponds to $T_g + 3.0 \le T \le T_g + 26.1$ °C with $T_g = 93$ °C. See also Figure 5 here. On the other hand, by inspection of Figure 1 or Figure 4 here, the corresponding temperature range for PIB I-7 in which the steady-state compliance $J_e{}^\circ$ can be reached in the same experimental time window is $-59.4 \le T \le -3.5$ °C, or $T_g + 17.0 \le T \le T_g + 72.9$ °C with $T_g = -76.4$ °C. An even more appropriate comparison of the two temperature ranges can be achieved by normalizing temperature to the respective T_g. We have then

$$1.01 \le T/T_g \le 1.07 \quad (21)$$

for PS A-61 and

$$1.09 \le T/T_g \le 1.37 \quad (22)$$

for PIB I-7. The scaled temperature ranges clearly indicate that the steady-state compliance, $J_e{}^\circ$, can still be reached within the experimental time window at temperatures as low as 1% above T_g in PS. This figure is to be contrasted with the corresponding figure of 9% above T_g in PIB. It is challenging to explain why in PS A-61 we can get closer

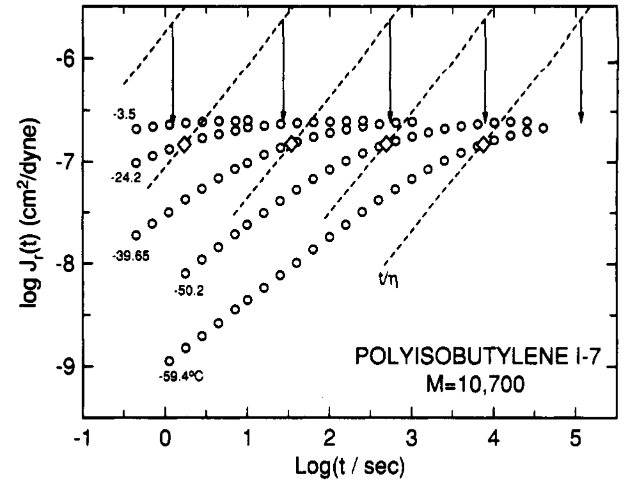

Figure 4. Relationship of the viscous contribution to the shear creep compliance, $J(t)$ (dashed lines), shown relative to the recoverable compliance, $J_r(t)$ (data points), for PIB I-7 plotted logarithmically as a function of log t. Open diamonds indicate the compliance levels where the viscous and recoverable deformations are equal. The arrows indicate the time t_e at which the condition $t/\eta = 10J_r(t)$ is satisfied. At t_e, $J_r(t)$ has reached a value within a few percent of $J_e{}^\circ$. Note that $J_r(t_e)$ is almost temperature independent.

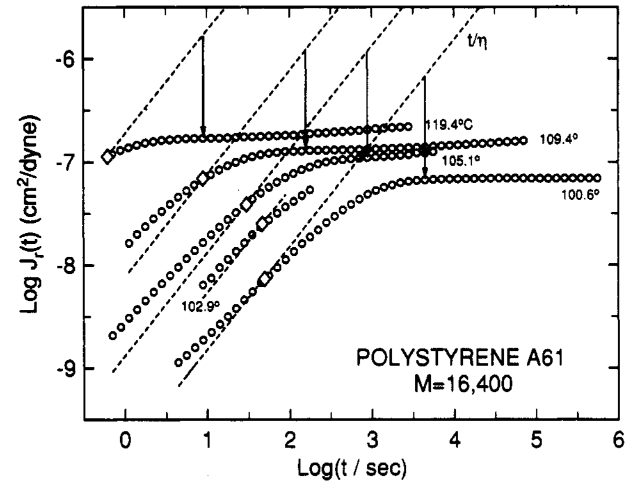

Figure 5. Plot for PS A-61 (3) similar to that for PIB I-7 in Figure 4. Note that $J_e(t_e)$ so determined for PS A-61 (3) is temperature dependent. This is to be contrasted with the temperature independence of the same quantity in PIB I-7.

