Breakdown of Time−Temperature Superposition Principle and Universality of Chain Dynamics in Polymers

Yifu Ding[†] and Alexei P. Sokolov*

Department of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

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ABSTRACT: Detailed comparison of temperature dependences of segmental (τ_α) and chain (τ_n) relaxation times shows that decoupling of these relaxation processes occurs (the ratio τ_n/τ_α starts to drop) at a similar range of $\tau_\alpha \sim 10^{-5}-10^{-7}$ s regardless of a polymer and its molecular weight. The degree of decoupling depends on polymer and is stronger in more fragile systems. The most intriguing result is a rather universal temperature dependence of τ_n observed for the analyzed polymers when it is plotted vs T_g/T. These observations call for a revision of current models describing the microscopic friction coefficient in polymer melts.

Introduction

Polymers exhibit peculiar viscoelastic behavior due to chain relaxation that controls their viscosity, diffusion, and mechanical properties. Chain relaxation in polymers appears in addition to the main structural relaxation (so-called α-relaxation) that exists also in nonpolymeric materials. The structural relaxation in polymers is usually called segmental relaxation. The chain relaxation in polymer melts is described by the Rouse or reptation models.[1,2] According to these single-chain models, the friction coefficient ζ defines the chain relaxation time τ_n and its temperature variation.[1,2] The traditional assumption is that the friction coefficient is the same for various chain and segmental modes. Thus, different relaxation processes in a polymer are expected to have the same temperature dependence.[2] This leads to the so-called time−temperature superposition (TTS), the basic principle widely used for analysis of polymer dynamics.[2]

Using viscoelastic measurements, Plazek showed already in 1965 that TTS breaks down for many polymers when the temperature approaches the glass transition temperature, T_g.[3] Modern dielectric spectroscopy covers an enormous frequency range and provides the potential for accurate studies of chain and segmental dynamics in some polymers (so-called type A polymers) that have an accumulated dipole moment along the chain backbone.[4,5] These studies reveal that the segmental relaxation time (τ_α) has stronger temperature dependence than the chain relaxation time in poly(propylene glycol) (PPG)[6] and polyisoprene (PIP).[7] The same phenomenon has been reported for atactic polypropylene (aPP) from collection of data obtained by different techniques.[8] Despite all these experimental observations, the TTS principle and the assumption that segmental relaxation defines the chain friction coefficient remain one of the cornerstones in polymer science.

In this work, we analyze the temperature dependence of τ_α and τ_n for several polymers. Surprisingly, τ_α and τ_n seem to decouple (start to have different temperature dependence) at a similar range of $\tau_\alpha \sim 10^{-5}-10^{-7}$ s for all the polymers analyzed. The extent of the decoupling depends strongly on the chemical structure of the polymers. More fragile systems (or systems with more rigid backbones) exhibit stronger decoupling. The most intriguing result is that all studied here polymers display similar dependence of τ_n on T_g/T, while they differ strongly in behavior of τ_α (fragility). We speculate that a decoupling of translational and rotational motions may be the reason for the observed decoupling of chain and segmental dynamics. A possible explanation for rather universal temperature dependence of the chain dynamics is discussed at the end.

Experimental Section

The broadband dielectric spectrometer Concept 80 (from Novocontrol) was used for the measurements, covering a broad frequency range: $10^{-2}-10^{8}$ Hz. Two monodisperse samples of PIP from Scientific Polymers, $M_n = 2460$ with polydispersity (PDI) = 1.08 and $M_n = 21\,200$ with PDI = 1.32, were used for dielectric measurements. Parallel plates geometry was used for all the measurements. Figure 1 illustrates the dielectric loss spectrum of *cis*-PIP with $M_n = 2460$ at several temperatures. The segmental and normal modes correspond to the higher and lower frequency of the relaxation peak, respectively. Characteristic relaxation times were obtained as the reciprocal of the frequency of the maximum in $\epsilon''(\nu)$ (Figure 2a). Both τ_α and τ_n increase with the increase of molecular weight (Figure 2a), which is consistent with known literature data.[4,5,9]

