When Does a Molecule Become a Polymer?

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ABSTRACT: Using light scattering spectroscopy, we demonstrate that a transition from small molecular behavior to Rouse dynamics in poly(dimethylsiloxane) (PDMS) is a smooth function of molecular weight, M_w. The asymptotic Rouse behavior is achieved when the chain begins to display Gaussian behavior. Surprisingly, the molecular weight dependence of physical properties such as T_g and density also level off at the same molecular weight. A comparison of PDMS and polystyrene (PS) demonstrates that neither molecular weight between entanglement (M_e) nor Kuhn segment length l_K is important for T_g and density. We speculate that there may be a third important parameter of molecular weight, in addition to M_e and l_K, which characterizes chain statistics and determines the molecular weight dependence of some physical properties. We introduce the molecular weight of a random step, m_R, as such a parameter. m_R is estimated to be ∼560 for PDMS and ∼5100 for PS. The molecular weight dependence of T_g in PDMS and PS appears to be the same when presented as a function of M_w/m_R. Moreover, our analysis shows that a molecule becomes a polymer (approaches Gaussian coil) at $M_w \sim 10-20m_R$.

I. Introduction

The most significant difference between polymers and other materials appears in the viscoelastic properties at times longer than the structural relaxation time τ_α (α-process or segmental relaxation in polymers). Segmental motion is slowed down due to chain connectivity and is usually described by the Rouse model for an unentangled chain and the reptation model for a long entangled chain.[1−3] While a crossover from the Rouse-type behavior to reptation-like motion has been intensively discussed,[1,4−7] a crossover from the small molecule behavior to the Rouse regime has received relatively little attention.[8] The Rouse dynamics, however, is a general property of polymer melts.[1,5] The Rouse model considers a flexible chain of N segments and, assuming Gaussian statistics for the chain, predicts that the mean-squared displacement of a monomer on a time scale shorter than diffusion of the whole molecule should increase as $\langle r^2\rangle \propto t^a$ and that the mechanical loss modulus should change as $G(\nu) \propto \nu^a$ with $a = 0.5$.[1−3,5] For comparison, small molecules exhibit normal diffusion, $\langle r^2\rangle \propto t$, and $G(\nu) \propto \nu$ in this time (frequency) range, $t > \tau_\alpha$. The assumption of Gaussian chain statistics is a fundamental concept in polymer physics,[1,3] and when a molecule is still too short to display Gaussian statistics, one would expect the value of the exponent a to be in the range between 1 and 0.5. Thus, by changing the molecular weight of a chain (M_w), one can observe a transition from behavior characteristic for small molecules to the Rouse dynamics characteristic for polymers. This transition in dynamic behavior should occur at a value of M_w above which molecules exhibit Gaussian statistics and become "polymers".

The predictions of the Rouse model have been tested in many experiments on polymer melts and have been found to be in reasonable agreement, even on a quantitative level.[1,3,6] Recent analytical studies[9] on a model chain (without entanglements) show that the mean-square displacement of the segment varies as $\langle r^2\rangle \propto t^a$, $a = 0.6$ for a chain with $N = 10$ Kuhn segments, but reaches 0.5 for a chain with $N = 100$ Kuhn segments. One should keep in mind that N is not the number of repeat units, X_n, in a real polymer. N corresponds to the number of Kuhn segments in the chain. Each Kuhn segment may consist of a few repeat units depending on the flexibility of the real chain. In contrast, computer simulations[8,10,11] demonstrated that the value of the exponent a varies from ∼0.6 to 1, depending on the length of the chain simulated, but does not reach the asymptotic value of 0.5. For example, Padding et al.[12,13] found in simulations of polyethylene (PE) deviations from the Rouse behavior even for the $C_{120}H_{240}$ chain, which is near the molecular weight between entanglements, M_e. Moreover, results of computer simulations presented in ref 14 suggest that a chain hits reptation behavior before reaching the asymptotic Rouse behavior.

This contribution presents analysis of depolarized light scattering spectra of poly(dimethylsiloxane) (PDMS) with various molecular weights. A smooth transition from behavior characteristic for small molecules to Rouse-type dynamics is observed. We demonstrate that the asymptotic Rouse exponent ∼0.5 is achieved at the molecular weight at which Gaussian statistics is achieved. More importantly, we found that this change in dynamics and in the chain statistics correlates with changes in the glass transition temperature, T_g. We speculate that there is a third parameter of a polymer chain important for Rouse dynamics, segmental relaxation, and T_g in addition to traditionally used M_e and Kuhn segment length l_K.

