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Modes of Molecular Motion in Low Molecular Weight Polystyrene

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ABSTRACT: The variations with temperature of the viscosity, η , and the relaxation times for various low molecular weight, unentangled polystyrenes (PS) are analyzed. We find that the temperature dependence of η does not directly reflect the behavior of the global chain modes. Depending on molecular weight and temperature, η can exhibit a stronger temperature dependence than even the local segmental modes. However, this is only a consequence of the strong temperature dependence of the recoverable compliance J_s . The Rouse relaxation time, τ_1 , deduced from the product of the viscosity and the recoverable compliance, has the expected behavior. For example, this Rouse time for a PS of molecular weight equal to 2 kg/mol has the same temperature dependence as that for self-diffusion; hence, there is no enhancement of translational diffusion in the polymer. The same conclusion was reached by Urakawa et al. [Urakawa, O.; Swallen, S. F.; Ediger, M. D.; von Meerwall, E. D. *Macromolecules* **2004**, *37*, 1558], although the analysis leading to it was different. The conclusion is consistent with two extant explanations of the enhancement of translational diffusion in small molecular glass-formers, one which invokes spatially heterogeneous dynamics and the other ascribing the effect to the different coupling parameters for the translational and rotational correlation functions.

Introduction

Characterizing the dynamics of polymer chains is the sine qua non for understanding and predicting most of their physical properties. The gigantic size of polymer molecules implies an enormous number of degrees of freedom, which in turn gives rise to motion encompassing many decades of time over a correspondingly broad range of length scales. The usual approach to unraveling the viscoelasticity of polymers is to express the relaxation and transport dynamics in terms of modes, whose summation yields the macroscopic behavior. The starting point for analysis of the low-frequency motions is the Rouse model, generalized for undiluted polymer. According to the Rouse model, the chain is approximated as a collection of submolecule units ("beads"), connected by linear springs, with a friction coefficient ζ . The chain motions are described in terms of a superposition of independent modes, each having a relaxation time given by^{1,2}

$$\tau_p = \frac{b^2 N^2 \zeta}{3\pi^2 k T p^2} \quad (1)$$

where N is the number of segments in the chain and b is the Kuhn step length. The $p = 0$ mode measures the position of the center of mass; thus, the translational relaxation time for Rouse chains is related inversely to the self-diffusion constant, D ²

$$\tau_0 = \frac{\langle r^2 \rangle}{3\pi^2 D} \quad (2)$$

where $\langle r^2 \rangle$ is the mean-square end-to-end chain length. The terminal Rouse relaxation time ($p = 1$) can be evaluated from the relaxation modulus, $G(t)$

$$\tau_1 = (15/\pi^2) \int_0^\infty t G(t) dt / \int_0^\infty G(t) dt \quad (3)$$

It is proportional to the product of the zero-shear viscosity, η , and the equilibrium recoverable compliance, J_s ¹

$$\tau_1 = (15/\pi^2) \eta J_s \quad (4)$$

J_s , a measure of the elastic deformation during steady-state flow, is also related to the relaxation modulus

$$J_s = \int_0^\infty t G(t) dt / \left(\int_0^\infty G(t) dt \right)^2 \quad (5)$$

whereby from eq 4

$$\eta = \int_0^\infty G(t) dt \quad (6)$$

At temperature sufficiently higher than the glass temperature T_g , the Rouse model accurately predicts J_s .^{1,3} Since J_s varies only very weakly with temperature, τ_0 , τ_1 , and η have essentially the same temperature dependence. However, as T_g is approached by cooling, there is a marked decrease in the recoverable compliance,³ with a concomitant decrease in the quantity τ_1/η .