Results and Discussion

In both samples, τ_α shows a stronger temperature dependence than τ_n as temperature approaches T_g. The temperature dependences of the relaxation times for both modes agree well with many previous dielectric measurements of PIP with various molecular weights.[10−16] As an example, measurements from Doxastakis et al. for molecular weight 1350 are included in Figure 2b.[15] The difference in the behavior of τ_α for chains with different molecular weights is removed when temperature is scaled by T_g (Figure 2b). The vertical shift $A = -\log 309 = -2.49$ has been applied to τ_n for $M_n = 21\,200$ in order to match it to τ_n for $M_n = 2460$. This shift factor agrees with earlier analysis performed by Adachi et al., using empirical parameters, $M_c = 10\,000$ and exponent 3.7,[4,11] $A = \log(M_1/M_c)^{3.7}(M_c/M_2)^2 \approx \log(266) = 2.43$, or can be explained by the scaling predicted by the reptation model: $\log(M_1/M_e)^3(M_e/M_2)^2 = \log(21200/5097)^3(5097/2460)^2 = \log(309)$ (for PIP, $M_e = 5097$).[17] Similarly, a shift factor of $\log(2460/1350)^2 = 0.52$ is applied to $M_n = 1350$. Consistent with earlier reports,[7] the analysis (Figure 2b) shows no significant difference in the temperature

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[†] Current address: Polymer Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8541.

* Corresponding author: e-mail alexei@uakron.edu; phone 330-972-8409; fax 330-972-5290.

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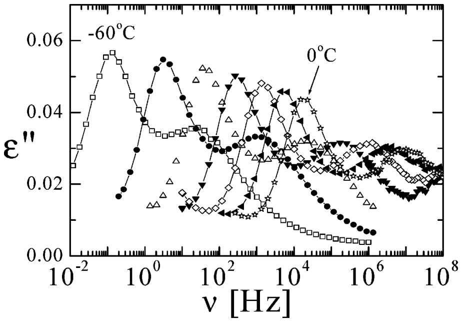

Figure 1. Dielectric loss spectrum for *cis*-PIP with $M_n = 2460$ at different temperatures. Temperature increases from −60 to 0 °C, with the step 10 °C.

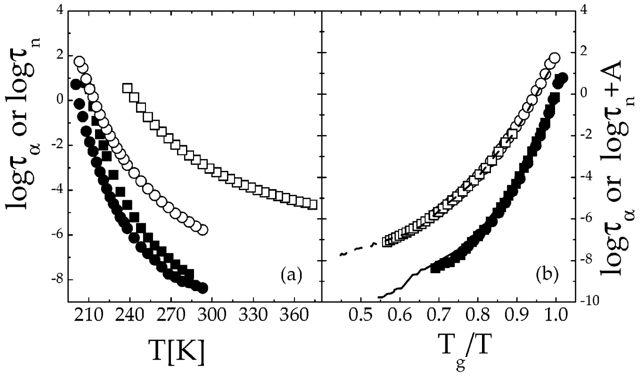

Figure 2. (a) Temperature dependence of relaxation times for *cis*-PIP: $M_n = 2460$, (●) τ_α and (○) τ_n; $M_n = 21\,200$, (■) τ_α and (□) τ_n. (b) T_g scaled temperature dependence of both τ_α and τ_n, the symbols are the same as in (a). Solid and dashed lines represent τ_α and τ_n of PIP with $M_n = 1350$ from ref 16. Here T_g is defined as the temperature where $\tau_\alpha = 1$ s, $T_g(M_n = 2460) = 202.5$ K, $T_g(M_n = 21\,200) = 211.7$ K, and $T_g(M_n = 1350) = 200.5$ K. To compare the temperature dependence, a vertical shift is applied to τ_n of $M_n = 21\,200$ and $M_n = 1350$; see text for details.

dependence of τ_n for so different molecular weights (range from 1350 up to 21 200) when scaled by T_g, at least in the range where τ_n overlaps. We note that dielectric relaxation data covering broader range of temperature and molecular weights are necessary to clarify this point.