II. Experimental Results

We choose PDMS because it is considered to be the best chain to display Rouse dynamics even down to very small length scale.[15,16] Methyl-terminated PDMS with molecular weight from 162 (the degree of polymerization $X_n = 1$, without including the end groups) up to 166 500 ($X_n = 1573$) was purchased from Gelest with typical polydispersity 1.5−2.0.[16] The samples were placed in an optical cryofurnace (Janis ST-100 model). Depolarized light scattering spectra were measured in the backscattering geometry, using a tandem interferometer (Sandercock model) at frequencies below ∼300 GHz and a Raman spectrometer (JY T64000) at higher frequencies. An Ar ion laser with a wavelength of 514.5 nm and power of 200 mW was used for the measurements. Spectra were measured at two temperatures, 296 and 400 K, to analyze any possible energetic effects.

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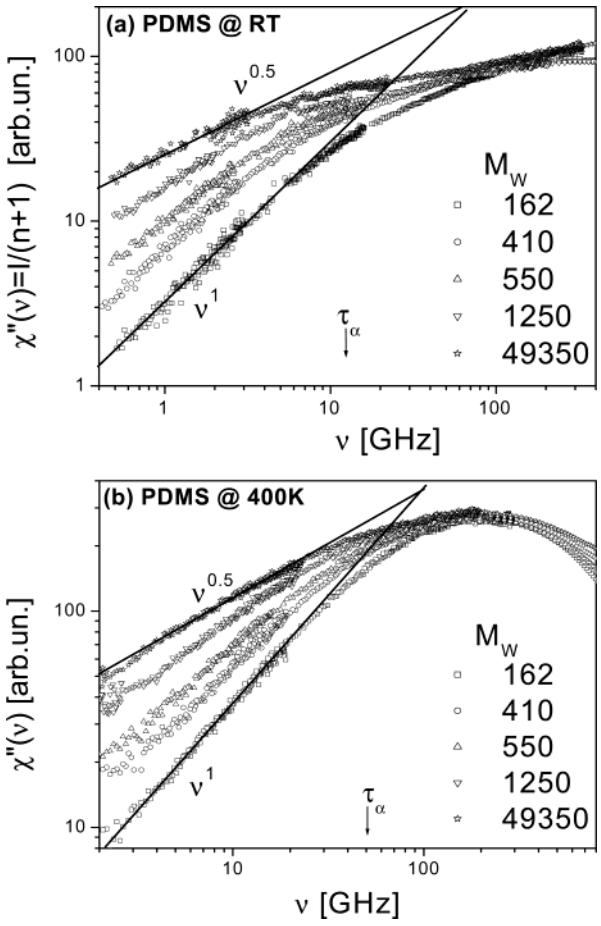

Figure 1. Depolarized light scattering spectra of PDMS with various molecular weight at (a) $T = 296$ K and (b) $T = 400$ K. The spectra are presented as the imaginary part of the susceptibility. The segmental relaxation frequencies at both temperatures are marked with the arrows. The solid lines present slopes characteristic for small molecules $\chi''(\nu) \propto \nu$ and for the Rouse dynamics $\chi''(\nu) \propto \nu^{0.5}$.