The submolecule itself ($p = N$ mode) must be sufficiently long to exhibit Gaussian statistics for its end-to-end distribution. Dynamics transpiring on a smaller length scale (faster than τ_N) are thus referred to as sub-Rouse modes.^{3,4} At sufficiently short range, only a few backbone bonds are involved, and this comprises the local segmental motion (dielectric α -process) associated with the glass transition (structural relaxation). Williams⁵ proposed for polystyrene that five repeat units are required for the submolecule to exhibit Gaussian behavior. If this estimate is correct, then the Rouse model and eq 4 are relevant for the description of chain relaxation for all the molecular weights of polystyrene discussed in this work. In the event that the molecular weight is too small and the sub-Rouse modes replace

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the Rouse modes, eq 4 still gives a value proportional to the terminal sub-Rouse relaxation time.

Resolving the various modes of motion from experimental data is difficult. For polymers lacking a dipole moment parallel to the chain axis, the normal modes are dielectrically inactive, whereby the local segmental relaxation (α -process) would be isolated in the dielectric relaxation spectrum. This is not the case for mechanical measurements, in which the response from the chain modes overlaps the local segmental process. This manifests in the well-known breakdown of time–temperature superpositioning in the transition zone of the viscoelastic spectrum of polymers.³ Read⁶ and Inoue and co-workers^{7,8} have proposed a method of extracting the segmental (“G-component”) and chain mode (“R-component”) contributions by combining mechanical and birefringence measurements. The underlying assumption of the method is that the various modes are additive in the stress. This assumption is at odds with various experimental facts, as detailed elsewhere.^{9,10}

The present work is motivated by a recent publication by Urakawa et al.,¹¹ in which relaxation and transport properties of unentangled polystyrene (PS2K, molecular weight = 2 kg/mol) were reported. In their analysis, Urakawa et al.¹¹ identified the terminal viscosity with the G -component of Inoue et al.⁸ and reported that η_0/T had the same T dependence as the segmental dynamics. This is surprising since the viscosity is measured at low frequencies, long past the softening zone of the viscoelastic spectrum and the “ G -component”. In fact, according to the Rouse model, 60% of the viscosity of an unentangled polymer comes from the terminal Rouse mode.¹ Since all Rouse modes have the same friction coefficient, all Rouse modes, as well as the viscosity, will have the same temperature dependence. On the other hand, segmental relaxation, which defines the glass transition, represents motion at length scales smaller than the shortest Rouse mode. Common practice is to define a segmental relaxation time, τ_{seg} , as the inverse of the frequency of the loss modulus maximum occurring near the glass transition. In terms of the relaxation modulus

$$\tau_{\text{seg}} = \int_0^\infty \sin(t/\tau_{\text{seg}}) t G(t) dt / \int_0^\infty \cos(t/\tau_{\text{seg}}) G(t) dt \quad (7)$$

It is often assumed that segmental relaxation and the Rouse modes are governed by the same monomeric friction coefficient and hence have the same time–temperature shift factors. Experimentally, this is found to be true only at high temperatures.^{1,3,12} At lower temperatures, the Rouse model prediction for J_s breaks down, and the segmental relaxation time varies more with temperature than do the Rouse modes.

Herein we analyze existing data on unentangled PS (molecular weights in the range from 2 to 13 kg/mol) to compare the respective temperature dependences of the Rouse relaxation times, the viscosities, and the segmental relaxation times. We find, in agreement with Urakawa et al.,¹¹ that the Rouse and translational relaxation times (the latter obtained from diffusion measurements) have the same temperature dependence. However, particularly at lower temperatures, the viscosity exhibits a stronger T dependence, consistent with the decreasing magnitude of J_s . Quantities involving chain modes—Rouse relaxation times and diffusion coefficients—vary less with temperature than does the local segmental relaxation.