to T_g than in PIB I-7 and can still observe the steady-state compliance being reached within the same experimental window. The reason for this difference is because the encroachment of τ_α^* into the neighborhood of the Rouse spectrum is much more severe in PS than in PIB, as illustrated by Figure 3. This is also evident in Figure 2 which shows that the separation between the local segmental relaxation (located roughly at $\log t/a_T = 0$ for both) and the terminal region is significantly shorter for PS A-61 than for PIB I-7. The larger separation between the two viscoelastic mechanisms in PIB I-7 can also be inferred from the much larger viscosity measured near T_g in PIB I-7 ($\log \eta = 13.78$ at $T = -75.2$ °C) than near T_g in PS A-61 ($\log \eta = 11.09$ at $T = 96.0$ °C) and from the fact that both samples have comparable J_e°'s. At T_g the terminal zone retardation time, ηJ_e°, is thus much longer than the local segmental relaxation time, $\tau_\alpha^*(T_g)$, for PIB I-7 than for PS A-61, since by definition $\tau_\alpha^*(T_g)$ is the same, independent of polymer. Hence we can conclude, at T_g, the two viscoelastic mechanisms are much more widely separated in PIB I-7 than in PS A-61. It is generally known that the closer the temperature is to T_g, the stronger is the temperature variation of the friction coefficient. As a consequence of this property the ratio $\zeta_0(T_o)/\zeta_0(T)$ decreases much more in the temperature range (21) of PS A-61 than in the temperature range (22) of PIB I-7. Both the larger variation of the ratio $\zeta_0(T_o)/\zeta_0(T)$ and the increase in size of the exponent h when going from PIB I-7 to PS A-61 act in concert in eq 19 to make the decrease in J_e° prominent in PS A-61 but negligible in PIB I-7. This is indeed what we have observed experimentally (see Figure 2). From the discussion above it is clear that these results are consequences of the disparity in the size of the coupling parameter, n_α of the local segmental motion for these two polymers, which ultimately is due to the difference in their monomer molecular structures.

(b) Method Based on a Principle of Viscoelasticity. There is an alternative way to see why the steady-state recoverable compliance, J_e°, decreases drastically as temperature is decreased to approach T_g in polymers such as PS which has a large coupling parameter for the local segmental motion. Let us start by reviewing the physical interpretation of viscoelasticity. The steady-state recoverable compliance reflects the limiting state of orientation per unit stress. It is determined by a dynamic balance between the orienting drag forces and the thermal diffusion drift toward spherical conformations of the polymer coils, i.e. maximum entropy. The shearing stress determines the orientational drag force. Whenever the viscous flow starts to dominate the deformation (i.e. $t/\eta \geq 10J_r(t)$), the limiting amount of orientation of a monodisperse polymer has been reached. The entire energy input is dissipated by the viscous deformation and none is available for further orientation. If t_e denotes the time at which

$$t_e/\eta = 10J_r(t_e) \tag{23}$$

the argument given above suggests that $J_r(t)$ ceases to increase for $t > t_e$ and $J_r(t_e)$ is approximately J_e°. See Figures 4 and 5 for illustrations.

If all viscoelastic mechanisms, from the local segmental motion zone to the terminal zone have the same shift factor, the two terms t/η and $J_r(t)$ when plotted logarithmically against $\log t$ will shift horizontally by the same amount, $\log a_T$, if temperature is lowered from a reference temperature, T_o, to T. The relation that determines J_e° at T, $[a_T t_e(T_o)/a_T \eta(T_o)] = 10J_r(a_T t_e(T_o),T)$, is the same as the corresponding one that determine J_e° at T_o, i.e. $t_e(T_o)\eta(T_o) = 10J_r(t_e(T_o),T_o)$. Thus J_e° determined in this manner is essentially independent of temperature for ideal polymers that are thermorheologically simple, as it should be.

Among linear amorphous polymers, PIB is at present the best candidate for thermorheological simplicity. PIB has the smallest local segmental coupling parameter known thus far in amorphous polymers.[1,6] As discussed before, the departure from thermorheological simplicity indicated by eq 7 is minimized for polymers with smaller n_α like PIB. Moreover, as has also been pointed out in the discussion following eqs 21 and 22, there is negligible encroachment of τ_α^* into the neighborhood of the Rouse spectrum in PIB I-7. It can be seen by inspection of Figure 3, throughout the temperature range $T_g + 17.0 \leq T \leq T_g + 72.9$ °C defined by eq 22, the two shift factors, a_T and $\eta J_e^\circ/\eta(T_o)J_e^\circ(T_o)$, are effectively identical. Consequently, J_e° given approximately by $J_r(t_e)$ determined by eq 23 is independent of temperature. In Figure 4, some of the recoverable compliance data of PIB I-7 are replotted together with the permanent viscous deformations, t/η. The solutions of eq 23 determine t_e and $J_r(t_e)$. These are illustrated graphically in Figure 4 for several temperatures. Indeed, the results indicate that to a good approximation J_e° can be taken to be $J_r(t_e)$, and it is nearly temperature independent in PIB I-7.