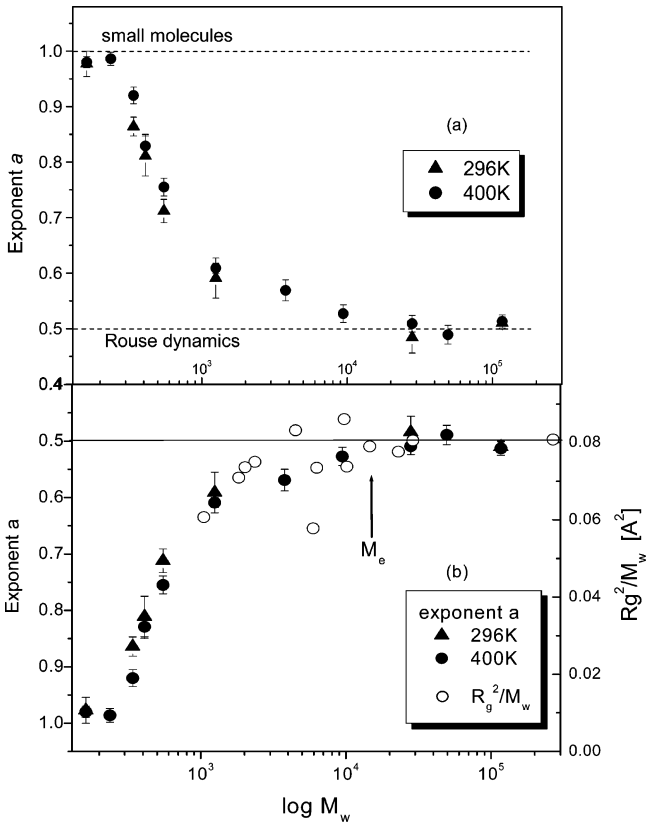

Figure 2. (a) Molecular weight dependence of the exponent a in PDMS at $T = 400$ K and $T = 296$ K; dashed lines show limits $a = 1$ for small molecules and $a = 0.5$ for the Rouse dynamics. (b) Molecular weight dependence of the exponent compared to the molecular weight dependence of R_g (data from refs 36 and 37). The arrow marks M_e.

Figure 1 presents light scattering susceptibility spectra $\chi(\nu) = I(\nu)/[n(\nu) + 1]$ at two temperatures. Here $I(\nu)$ is the light scattering intensity, and $n(\nu) = [\exp(h\nu/kT) - 1]^{-1}$ is the Bose temperature factor. The susceptibility presentation allows direct comparison of scattering data to dielectric $\epsilon''(\nu)$ or mechanic $G''(\nu)$ loss modulus data.[17] Figure 1 shows that the low-frequency tail of the relaxation spectra depends on molecular weight: $\chi(\nu) \propto \nu$ for short chain and reaches $\chi(\nu) \propto \nu^{0.5}$ for long chains. For a quantitative analysis of the slope, we fit the low-frequency part (2 GHz $< \nu <$ 25−30 GHz at $T =$ 400 K and ∼0.7 GHz $< \nu <$ 6−7 GHz at $T = 296$ K) of the spectra by a power law $\chi(\nu) \propto \nu^a$. The dependence of the value of the exponent a on degree of polymerization is presented in Figure 2a. There is no significant difference between the data obtained at $T = 400$ K and $T = 296$ K. An increase in temperature leads to a shift of the relaxation spectra to higher frequencies, but no variation in a is observed. The first change in the exponent is observed already in very short chains with degree of polymerization $X_n \geq 3-4$ ($M_w \sim 400$). The exponent decreases smoothly with increase in X_n and reaches the asymptotic Rouse value of 0.5 at $X_n \sim 50-100$ ($M_w \sim 4000-7500$).

III. Discussion

A. Rouse Dynamics in Depolarized Light Scattering Spectra. To verify that the observed low-frequency tail (Figure 1) is the expected Rouse regime, it is necessary to identify the frequency range of the Rouse dynamics. It should show up below the frequency of the segmental relaxation $\nu_\alpha = (2\pi\tau_\alpha)^{-1}$ but above the characteristic frequency of the longest Rouse relaxation time $\nu_{\text{Rouse}} = (2\pi\tau_R)^{-1}$. Recently, Arrighi et al.[18] analyzed the local dynamics of PDMS chain ($M = 92\,000$) at $T =$ 300 K using quasielastic neutron scattering and obtained for the segmental relaxation $\nu_\alpha = 0.05$ meV ≅ 12 GHz. This agrees well with the high-frequency limit for the observed Rouse regime at $T = 296$ K (marked in Figure 1a). Taking into account the Arrhenius temperature dependence with $E_a = 14.6$ kJ/mol, observed for the segmental relaxation of PDMS at high temperature,[18] ν_a for 400 K is estimated to be ∼50 GHz. This also agrees well with the spectra measured at $T = 400$ K (Figure 1b). Arbe et al.[15] measured the intermediate scattering function using neutron spin echo (NSE) and obtained the Rouse diffusion coefficient for PDMS melt ($M = 6462$) at 373 K, $D_R = 2.7$ Å^2 ns^{-1}. The longest Rouse relaxation time is estimated to be ∼0.95 ns (∼0.17 GHz), based on $\tau_R = R_g^2/(18\pi^2 D_R)$ with the radius of gyration $R_g = 21.3$ Å from their work. These estimates confirm that the observed low-frequency tail (Figure 1) falls exactly in the expected Rouse regime.