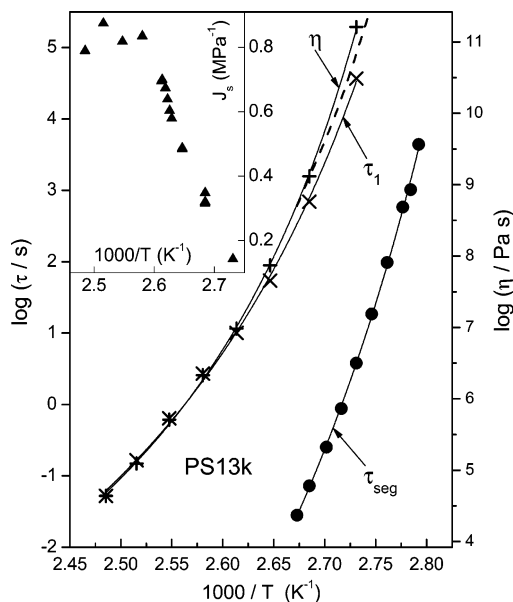


Figure 1. Arrhenius plot of Rouse relaxation times calculated using eq 4 (\times), steady-state creep viscosities ($+$), and segmental relaxation times (\bullet) for PS13K.¹³ The dotted line represents τ_{seg} shifted to coincide with η at higher T . Solid lines represent Vogel–Fulcher–Tammann–Hesse (VFTH) fits.¹ The respective ordinate scales have been adjusted to superpose τ_1 and η at the highest temperatures. The data were obtained by dynamic mechanical and shear rheometry measurements. The inset shows the steady-state recoverable compliance.¹³

Results

In Figure 1 are shown the local segmental relaxation times (\bullet , defined as the inverse of the circular frequency of the maximum in the loss modulus) and the viscosities ($+$) for PS13K¹³ ($M_w = 13$ kg/mol), along with the relaxation times calculated for the first Rouse mode (\times), using eq 4. The experimental values of J_s are shown in the inset. A marked decrease in J_s begins at $\tau_1 \sim 10$ s. This change in J_s amplifies the variation of η with temperature (eq 4), so that η exhibits a stronger T dependence than does τ_1 , as seen at lower temperatures in Figure 1. We have also shifted the segmental relaxation times (dashed line) to allow comparison to the viscosity. The variation of η with temperature also exceeds that of τ_{seg} . Since the behaviors are all non-Arrhenius over this range, the differences in temperature dependences will vary with temperature.

In Figure 2 are shown results similar to above, but for a lower molecular weight PS ($M_w = 3.4$ kg/mol).^{14,15} For PS3.4K, the decrease in J_s (shown in the inset) occurs at higher temperatures, for τ_1 on the order of 10^{-3} s. The consequence again is a stronger temperature dependence of η in comparison to τ_1 . However, the local segmental relaxation times exhibit more variation with temperature than does η or τ_1 , in contrast to the behavior of the PS13K in Figure 1. The stronger T dependence for the shorter time (involving shorter length scales) mode is the source of the well-known breakdown of time–temperature superpositioning in the glass transition zone. Thermorheological complexity is observed in that region of the viscoelastic spectrum because the relaxation times for the chain modes and segmental motion are sufficiently close that contributions from both mechanisms can be seen in isothermal viscoelastic measurements. Note that for $T > 385$ K, η and τ_1 have the same temperature dependence, consistent with the more nearly constant value of J_s at higher

