Influence of Molecular Weight on Fast Dynamics and Fragility of Polymers

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ABSTRACT: The molecular weight dependence of the fast dynamics, sound velocity, and fragility has been studied for polystyrene (PS) and polyisobutylene (PIB). These different physical properties vary with molecular weight (M_n) and level off near the same chain length where T_g becomes independent of M_n. The latter differs significantly between PS and PIB. The results suggest that neither Kuhn segment length nor molecular weight between entanglements is an important parameter for the molecular weight dependence of these properties. The most intriguing result is that the molecular weight dependencies of the fast dynamics and sound velocity observed in PS are opposite to the one observed in PIB, although T_g increases with M_n in both cases. Moreover, there are some indications that even variations of fragility with molecular weight in PIB might be opposite to the variations observed in PS. We speculate that difference in symmetry of the monomer structures is responsible for the opposite behavior. On the basis of this idea, predictions for dependence of the fast dynamics and fragility in various polymers on molecular weight and tacticity are formulated.

I. Introduction

It is known that many physical properties of polymers depend on their molecular weight, M_n. In particular, viscoelastic properties of polymer melts show strong variations with M_n and can be reasonably well described by the reptation model for entangled chains and the Rouse or Zimm models for unentangled chains.[1,2] The influence of molecular weight on the glass-transition temperature, T_g, and segmental relaxation is also well investigated,[2] although it is still not well understood.[3−5] Gibbs-DiMarzio theory and chain-end free volume model provide a good description of the molecular weight dependence of T_g (the authentic glass-transition temperature T_2 in the case of Gibbs-DiMarzio theory) for some polymers but fail in other cases.[3] Even less is known about faster dynamics, namely, the influence of molecular weight on secondary and fast relaxations and low-frequency vibrations—the so-called boson peak. It is not clear whether molecular weight between entanglements, M_e, Kuhn segment, l_K, or some other characteristic parameter of a polymer chain is important for the fast dynamics.

Recent analysis of dielectric relaxation in poly(propylene glycol)-based dimethyl ethers reveals that relaxation time of the β-process, τ_β, has a much weaker dependence on M_n than τ_α of segmental relaxation (α-process).[6] Moreover, the molecular weight dependence of τ_β saturates at much lower $M_n \approx 400$ than the dependence of τ_α.[6] Controversial results can be found in the literature concerning the boson peak dependence on molecular weight. It has been shown that the boson peak frequency, ν_{BP}, decreases with increase in molecular weight of polystyrene (PS) up to $M_n \approx 1000$.[7] However, opposite behavior, i.e., an increase of the boson peak frequency with an increase in M_n, has been observed in the case of polyisobutylene (PIB).[8] The dependence of ν_{BP} in PIB saturates at $M_n \approx 5000$.[8] No significant variations of the fast dynamics have been observed in 1,4-polybutadiene (PB) for molecules with $2000 < M_n < 100\,000$.[4] Thus, no clear picture of the molecular weight dependence of the fast dynamics emerges from analysis of literature data.

The main goal of the present contribution is a detailed analysis of the molecular weight dependence of the fast dynamics in PS and PIB. In addition, the sound velocity and fragility of the polymers are analyzed. Surprisingly, all parameters show similar dependence on molecular weight that saturates around the same M_n (∼5000−10 000 for PIB and ∼100 000 for PS) where the molecular weight dependence of T_g levels off. However, the dependence of the fast dynamics and sound velocity on molecular weight in PS is opposite to that observed in PIB. We speculate that the symmetry of the monomers is the main reason for the observed difference between the behavior of PS and PIB. From this idea, an influence of molecular weight and tacticity on fragility of polymers is predicted.

II. Experimental Section

Monodisperse polystyrene (M_n from 197 to 200 600) was purchased from Scientific Polymers. Samples of polyisobutylene with molecular weight M_n from 370 to 64 780 were purchased from Polymer Standard Service and $M_n = 200\,000$ from Aldrich. The number-average molecular weights and molecular weight distributions are listed in Table 1.