It is not obvious how Rouse dynamics should show up in the light scattering spectra. It might be that the presented results (Figure 1) are the first observation of the Rouse-like dynamics in depolarized light scattering. The relationship between depolarized light scattering spectra and density fluctuations measured, for example, in neutron scattering remains unclear and is the subject of many papers.[19−21] It is known that mechanical stresses lead to change of refractive index (birefringence) of polymeric materials. Stress-induced birefrin-

gence is usually described by stress−optical rules and is ascribed to orientation of main chain.[22] We expect that this stress−optical mechanism may be the reason for the appearance of the Rouse-like behavior $\chi(\nu) \propto G(\nu) \propto \nu^{0.5}$ in depolarized light scattering spectra.

We have found two earlier theoretical works that analyze depolarized light scattering mechanisms in polymers and predict two contributions:[23,24] (i) segmental reorientation (segmental relaxation or α-peak in our case), its amplitude depends on optical anisotropy of a monomer; and (ii) chain relaxations with amplitude that depends on photoelastic constants or optical anisotropy of subchains. This situation is similar to mechanical relaxation where also the sum of two contributions, segmental (glassy) and chain (rubbery), are assumed.[25−27] These two contributions to $G^*(\nu)$ differ strongly in amplitude because of much weaker elastic constant of the entropic spring of subchains. The depolarized spectra of PDMS (Figure 1) clearly show that the contribution of segmental relaxation (marked by τ_α) is weaker than the microscopic peak at $\nu \sim 300$ GHz. For most molecular systems such as glycerol, salol, and *o*-terphenyl the peak of the α-relaxation in the depolarized light scattering is much higher than the microscopic peak.[28−30] The same has been observed in depolarized light scattering spectra of many polymers, including poly(propylene glycol),[31] polyisobutylene (PIB),[32] polybutadiene, and polyisoprene.[33] The low amplitude of the α-relaxation peak in the depolarized spectra of PDMS (Figure 1) suggests rather low optical anisotropy of monomers. That might be the reason for relatively strong contribution of chain relaxation in depolarized spectra of PDMS. These questions together with a direct comparison of the light scattering data to $G^*(\nu)$ measured traditionally in the hertz−milihertz frequency range will be discussed in more detail elsewhere.[34]

Figure 2a shows that PDMS approaches asymptotic Rouse dynamics at length of the chain ∼50−100 monomers. Does that correspond to the molecular weight at which the chain approaches a Gaussian coil? This point can be verified from analysis of the molecular weight dependence of R_g. $\langle R_g^2\rangle/M$ usually increases with molecular weight and reaches a constant value when the coil approaches Gaussian statistics:[35]

$$\langle R_g^2\rangle = \frac{1}{6}\langle R_0^2\rangle = \frac{1}{6}C_\infty n l_0^2 = \frac{1}{6}C_\infty \frac{M}{m_0} l_0^2 \qquad (1)$$

Here R_0 is the end-to-end distance, n, m_0, and l_0 are the number of bonds in the chain, the mass associated, and the length of the bond, respectively, and C_∞ is the characteristic ratio. The latter defines the length of the Kuhn segment $l_K = C_\infty l_0$ and is considered to be a characteristic of the chain stiffness.[1,3] The molecular weight dependence of the exponent a agrees well with the data for $\langle R_g^2\rangle/M$ taken from the literature;[36,37] both saturate at approximately the same M (Figure 2b). This analysis gives further support for our interpretation of the extended low-frequency tail, $\chi''(\nu) \propto \nu^{0.5}$, as being a Rouse-like relaxation. These results suggest that a PDMS chain becomes a polymer, i.e., reaches Gaussian statistics and shows the Rouse-like chain dynamics, at a rather small degree of polymerization $X_n \sim 50-100$. We should emphasize that achieving the Gaussian coil is strictly speaking an asymptotic process. We will use the term "approaching Gaussian statistics (coil)" when the quantities analyzed become constant (independent of M) within experimental accuracy.

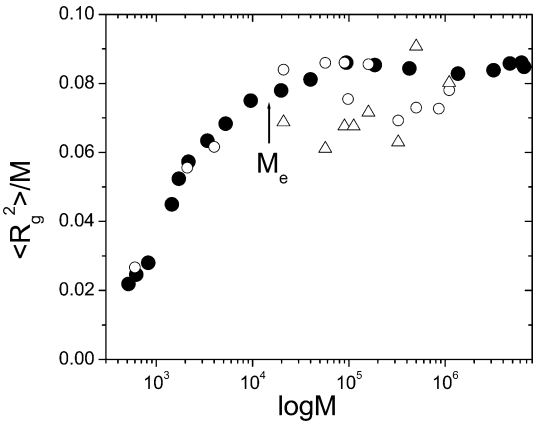

Figure 3. Molecular weight dependence of the ratio $\langle R_g^2\rangle/M$ in PS: (●) SAXS data for PS θ-solutions from ref 38; (○) SANS data for PS θ-solutions from ref 41; and (△) SANS data for PS melts from refs 39 and 40. The arrow marks M_e.