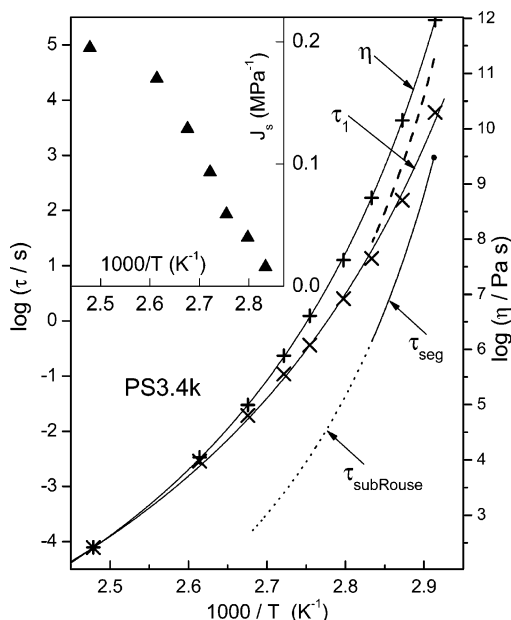


Figure 2. Arrhenius plot of Rouse relaxation times calculated from eq 4 (×), steady-state creep viscosities (+),¹⁵ and segmental relaxation times¹⁴ (single point designated by ●, with solid line representing shift factors for higher temperatures) for PS4.3K. Dashed line extending from τ_{seg} at higher temperatures represents shift factors for the sub-Rouse modes (see text). The dotted line represents τ_{seg} shifted to coincide with τ_1 at higher T . Solid lines are VFTH fits to the respective data points. The respective ordinate scales have been adjusted to superpose τ_1 and η at the highest temperatures. The data were obtained from creep recovery experiments.¹⁵ The inset shows the steady-state recoverable compliance.

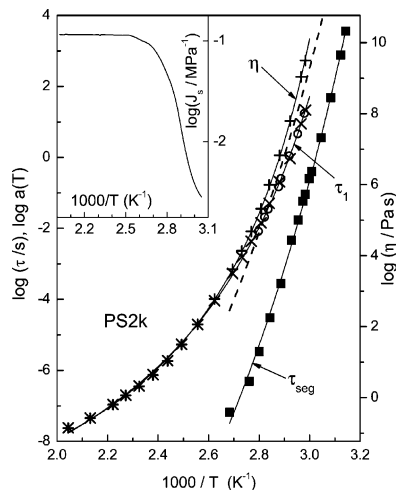


Figure 3. Arrhenius plot of the Rouse relaxation times (×), local segmental relaxation times¹⁴ (■), zero-shear rate dynamic viscosities¹¹ (+), and shift factors for the translational relaxation times calculated from the D in ref 11 (○) for PS2K. The respective ordinate scales have been adjusted to superpose τ_1 and η at the highest temperatures. The solid line is the VFTH fit to τ_{seg} , and the dotted line is this same curve shifted to overlap the data for τ_1 . The inset shows the steady-state recoverable compliance.

temperatures. Also, for $T > 350$ K, the creep compliance is no longer unambiguously dominated by the segmental modes, and thus we refer to these data as the sub-Rouse relaxation times.

In Figure 3 relaxation times¹⁴ and viscosities¹¹ are plotted for a lower molecular weight polystyrene, PS2K ($M_w = 2$ kg/mol). The steady-state recoverable compliance displayed in the inset was obtained by interpola-

tion ($J_s \propto M_w$) between published values¹⁵ for PS having molecular weights bracketing 2 kg/mol. The conspicuous decrease in J_s corresponds to a value of $\tau_1 \sim 6 \times 10^{-4}$ s at $T \sim 370$ K. At temperatures below this, the viscosity (+) varies more with temperature than does τ_1 (×), while the curves for η and τ_{seg} (■) are roughly parallel. Again, the recoverable compliance contributes significantly to the temperature dependence of the viscosity.

Also included in Figure 3 are shift factors for the translational relaxation time, τ_0 (○), obtained from the published¹¹ self-diffusion coefficients for PS2K. The shift factors were chosen so that they overlap with the τ_1 in Figure 3. This makes evident that the two Rouse relaxation times have essentially identical temperature dependences.

From eq 2, we can obtain a lower bound on $\langle r^2 \rangle$, which must be greater than the quantity $3\pi^2 D\tau_1$, since $\tau_0 > \tau_1$. The result is $\langle r^2 \rangle > 290 \text{ \AA}^2$. The mean-square end-to-end length of a chain with i backbone bonds is also given by

$$\langle r^2 \rangle = C_i l^2 \quad (8)$$

where C_i is the characteristic ratio, l ($=1.54 \text{ \AA}$) the carbon-carbon bond length, and $i = 38$ for PS2K. The value of C_i for PS2K is unavailable. Using the high M_w limiting value of the characteristic ratio, $C_\infty = 10.3 \text{ \AA}$, provides an upper bound, so that we obtain $17 \text{ \AA} < \langle r^2 \rangle^{1/2} < 30 \text{ \AA}$. This is consistent with the value reported by Abe et al.,¹⁶ $\langle r^2 \rangle^{1/2} = 25 \pm 2 \text{ \AA}$, and thus supports our application of the Rouse model to polystyrene with $M_w = 2$ kg/mol.