According to the TTS principle, the ratio τ_n/τ_α should remain constant with the variation of temperature or relaxation time.[2] This ratio as a function of τ_α is shown in Figure 3a, and we observe that TTS in *cis*-PIP breaks down around $\tau_\alpha \sim 10^{-6}$ s. This agrees with earlier analysis performed by Adachi et al.[15] Literature data suggest that TTS breaks down around the same range of τ_α for PPG [6] and aPP.[18] Figure 3b presents the ratio τ_n/τ_α for six different polymers. Except for polycarbonate (PC), all the data for polymers are directly obtained from the references shown. In the case of PC, we were not able to find direct measurements of τ_n and used temperature dependence of viscosity, $\eta(T)$,[23] to estimate $\tau_n(T) = \eta(T)J_e = \eta(T)/G_N$. We assumed that the plateau modulus G_N (or steady-state compliance J_e) is temperature independent.[2] Plazek et al. have shown that J_e decreases as temperature approaches T_g, but this effect is weak for large molecular weights.[24] Thus, assuming temperature-independent G_N, the ratio τ_n/τ_α for PC might be slightly overestimated at temperatures close to T_g. Its temperature dependence might be slightly stronger than the one shown in Figure 3b, making the decoupling even more pronounced. From the noisy data collected in Figure 3b it is difficult to identify unambiguously range of τ_α at which the time−temperature superposition starts to break down. However, it seems that τ_n/τ_α for the presented polymers starts to drop at a similar range of segmental relaxation time, $\tau_\alpha \sim 10^{-5}-10^{-7}$ s (it is not clear for PC due to the limited range of τ_α). Recent measurements on different molecular mass POB showed that the ratio of τ_n/τ_α does not depend on temperature.[25] However, the lowest temperature investigated (~225 K) is still much higher than T_g (199 K), where the effect of decoupling is not evident. Moreover, the strength of decoupling between segmental and chain dynamics depends strongly on the polymer (Figure 3b). Specifically, the deviation from the TTS follows the order POB ~ PPG < *cis*-PIP < aPP < PS < PC, suggesting that polymers with more rigid backbones have a stronger difference in temperature dependence of chain and segmental relaxation. Similar observations were reported by Plazek et al. from the comparison of TTS between PS and polyisobutylene (PIB): PS exhibits strong difference in temperature dependencies of τ_n and τ_α, while high molecular weight PIB seems to show similar variations in τ_n and τ_α.[26]

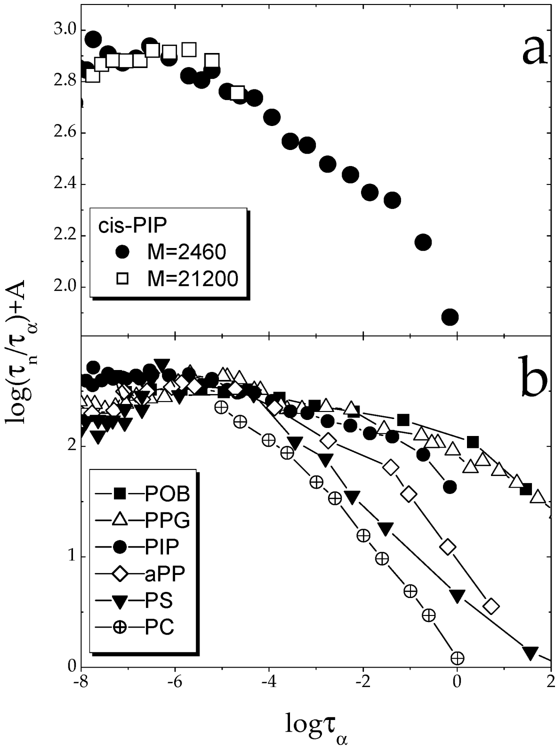

Figure 3. Ratio of chain (τ_n) to segmental (τ_α) relaxation times as a function of τ_α. (a) For *cis*-PIP with two different molecular weights. (b) For several polymers: polyoxybutylene (POB),[19] PPG,[5] PIP, atactic PP,[8] polystyrene (PS) (τ_α from ref 20 and τ_n from ref 21), polycarbonate (PC) (τ_α from ref 22 and τ_n from ref 23). Vertical shifts are applied to τ_n to match the values at high temperature (small τ_α).