Figure 3 shows the molecular weight dependence of $\langle R_g^2\rangle/M$ in another polymer, polystyrene (PS).[38−41] Unfortunately, small-angle neutron scattering (SANS) data for PS melts are very limited, and we did not find any data for melts of short ($M_w < 10\,000$) chains. It is usually expected that the chain statistics in θ-solution is identical to the chain statistics in the melt.[35] This assumption has been confirmed by many SANS measurements and simulations.[39−42] In particular, SANS measurements[39−41] have found no difference in R_g of PS chains in θ-solution and in the melt (Figure 3), although no comparison for short chains has been performed. On the basis of this traditional assumption, we use the most complete data set for the molecular weight dependence of $\langle R_g^2\rangle/M$ in PS from ref 38. These data are based on small-angle X-ray scattering (SAXS) measurements of PS in a θ-solvent.

One surprising result in Figure 3 is that $\langle R_g^2\rangle/M$ in PS reaches saturation at much higher $M \sim 100\,000$ ($X_n \sim 1000$) than in PDMS. We will discuss this point in more details in the next section. What is more interesting here is that the Gaussian statistics in PS is reached at M_w much higher than molecular weight between entanglements $M_e \sim 13\,000$.[43] It means that PS chain becomes entangled before achieving Gaussian coil. In this case we expect that the exponent a will not reach the asymptotic value of 0.5, but instead stop at a higher value of $M_w \sim M_e$. This idea agrees with the results of recent computer simulations[14] where the exponent ∼0.6 (significantly higher than the asymptotic Rouse value of 0.5) has been observed for mean-squared displacements of monomers even in entangled chains. This observation might provide an explanation for a long-standing experimental puzzle in mechanical measurements of polymers where the asymptotic Rouse prediction, $G'(\nu) = G''(\nu) \propto \nu^{0.5}$, has not been found.[5] Chain between entanglements for many polymers might not be long enough to reach Gaussian coil. This idea suggests that the asymptotic Rouse predictions might not be applicable for many polymers; instead, an exact summation of a limited number of subchain modes should be used.

B. Chain Statistics and the Glass Transition. Figure 4 compares the molecular weight dependencies of the glass transition temperature T_g and of the chain size $\langle R_g^2\rangle/M$ for PDMS and PS. Surprisingly, the molecular weight dependence of T_g for both polymers follows well the chain statistics; it saturates at the same

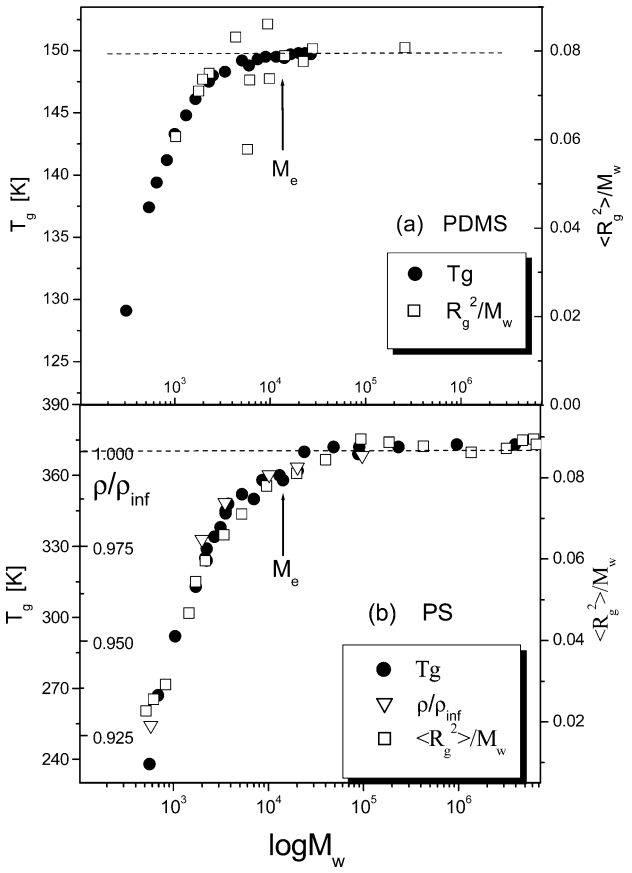

Figure 4. Molecular weight dependence of T_g and of $\langle R_g^2\rangle/M$ (a) for PDMS (T_g data from refs 44 and 45) and (b) for PS (T_g data from ref 46). Also, the molecular weight dependence of density ρ (data from ref 47) in PS is shown in (b). The arrows mark M_e.