Discussion and Summary

From an analysis of various data for PS2K, Urakawa et al.¹¹ concluded that the viscosity of low molecular weight PS is dominated by segmental motion, which they identified with the "glassy" or G-mode of Inoue et al.¹⁷ The results in Figures 1–3 show that this is not necessarily the case. There are small, but significant, differences in T dependences of τ_{seg} and η , at least for the two higher molecular weight samples. The viscosity is dominated by the chain modes. At lower temperatures, approaching T_g , there is a decrease of the recoverable compliance, J_s . This decrease is accompanied by an additional temperature dependence to η . Both reflect the variation of the relaxation modulus with T (eqs 5 and 6). A consequence is that the variation of η with T becomes greater than the variation of τ_1 . The implication is that the viscosity may be a less useful quantity, at least when assessing temperature dependences of rheologically complex materials, including low molecular polymers at lower temperatures. For high polymers, and/or well-above T_g , there is no change of J_s with temperature and hence no significant difference between the T dependences of η and τ_1 . Note that the decrease in J_s for unentangled polymers at low temperature is contrary to the behavior expected from the pure Rouse model. The effect has been ascribed to the loss of the longer chain modes due to encroachment from local segmental relaxation.¹⁸ Most important herein is that eq 4 still gives a valid measure of the terminal relaxation time.

We show herein that for unentangled PS ($2 \leq M_w$ (kg/mol) ≤ 13) the T dependence of η can be less than, equal to, or even greater than the variation of the local segmental relaxation times with temperature. The

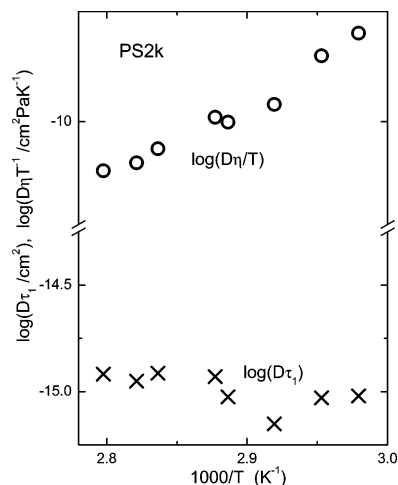


Figure 4. Product of the diffusion constant times the Rouse relaxation times (x) and the diffusion constant times the viscosity divided by T (O) for PS2K.

behavior is reflected in the temperature variation of J_s . The viscosity is a low-frequency, global quantity, which cannot be identified with either local segmental motion or the “glassy mode” of Inoue et al.⁸ τ_1 is the “terminal” Rouse time for the reorientation of the chain end-to-end vector, and it, as well as τ_0 , may be less affected by the temperature variations of $G(t)$, in comparison to the steady-state compliance (viz. eqs 3 and 4). Together with the fact that that τ_1 and τ_0 are both Rouse relaxation times, this leads immediately to the conclusion that τ_1 has the same T dependence as τ_0 .

In Figure 4, the product of τ_1 and the D from ref 11 are plotted vs temperature for PS2K. There is no significant variation, supporting a principal finding of Urakawa et al.¹¹ that D ($\propto \tau_0^{-1}$) has the same temperature dependence as the terminal (longest Rouse) relaxation time. This conclusion is reached herein directly from experimental viscoelastic quantities (i.e., η and J_s), without recourse to the R-mode analysis of Inoue et al.⁸ As has been discussed elsewhere,^{9,10} the deconvolution of the dynamic modulus into distinct glassy and rubbery components,⁷ originally proposed by Read,⁶ relies on a stress-additivity assumption which is questionable.^{19,20}