The steepness of temperature variations of τ_α at T_g is traditionally described by the "fragility" parameter m defined as[28]

$$m = \left.\frac{\mathrm{d}\log\tau_\alpha}{\mathrm{d}(T_g/T)}\right|_{T=T_g} \tag{1}$$

We estimated the fragility of the analyzed polymers from temperature dependence of segmental relaxation m_α using both eq 1 and the slope of $\log\tau_\alpha$ vs T_g/T in the range $T_g/T = 0.95-1$ (Figure 4, Table 1). The polymers display fragility m_α in the order *cis*-PIP ~ POB < PPG < aPP < PS < PC, consistent with the literature values of m.[29] The most intriguing observation is similar dependence of τ_n on T_g/T for all the presented polymers (Figure 4). It is known that no master curve exists for viscosity of different polymers when it is plotted as $T -$

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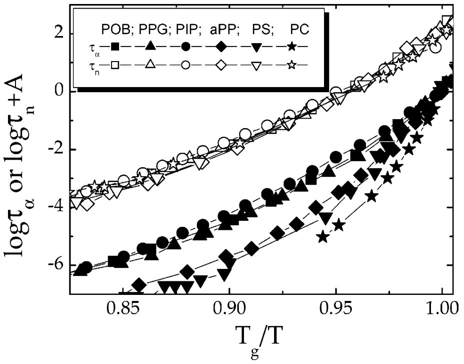

Figure 4. Dependence of the chain and segmental relaxation on T_g/T. Vertical shift is applied to τ_n. T_g is defined as $\tau_\alpha \sim 1$ s.

T_g.[30] The latter scaling is the most common way used to remove the differences in T_g's for comparison of different polymers or different molecular weights of the same polymer and is based on free volume arguments. We emphasize that scaling T_g/T has the physical meaning of scaling the temperature by an energetic parameter that affects friction coefficient. This scaling reveals rather universal temperature behavior for chain relaxation, at least in the polymers analyzed here. It would be important to verify whether this universality will also hold for chain relaxation in other polymeric systems.

We used the same definitions to estimate the "fragility" of the chain relaxation m_n (Figure 4, Table 1). It appears that m_n does not vary much (from ~42 up to ~50) in this group of polymers, while their segmental relaxation exhibits strong variation in fragility (from ~59 up to ~175). This result suggests that the observed difference in breakdown of TTS (Figure 3b) comes from the difference in temperature variation of τ_α, i.e., from fragility of the polymers: More fragile polymers show stronger decoupling. Moreover, the estimated value of m_n is close to the fragility value of high molecular weight PIB, $m_\alpha \sim 46$.[29] This explains why no significant breakdown of TTS has been observed for PIB.[26] The observed behavior is also consistent with earlier observation of stronger decoupling between chain and segmental relaxation in materials with broader segmental relaxation peak[27] because the width of the peak is known to be correlated to fragility.

The temperature dependence of viscoelastic properties is usually described by the VFT equation

$$\tau(T) = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right) \qquad (2)$$

and the ratio T_0/T_g also characterizes fragility:[28]

$$T_0/T_g \approx 1 - \frac{17}{m} \qquad (3)$$

Figure 5 shows the molecular weight dependence of T_0/T_g for PS with T_0 obtained from VFT fit of temperature variation of viscosity[31] and τ_α.[32] The ratio obtained from τ_α increases with the increase of molecular weight, consistent with the increase in fragility.[32] On the other hand, the ratio obtained from viscosity is independent of molecular weight, suggesting that viscosity of different molecular weight PS has a similar temperature dependence when scaled by T_g. The presented results (Figures 4 and 5, Table 1) show that estimates of fragility in polymers using viscoelastic properties dominated by the chain relaxation process will differ from the estimates based on analysis of segmental relaxation. Moreover, the dependence of chain relaxation on T_g/T appears to be less sensitive to molecular weight and chemical structure of the polymer than the dependence of segmental relaxation (Figures 4 and 5).