M_w at which the chain approaches Gaussian coil (i.e., $\langle R_g^2\rangle/M \approx$ constant). The same is observed for the molecular weight dependence of density in PS (Figure 4b). These results (Figures 2−4) suggest that when a polymer chain becomes long enough to exhibit Gaussian behavior, the asymptotic Rouse dynamics emerges and the molecular weight dependence of many physical properties, such as T_g and density, saturate.

Both polymers, PDMS and PS, have similar values of molecular weight between entanglements, $M_e \sim$ 13 000−15 000,[43] and slightly different Kuhn segment length l_K or C_∞: $l_K \sim 5-6$ monomers and $C_\infty \sim 6.5$ in PDMS, while $l_K \sim 8-9$ monomers and $C_\infty \sim 9.5$ in PS.[37,48] Nevertheless, a PS chain must have ∼7−15 times more monomers or ∼5−10 times more Kuhn segments than a PDMS chain in order to reach Gaussian coil. The same tendency is observed in the molecular weight dependence of T_g (Figure 4). This comparison demonstrates that M_e and l_K (or C_∞) are not important parameters for the glass transition in polymers. Instead, a new parameter—the molecular weight at which the Gaussian coil is achieved—is crucial for T_g, density, and perhaps segmental relaxation in polymers.

It is not clear why PDMS approaches Gaussian statistics at much shorter chain length ($X_n \sim 50-100$) than PS does ($X_n \sim 1000$), especially since size of the coils in these polymers does not differ much: $\langle R_g^2\rangle/M \sim$ 0.08 Å^2 in PDMS and $\langle R_g^2\rangle/M \sim$ 0.09 Å^2 in PS (Figure 4). There are a few other experimental evidences suggesting that traditionally defined Kuhn segment length might disagree with a bead size. Using the neutron spin echo technique for analysis of chain dynamics in polymer solutions, the authors of ref 49 estimated bead size to be ∼16 Å for PDMS and ∼38−55 Å for PS. Arbe et al.[15] used neutron scattering spectroscopy to compare the chain dynamics of PDMS and PIB. They found that Rouse model describes PDMS chain dynamics up to $Q \sim 0.4$ Å^{-1}, while it fails to describe PIB chain dynamics already at $Q > 0.15$ Å^{-1}. Apparently the dynamic (Rouse) bead is much shorter in PDMS than in PIB, although both molecules have very similar l_K ($C_\infty \sim 6.5$ for both[15]). Similar results have been found by Somoza et al. from the measurements of rotational relaxation time of small probe molecules in PIB and PDMS melts.[16]

To analyze this contradiction, let us go back to the basic definition of the Kuhn segment length and chain statistics (eq 1). The Kuhn segment length is traditionally estimated using the length of a completely extended chain R_{max}:[1,3]

$$R_{max} = Nl_K = nl_0 \tag{2}$$

Rewriting eq 1

$$\langle R_0^2\rangle = Nl_K^2 = C_\infty nl_0^2 \tag{3}$$

and substituting the eq 2 in eq 3, one obtains the traditional relationship for the Kuhn segment, $l_K = C_\infty l_0$. However, eq 2 explicitly assumes that the chain inside of a single Kuhn segment is completely extended. This is not the case for most of the polymers. Equation 3 can be rewritten

$$\langle R_0^2\rangle = N_R l_R^2 = \frac{M}{m_R} l_R^2 = C_\infty nl_0^2 = C_\infty \frac{M}{m_0} l_0^2 \tag{4}$$