Also shown in Figure 4 is the quantity $D\eta/T$ (the viscosity is divided by temperature in accord with the Stokes–Einstein rule). This quantity increases with decreasing temperature, a manifestation of the well-known enhancement of translational motion near T_g .¹¹ Our analysis herein obviates the need to invoke the argument that dynamic heterogeneity of segmental relaxation is averaged out due to the larger size of the PS2K molecule relative to the length scale for spatial heterogeneity.¹¹ While this argument is needed to rationalize the absence of enhancement of translation diffusion in PS2K in comparison to the terminal relaxation rate $1/\tau_1$ (corresponding to $1/\tau_{\text{term}}$ in ref 11), the present approach arrives at the same conclusion directly. Spatially heterogeneous dynamics has been proposed²¹ as the cause of the enhancement in small-molecule glass-formers of translation diffusion compared to the rate of rotational relaxation. The inference of Urakawa et al.¹¹ is that the PS2K molecules experience an average environment, which diminishes or even eliminates enhancement of their translation diffusion. Accordingly, the plausibility of the spatially heteroge-

Table 1. Activation Energies for Polyethylene and Hydrogenated Polybutadiene ($T \gg T_g$)

variable	E_a (kJ/mol)	
	polyethylene	hydrogenated polybutadiene ^a
η	26.6 ²²	30 ²⁴
D	22.9 ²³	25.9 ²⁵

^a 8% vinyl content.

neous dynamics explanation of enhanced translational diffusion for small molecular glass-formers²¹ is consistent with the absence of it in PS2K. However, this explanation in terms of heterogeneity length scales does not address the situation for polymers of high molecular weight. For entangled chains, the viscosity and self-diffusion coefficient exhibit different temperature dependences. For example, as shown in Table 1, the activation energy for the viscosity of polyethylene²² is larger than E_a for self-diffusion.²³ The same is true for (the structurally similar) hydrogenated polybutadiene.^{24,25} These molecules, of course, are larger in size than PS2K, and so the putative averaging of spatial heterogeneities still occurs. However, the decoupling of η and D in high- M_w polymers is observed at high temperatures, $T > T_g$, where dynamic heterogeneity is not expected to be an issue. Thus, an explanation based on spatially heterogeneous dynamics is not operative in this regime.

There is, however, an alternative hypothesis regarding the decoupling between translational diffusion and rotational motion observed in small molecules. One obvious difference is that D involves the correlation of the center of mass (one point), while τ_c is determined by the time correlation of the transition dipole of the molecule, \bar{u} , a vector. Thus, a priori, there is no reason to expect their correlation functions to be the same. Moreover, from the fact that the vector \bar{u} is defined by two points in space, one expects intermolecular constraints to be more effective in slowing the rotation of \bar{u} than the motion of the center of mass. The coupling model explanation of the decoupling is based on the difference in the correlation functions (and hence coupling parameters) for self-diffusion and rotation.²⁶ According to this approach, the same mechanism underlies the decoupling seen in small molecular liquids near T_g and in entangled polymers at high temperature.

However, is the lack of this decoupling in PS2K consistent with this alternative explanation? The answer is in the affirmative and is easily arrived at as follows. As formulated, in the Rouse model for undiluted polymers, the relaxation modes of each Rouse chain are independent of those for other chains. Hence, by definition, all Rouse modes, including τ_0 (self-diffusion) and τ_1 (rotation) in unentangled PS, experience no intermolecular coupling, and thus their coupling parameters equal zero.²⁷ Moreover, since their coupling parameters are the same, it follows that τ_0 and rotation τ_1 have the same temperature dependence;²⁶ there is no decoupling in PS2K, in accord with the finding of Urakawa et al.¹¹ Although for Rouse chains near T_g , self-diffusion is not enhanced relative to terminal relaxation, for high molecular weight polymers, reorientation and self-diffusion are associated with different (nonzero) coupling parameters, again due to different correlation functions (reflecting different weighting of entanglement interactions). From the dependence of the relaxation time on the magnitude of the coupling parameter, the differ-

ences in temperature dependences of viscosity and self-diffusion (viz. the E_a in Table 1) can be accounted for.²⁸

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