Depolarized light scattering spectra were measured using a Raman spectrometer (Jobin Yvon T64000 triple-monochromator) and a tandem Fabry−Perot interferometer (Sandercock model) with free spectral range (FSR) ∼360 GHz (∼12 cm^{-1}). Polarized Brillouin spectra were measured using the interfero-

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Table 1. Sample Information

polystyrene[a]		polyisobutylene[b]	
M_n	M_w/M_n	M_n	M_w/M_n
197	1.02	370	1.06
550	1.07	640	1.06
990	1.12	3470	1.16
2170	1.07	13 300	1.04
3400	1.08	30 000	1.13
8000	1.05	51 000[c]	1.80
12 400	1.06	64 780	1.13
29 100	1.09	200 000	2.50
105 300	1.05		
200 600	1.11		

[a] From Scientific Polymers (USA). [b] From Polymer Standard Service (Germany). [c] From Polymer Source (Canada).

meter with FSR ~50 GHz for PS and ~30 GHz for PIB. The samples were placed in optical cells and vacuum sealed. An optical cryofurnace (Janis ST-100 model) has been used for temperature variations. All scattering measurements were done in the backscattering geometry with a laser power 100 mW (Ar^{++}, $\lambda_0 = 514.5$ nm). Unfortunately, the Raman spectra of PIB samples at low temperatures had a large fluorescence contribution and no reliable measurements of the boson peak and fast relaxation were possible. The same problem appears for PS with molecular weight 197. In addition, we use inelastic neutron scattering spectra of PIB measured on the time-of-flight spectrometer IN6 at the ILL, Grenoble. Details of the measurements and data treatment have been published in ref 8.

III. Results and Their Analysis

Figure 1 presents depolarized light scattering spectra of PS at two temperatures, $T \approx T_g$ (a) and $T = 80$ K (b). The spectra are shown in a spectral density representation, $I_n(\nu) = I(\nu)/[\nu(n(\nu) + 1)]$, and are normalized to the intensity of the microscopic mode at $\nu \approx 80$ cm^{-1} (inset, Figure 1b). Here, $I(\nu)$ is the measured intensity and $[n(\nu) + 1] = [1 - \exp(-h\nu/kT)]^{-1}$ is the temperature Bose factor. Three factors common for the spectra of polymers are visible in Figure 1: (1) A so-called microscopic vibrational mode around 70−80 cm^{-1} that is most visible as a peak in the susceptibility spectra $\chi''(\nu) = I(\nu)/[n(\nu) + 1]$ (inset, Figure 1b); (2) low-frequency collective vibrations, the boson peak, at $\nu \approx 10-20$ cm^{-1}; (3) quasielastic light scattering (contribution of the fast relaxation) that dominates the spectral density at $\nu < 6$ cm^{-1}.

Figure 1 reveals that the quasielastic scattering increases significantly with an increase of molecular weight and dominates the spectral density at $T \approx T_g$. The boson peak at these temperatures is clearly visible only in the sample with $M_n \approx 550$. The quasielastic contribution is suppressed and the boson peak appears clearly for all the samples at $T = 80$ K, well below T_g. The frequency of the boson peak maximum, ν_{BP}, decreases with an increase in molecular weight. Also, the frequency of the microscopic peak, ν_{micro}, decreases with an increase in M_n (inset, Figure 1b). The opposite trend is observed for PIB (Figure 2): ν_{BP} increases and the quasielastic intensity decreases with an increase in molecular weight.

Figure 3 presents Brillouin scattering spectra of PS (Figure 3a) at $T = 80$ K and PIB (Figure 3b) at $T = 100$K. Peaks in the polarized Brillouin scattering are due to the scattering of light by longitudinal acoustic phonons. The frequency of the peak is related to the longitudinal sound velocity V_l