Although the breakdown of TTS in polymers is well established, its microscopic mechanism remains unclear. Two models, coupling model (CM) by Ngai[6,33] and dynamic disordered Rouse model (DDR) by Loring,[34] addressed this question. According to CM, the temperature dependence of a relaxation process (segmental or chain) depends on the temperature dependence of some primitive relaxation and a coupling parameter *n*. The difference in the coupling parameter for chain and segmental relaxation processes leads to the difference in their temperature variations.[33] Specifically, the segmental mode has a stronger coupling than the chain modes, resulting in stronger temperature dependence.[6,33,35] In this model, the coupling parameter also controls stretching of the relaxation process and is known to increase with increase in fragility for segmental relaxation. Thus, stronger decoupling in more fragile polymers (Figure 3b) can be related to higher coupling parameter (stronger stretching) for their segmental relaxation. However, deeper analysis is needed for comparison of the model predictions to the observed similarity of the chain relaxation temperature dependence.

The DDR model relates the temperature dependence of the chain modes to the equilibrium concentration of mobile beads, *C*.[34] *C* for each Rouse bead fluctuates between 0 and 1 and is equivalent to temperature. Characteristic relaxation times depend on $C - C^*$ in a sense similar to VFT eq 2 with the threshold $C^* \sim 0.17$ being equivalent to T_0.[34] This model predicts that TTS breaks down sharply when *C* decreases below $C_1 \sim 0.3$,[34] and the longest chain mode should have a weaker dependence on *C* (or *T*) than the segmental mode below C_1 (Figure 4). Assuming a universal value of C_1, one can explain the observed universal value of $\tau_\alpha \sim 10^{-6}$ s at which TTS in various polymers starts to break down (Figure 3b). The model, however, does not explain why decoupling between chain and segmental dynamics is stronger in more fragile polymers (Figure 3b) as well as it cannot address the observed similarity in temperature dependence of chain dynamics for the polymers studied (Figure 4).

Spiess and co-workers found that, for some fragile polymer melts, the conformational memory effect exists for the structure relaxation (τ_α).[36] In other words, at time scale longer than structural/segmental relaxation, the backbones retain some degree of the orientation. The rate of losing this orientation is described as another relaxation time scale, i.e., so-called randomization time, τ_{RAN}. Surprisingly, τ_{RAN} shows a weaker temperature dependence than τ_α at temperature close to T_g, an observation similar to τ_n (Figure 2).[36] The connection between the randomization of the backbone and the chain relaxation is not clear. However, similarity in their temperature variations suggests that both processes might be controlled by the same molecular mechanism. A more detailed study of the randomization process for different polymers and its relationship with chain relaxation will be helpful.

We want to emphasize that the range of τ_α where TTS seems to break down for all the presented polymers, $\tau_\alpha \sim 10^{-5}-10^{-7}$ s (Figure 3b), is close to the range of structural relaxation time around the so-called crossover temperature, $\tau_\alpha \sim 10^{-7\pm1}$ s.[18,37] The latter marks the crossover in dynamics of glass forming systems and has been found to be rather universal for various molecular, polymeric, covalent, ionic, and hydrogen-bonding systems.[18,37] It is known that decoupling of various relaxation processes, including rotational and translational motion, appears below this temperature range.[38-40] Thus, the decoupling of chain and segmental dynamics might be related to the dynamic

Table 1. Fragility of the Analyzed Polymers, m_α for Segmental and m_n for Chain Relaxation, Estimated Using Eq 1 or as a Slope of log τ vs T_g/T in the Range $T_g/T = 0.95-1$ (Marked as m^*)[a]

	POB	PIP	PPG	aPP	PS	PC
m_α (m_α*)	59 (59)	62 (50)	68 (61)	105 (76)	126 (85)	175 (96)
m_n (m_n*)	45 (47)	42 (39)	49 (50)	46 (48)	50 (46)	48 (51)
T_g (K)	199	202.5/211	206.5	265−269	∼373	427
M_n	4.8K	2.46K/21K	60K	26K−371K	11K−180K	35K

[a] T_g and molecular weights of the corresponding polymers in Figure 4 are listed. See the details in the corresponding references in Figure 4.