Here we specially introduce N_R as the number, l_R as the length, and m_R as the mass of the random step in order to differentiate them from traditionally defined Kuhn parameters. Equation 4 gives a relationship between the length of the random step and l_0:

$$l_R^2 = C_\infty \frac{m_R}{m_0} l_0^2 \tag{5}$$

The above relationship differs significantly from the standard definition of the Kuhn segment. More importantly, there is an additional parameter, m_R, which enters the relationship. This might explain why polymers with similar C_∞ have large difference in the length of a dynamic bead. C_∞ characterizes the size of a polymer coil (eqs 1 and 4), while m_R (or l_R) characterizes the mass (or the length) of a single bead. These two parameters are not directly related (in contrast to the assumption used for the definition of the Kuhn segment). As a result, polymers with similar C_∞ may approach Gaussian coil at different molecular weights, as we see in the case of PDMS and PS (Figure 4). Recent theoretical analysis presented in ref 50 supports this idea. Moreover, using the rotation isomeric state model, the authors[50] have shown that a PDMS chain approaches infinite chain limit nearly twice faster than PIB does, although they have similar C_∞.

We can verify the proposed relationship (eq 5) assuming that the lengths of the beads estimated using neutron spectroscopy in ref 49 are correct. In the case of PDMS ($l_R \sim 16$ Å, $C_\infty = 6.5$, $l_0 = 1.64$ Å, $m_0 = 38$) it gives $m_R \sim 560$, i.e., ∼7.5 monomers. This estimate is

not very far from traditionally used Kuhn segment length. However, in the case of PS ($l_R \sim 47$ Å, $C_\infty = 9.5$, $l_0 = 1.54$ Å, $m_0 = 52$) the relationship (eq 5) gives $m_R \sim 5100$, i.e., ~50 monomers. This is significantly larger than traditionally used Kuhn segment length ~8−9 monomers.[48] It is interesting to note that earlier Monte Carlo simulations and careful SANS measurements of partially deuterated chains have shown that peculiarities of PS monomeric structure remain important up to distances ~50 Å,[51,52] i.e., at length scales much larger than a single Kuhn segment. There were also a few estimates of the dynamic bead in PS solutions from the fit of mechanical relaxation and oscillatory flow birefringence (OFB) data to a bead−spring model.[53,54] In both cases the authors obtained an estimate ~50 monomers that agrees well with results of our analysis.

However, we should emphasize that the situation with estimates of dynamic bead size in PS melt is less clear. It is usually assumed to be of the order of the Kuhn segment length,[5,47] although many authors admitted failure of the Rouse model to describe mechanical properties of short PS chains.[5,26,47] Analyzing dynamic mechanical and birefringence data of PS solutions, Inoue et al. concluded[27] that the molecular weight of the dynamic segment decreases with the increase of concentration and reaches the value of Kuhn segment in the bulk, although they admit that the size of an optical segment remains the same at any concentration. The estimate of the dynamic bead size in this case was indirect, through an extrapolation of a chain contribution to mechanical modulus at infinitely high frequency. Using the same analysis, Ionue and Osaki[25] estimated the dynamic bead size for more than 10 different polymers. A reasonable agreement between the bead size and standard Kuhn segment has been found for all the polymers where the data were available.[25] These results contradict a few publications where more direct measurements of the length scale were involved. As we have mentioned above, the comparison between PDMS and PIB melts by neutron measurements[15] and small probe rotation in PDMS, PE, and PIB[16] indicated that the dynamic segment differs significantly for polymers with a similar Kuhn segment length. In particular, neutron measurements by Richter et al.[55] showed failure of the Rouse model for PIB already at $Q \sim 0.2$ Å^{-1}, which corresponds to a length scale much beyond the Kuhn length. Moreover, recent analysis by Siline and Leonov[56] show that the flow segment might differ significantly from the Kuhn segment. In particular, extremely large flow segment appears for a PS melt. Also, recent rotational isomeric state calculations for PE, PDMS, and PIB show that even for the static chain properties, Kuhn length alone cannot describe the chain statistics.[50] Therefore, at present, results remain contradictory, and more theoretical and experimental efforts should be made to give a consistent picture of a size of dynamic and static beads and their relationship to the Kuhn segment length in polymer melts. In particular, detailed SANS and neutron spin echo (NSE) measurements of PS melts might be extremely desirable. They can provide direct estimates of static (SANS) and dynamic (NSE) bead sizes. Both appear to be ~50 monomers, i.e., ~5 times larger than traditional Kuhn segment, in PS solutions. However, their value in PS melts might be different.