$$\nu_B = \frac{qV_l}{2\pi} \qquad (1)$$

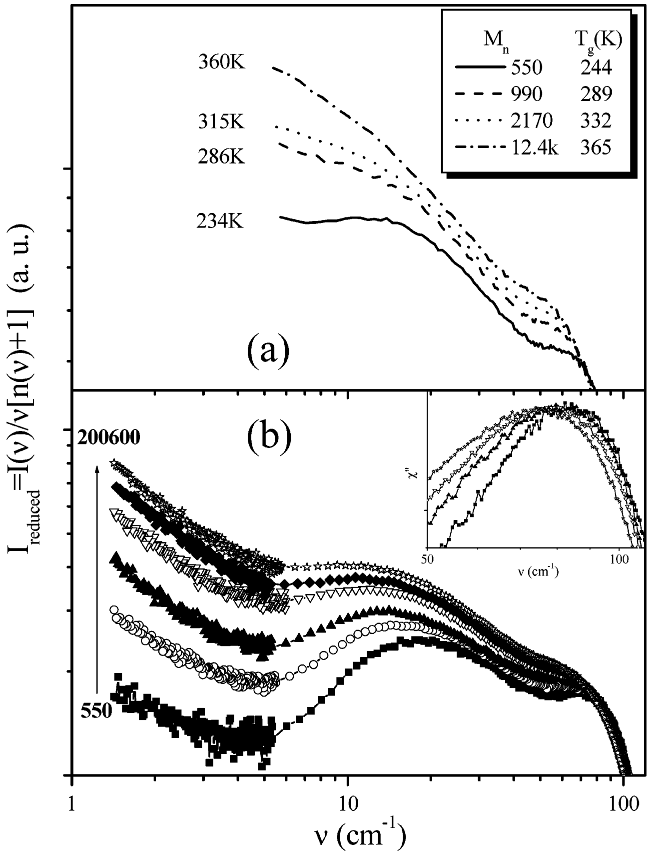

Figure 1. Depolarized light scattering spectra of PS with various molecular weights at (a) $T \approx T_g$ (for different molecular weight: (—) 550; (- - -) 990; (· · ·) 2170; (- · - ·) 12 400) and (b) $T = 80$ K. The inset of b is the imaginary part of susceptibility spectra $\chi(\nu) = I_n(\nu)\nu$, which shows the microscopic peak for PS with different molecular weight. (Different symbols in b represent PS with different molecular weights: (■), 550; (○), 990; (▲), 8000; (▽), 29 100; (♦), 105 300; (★), 200 600.)

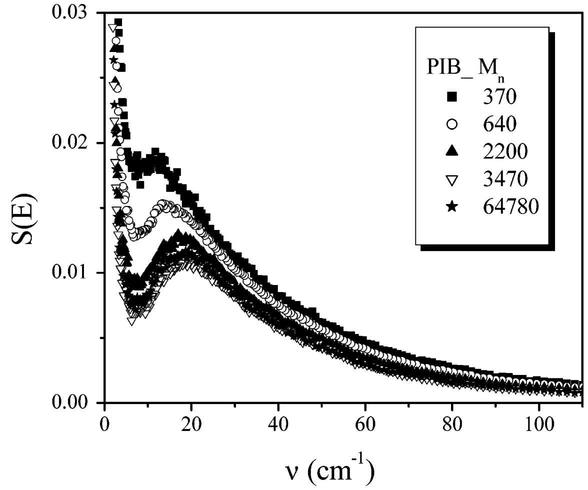

Figure 2. Inelastic neutron scattering spectra averaged over all scattering angles for PIB at 100 K for various molecular weights: (■) 370, (○) 640, (▲) 2200, (▽) 3470, (★) 64 780.

here q is the scattering wave vector, which in the backscattering geometry is equal to

$$|q| = \frac{4\pi n}{\lambda}$$

n is the refractive index, and λ is the wavelength of the incident light. Reviews of Brillouin scattering studies