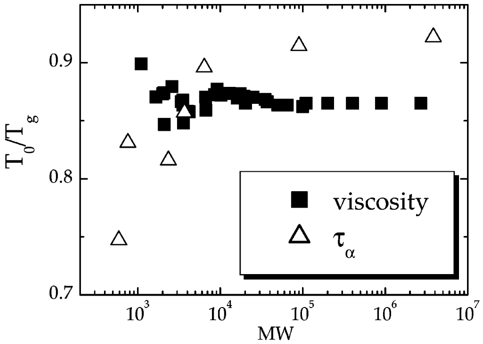

Figure 5. Ratio T_0/T_g for PS with different molecular weight. T_0 is estimated from the VFT fit of the temperature dependence of viscosity (■)[31] and τ_α (△).[32]

crossover and, in particular, to the decoupling of translational and rotational motions in polymer melts. We speculate that translational motion might contribute more toward chain dynamics while rotational motion might contribute stronger to segmental dynamics. Segmental dynamics include motions between various conformational and isomeric states that involve bonds rotation. That might explain stronger temperature variation of the segmental dynamics because it is known that rotational motion has a stronger temperature variation than the translational one.[39] The proposed explanation is also consistent with the recent analysis of rotational/translational decoupling in polymers: It has been demonstrated that the strongest decoupling happens in PC, with PS also showing strong decoupling and PIB showing only a weak effect.[39] Another explanation might be linked to a dynamic heterogeneity.[41−43] The stretching of the segmental relaxation spectra, fragility, and decoupling of rotational/translational motions are often related to dynamic heterogeneity in supercooled liquids.[41−43] The dynamic heterogeneity is believed to be strongly materials dependent and might affect significantly segmental relaxation but will be averaged out on the length scale of the chain relaxation.

Why the chain dynamics exhibits more universal temperature behavior than the segmental one (Figures 4 and 5) remains unclear. Recently, it was suggested [44] that fragility of short oligomers might be similar for chains of different chemistry because they all are small van der Waals molecules. On the basis of this suggestion, we speculate that temperature variations of chain dynamics might be defined by the van der Waals intermolecular interactions, and this is the reason for rather similar temperature variations of τ_n in different polymers. Ngai and Roland have shown that rigidity of the chain backbone affects significantly the temperature dependence of τ_α, i.e., fragility of polymers.[27] Similar observations were also made recently.[45,46] These intramolecular peculiarities might be unimportant on time and length scales of chain relaxation that are much longer than the ones of segmental dynamics. In another words, chemically specific intramolecular barriers and conformational states affect significantly behavior of segmental dynamics while they are averaged out on the time and length scales of the chain dynamics.

Conclusions

In summary, a detailed comparison of chain and segmental relaxation times for several polymers leads to two significant observations: (i) decoupling of their temperature variations seems to happen at a similar segmental relaxation time $\tau_\alpha \sim 10^{-5}-10^{-7}$ s and (ii) temperature dependence of chain dynamics is more universal than the dependence of segmental dynamics. As a result, fragile polymers exhibit stronger breakdown of TTS. We do not have any clear explanation for the observed results and speculate that decoupling of translational and rotational motions in polymer melts and/or dynamic heterogeneity on a segmental scale may be the main reasons for the difference in behavior of chain and segmental dynamics. Chemically specific intramolecular peculiarities that affect behavior of segmental dynamics are averaged out on the time and length scales of the chain dynamics. Apparently, polymer molecules appear as a flexible, chemically nonspecific chains on the time and length scale characteristic for chain relaxations. The presented results call to a revision of our microscopic understanding of the chain friction coefficient, one of the basic parameters in polymer dynamics. Also, more accurate comparison of temperature dependencies of segmental and chain dynamics for fragile polymers (e.g., PS and PMMA) might be very helpful in understanding the observed breakdown of TTS.

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