We are now turning back to analysis of the correlation between chain statistics and T_g (Figure 4). Figure 5 presents the molecular weight dependence of $T_g/T_g(\infty)$ for PDMS and PS as a function of M_w/m_R. Surprisingly, the dependence appears to be universal with no free adjustable parameters for both polymers (Figure 5). This analysis demonstrates the importance of the chain statistics for the glass transition. Moreover, it explains why C_∞ (or l_K) is not directly related to dynamics (whether segmental or Rouse). Instead, m_R (or l_R) appears to be an important parameter that defines molecular weight dependence of segmental and chain (Rouse) dynamics and T_g. The above analysis (Figure 5) shows that a chain needs to be ~10−20 segments long to approach Gaussian coil, i.e., to become a polymer. This conclusion is consistent with results of simulations presented in ref 57, where comparison of statistics for a Gaussian chain and for a random walk with 10 random steps shows no significant difference. The presented results also explain why PS has one of the strongest dependence of T_g on molecular weight. Because of rather large size of the dynamic bead (~50 monomers), much lower values of M/m_R can be achieved for short oligomers (see Figure 5).

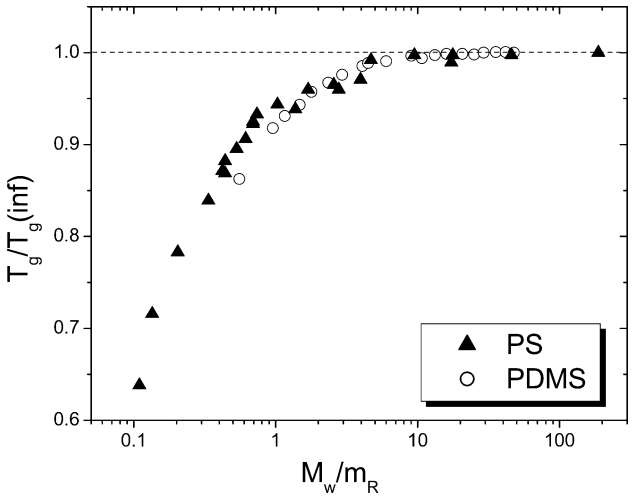

Figure 5. $T_g/T_g(\infty)$ as a function of molecular weight scaled by the mass of random step m_R. $m_R \sim 560$ for PDMS and $m_R \sim 5100$ for PS (see the text for definition of m_R).

How does our finding (Figure 5) compare to traditional approaches for description of the molecular weight dependence of T_g in polymers? It is not obvious for us how the chain statistics enters the Gibbs−DiMarzio approach,[58] and it is worth exploring that in the future. Another traditional approach is the chain-end free volume model.[59] Chain statistics does not enter the end-free volume model. So, this model cannot describe our observation (Figure 5). We also want to emphasize that our recent analysis of dynamics of linear and star polybutadiene[60] shows a failure of the chain-end free volume approach. We expect that chain-end free volume effects might be important for chains with molecular weight $\sim m_R$ (that is not small for PS, for example), but chains statistics becomes more important at higher M_w. We speculate that the packing of polymer chains (i.e., density of a polymer melt) depends on molecular weight until the point when the chain becomes Gaussian. The Gaussian chain has regular scaling behavior that makes the density of the melt independent of the length of the chains. This simple consideration might provide a qualitative explanation of the observed correlation between dependence of dynamics, density, and T_g on M_w.

IV. Conclusion

We have analyzed a transition from dynamics characteristic for small molecules to the Rouse dynamics characteristic for polymers. The dynamics appear to vary smoothly as a function of molecular weight of the PDMS chain and reach the asymptotic Rouse behavior at the same molecular weight, M_G, at which a chain begins to display Gaussian statistics. The important observation is that the molecular weight dependence of some physical properties of polymers, such as T_g and density saturates at the same $M_w \sim M_G$. It appears that M_G depends strongly on the chemistry of a polymer chain, might be higher or lower than the molecular weight between entanglements M_e, and does not correlate to Kuhn segment length l_K or characteristic ratio C_∞. We show that there is a deficiency in the traditional definition of the Kuhn segment length: the one parameter (C_∞) function is not enough, at least one additional parameter, mass of a random step, m_R, should be introduced in order to characterize the chain statistics. We emphasize that molecular weight dependencies of some physical properties (such as T_g and density) are not sensitive to M_e and l_K. Instead, as it appears from our analysis, the molecular weight dependence is sensitive to m_R. Above the molecular weight $M_G \sim 10-20m_R$, a chain becomes Gaussian, its dynamics should follow the Rouse predictions (if M_G is smaller than M_e), and density and T_g become independent of molecular weight. Apparently, more experimental, theoretical, and computational work is required to clarify the questions of the chain statistics and its importance for segmental and chain dynamics in polymers.

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