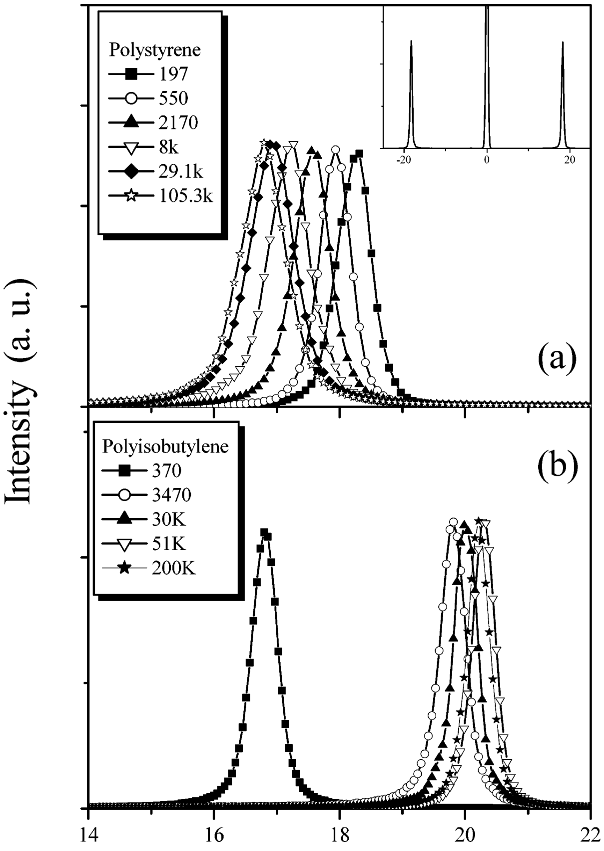

Figure 3. Brillouin scattering spectra of (a) PS at 80K and (b) PIB at 100K with different molecular weights (shown by numbers). Inset of a represents a typical Brillouin spectrum with doublet (±$\Delta\nu$) at both sides of the elastic line (ν_0).

in polymers can be found in ref 9. The data in Figure 3 show that ν_B decreases with molecular weight in PS while it increases in PIB.

For a more quantitative analysis of the boson peak frequency we fit the depolarized light scattering and the inelastic neutron scattering spectra by a simple approximation

$$I_n(\nu) = \frac{A\nu_0}{{\nu_0}^2 + \nu^2} + B\exp\left\{-\frac{[\ln(\nu/\nu_{BP})]^2}{2(W/\nu_{BP})^2}\right\} \qquad (2)$$

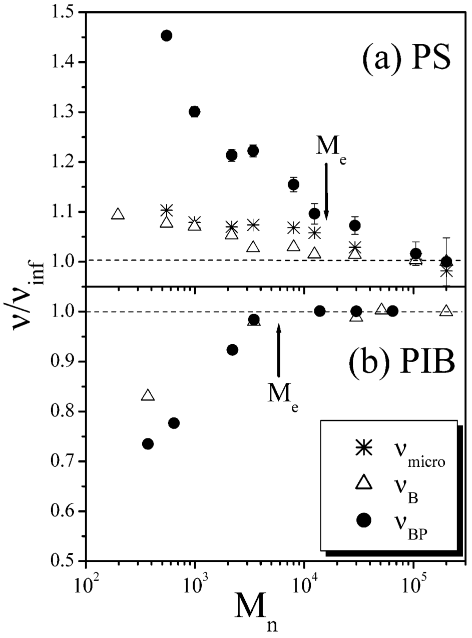

Figure 4. Molecular weight dependence of positions of microscopic peak ν_{micro} (*), Brillouin peak ν_B (△), and Boson peak ν_{BP} (●) for (a) PS at 80 K and (b) PIB at 100 K. All the frequencies are normalized by the value of the largest molecular weight ν_{inf}.

The first term in eq 2 describes the quasielastic contribution with the width ν_0 and the second term is the boson peak approximated by a log-normal function with width W. A log-normal distribution is a good approximation for the asymmetric shape of the boson peak.[10] We should emphasize that relaxation spectra of polymers have a complex spectral shape[11,12] and an approximation of the quasielastic contribution by a single Lorentzian is not appropriate for detailed analysis of relaxations. It is, however, sufficient for the purpose of our estimation of ν_{BP}. The frequency of the microscopic peak at ~80 cm^{-1} in PS, ν_{micro}, has been estimated using a simple Lorentzian fit of the susceptibility spectra near the maximum (inset, Figure 1b).