Polystyrene is a good example of an amorphous polymers that has a moderately large segmental coupling parameter. At temperatures near T_g, the local segmental relaxation time, τ_α^* has encroached significantly into the Rouse relaxation spectrum. This is clearly shown in Figure 3. At $T_g = 93$ °C τ_α^* has crept two and a half decades closer to the terminal relaxation when compared with the situation at a higher temperature of 119.4 °C. On the low-temperature side of the temperature range, $T_g + 7.6 \leq T \leq T_g + 26.1$ °C (corresponding to the measurement temperatures in Figure 5) the shift factor, a_T, of the transition portions of the recovery curves is much larger than the corresponding shift factor, $\eta(T)J_e^\circ(T)/\eta(T_o)J_e^\circ(T_o)$, of the terminal relaxation. We illustrate the solution of eq 23 in Figure 5 by plotting logarithmically the recoverable compliance, $J_r(t)$ of PS-A61, together with permanent viscous deformation, t/η. Graphical solutions to eq 23 are depicted. The viscous line continues to intersect the recovery curve at a lower compliance value as the temperature is decreased, a consequence of the encroaching local segmental relaxation due to the stronger temperature dependence of $a_{T,\alpha}$. $J_r(t_e,T)$ can be identified with $J_e^\circ(T)$, and it decreases as temperature is lowered toward T_g.

Figures 4 and 5 illustrate a method of determining J_e° by eq 23, obtained by applying a principle of viscoelasticity. This helps to clarify the anomalous decrease of J_e° in PS A-61 and the lack of it in PIB I-7. In addition to the two other methods based on analyses of the breakdown of the Rouse model (subsection a above and ref 8) this third method serves as an alternative route to explain why PS A-61 and PIB I-7 have very different viscoelastic behaviors. The basic physics used in all three alternative's approaches is the same and is essentially given by eq 7 from the coupling model.

Summary and Discussion

The shear creep and creep recovery behavior of a narrow molecular weight distribution polyisobutylene sample of low molecular weight are reported here as a function of temperature near and above the glass temperature. These measurements may be considered as natural extensions of previous measurements in low molecular weight polystyrene and poly(methylphenylsiloxane) samples. The choice of PIB here is guided by the previous work[1] in which we found that the viscoelastic properties of high molecular weight PIB and PS are very different. There we also showed that the coupling model can explain the difference. The same model predicts a consequential difference in behavior for low molecular weight PIB and PS. In these low molecular weight polymers the large decrease of the steady-state recoverable compliance, J_e°, observed in PS is predicted to be drastically reduced in PIB. The data reported here verify this prediction.

The contrasting differences in viscoelastic behavior of PS and PIB confirmed here stimulate further discussion of the basic physics behind the anomalous decrease of J_e° observed in PS and construction of additional methods to treat this problem. The basic physics is the intermolecular cooperative nature of the local segmental relaxation as brought out by the coupling model. The degree of intermolecular cooperativity of local modes is given by the coupling parameter, n_α. We expect the degree of intermolecular cooperativity and hence n_α to depend on the molecular structure of the monomer unit of the polymer. In establishing a correlation[6] between n_α and the steepness of the shift factor, $a_{T,\alpha}$, we examined many amorphous polymers. It was found that n_α varies over a considerable range and is larger in a polymer with a monomer molecular structure that has a larger capacity for intermolecular coupling. Polyisobutylene has small n_α because its molecular structure is compact and symmetric which should minimize intermolecular couplings between neighboring chains. On the other hand, polystyrene has a much larger n_α, as can be anticipated when its molecular structure is compared with that of PIB. In a polymer like PS with large n_α, the local segmental relaxation time, τ_α^*, increases much faster than the Rouse relaxation time spectrum as temperature is decreased toward T_g. It causes severe departure from thermorheological simplicity. As T is lowered toward T_g, the separation between τ_α^* and the Rouse spectrum continues to decrease. When τ_α^* has encroached into the neighborhood of the Rouse spectrum, it has a serious repercussion on the validity of the Rouse model which at high temperatures describes rather well the terminal relaxation of unentangled polymers.[9] We have provided two methods here in addition to a previous published one to deduce the consequences. Although the three methods are different, each has enabled us to arrive at the same conclusion that J_e° will decrease anomalously by a large amount as T is decreased towards T_g in polymers with large n_α such as PS. The coupling model also predicts that in polymers with small n_α like PIB, the departure from thermorheological simplicity is not large and the encroachment of τ_α^* toward the Rouse spectrum has not materialized at any temperature in which the steady-state recovery compliance has been reached inside the time window of our creep measurements.

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