The frequencies of the Brillouin peaks were estimated from the fit of the polarized spectra (Figure 3) by a simple Lorentzian. The final value of ν_B was obtained by averaging values obtained for energy-gain and energy-loss sides of the Brillouin spectra. Results of the fits are presented in Table 2 and Figure 4.

IV. Discussion

Molecular Weight Dependence of the Brillouin, Microscopic, and Boson Peak Frequencies. The decrease in the boson peak frequency with an increase of the molecular weight in PS (Figure 4a) is consistent with the earlier results presented in ref 7. However, our results show that the molecular weight dependence extends much beyond $M_n \approx 1000$. The peak frequencies,

Table 2. Boson Peak Position and Brillouin Peak Position Measured at T = 80 K for PS and at T = 100 K for PIB

polystyrene			polyisobutylene		
M_n (10^3)	ν_{Boson} (cm^{-1})	$\nu_{Brillouin}$ (GHz)	M_n (10^3)	$\nu_{Boson}{}^a$ (cm^{-1})	$\nu_{Brillouin}$ (GHz)
0.197		18.26	0.37	14.70	16.77
0.55	19.62	17.98	0.64	15.53	
0.99	17.56	17.87	2.2	18.47	
2.17	16.38	17.59	3.47	19.68	19.79
3.4	16.50	17.16	13.3	20.03	
8.0	15.59	17.19	30	20.01	19.96
12.4	14.80	16.95	51		20.26
29.1	14.48	16.93	64.6	20.02	
105.3	13.72	16.76	200		20.18
200.6	13.50	16.70			

[a] From ref 8; unit conversion: 1meV = 8 cm^{-1}.

ν_B and ν_{micro}, have very similar variations with molecular weight, while the boson peak frequency varies more strongly (Figure 4a). Similarity in variations of ν_B and ν_{micro} can be ascribed to the acoustic nature of both peaks. They simply reflect the molecular weight dependence of elastic constants in PS. The nature of the boson peak remains a subject of active discussion.[13−16] Many models relate these vibrations to quasilocal acoustic-like excitations.[13−16] However, ν_{BP} might depend not only on the elastic constants, but also on the characteristic radius and amplitude of fluctuations frozen in the glassy structure.[17,18] Thus, whatever parameter may govern the Boson peak position, a M_n-dependence of the Boson peak means a M_n-dependence of the controlling parameter. However, this discussion is out of the scope of the present paper. The most interesting observation is an opposite dependence of the fast dynamics and the Brillouin frequency (sound velocity) on molecular weight for PS and PIB. Another important difference is that the molecular weight dependence of ν_{BP} and ν_B approaches the infinite molecular weight limit at smaller M_n in PIB than in PS.

We should emphasize that the sound velocity depends on both modulus and density. Variations of modulus are usually much stronger than variations of density, ρ. It is known that the density of PS melts measured at T above 380 K increases with M_n,[19] and a similar trend is observed for the density of PIB melts.[20] However, there are no data for molecular weight dependence of densities in PIB and PS deep in the glassy state. These data might be interesting because it is possible that the density of PS and PIB deep in the glassy state will also have an opposite dependence on molecular weight. Using detailed density measurements presented for PS in ref 19, we estimate that the variations of ρ with molecular weight in PS at $T \approx T_g$ are smaller than 1%. Thus, we neglect this contribution and ascribe the molecular weight dependencies of V_l to variations of the modulus.

The presented results (Figure 4) clearly show that the fast dynamics and elastic constants of the polymers remain sensitive to the chain length even at rather high molecular weight. This result for the fast dynamics seems to be surprising. It is known that the molecular weight dependence of secondary relaxations usually saturates when M_n reaches a few hundreds (see, for example, ref 6). The fast dynamics are also expected to be localized, and one might expect them to be rather independent of M_n or have variations at very low M_n only (similar to the secondary relaxation). Experimental results, however, show significant dependence on M_n and raises the question of whether some characteristic lengths of polymers, like the Kuhn segment length, l_K, or the molecular weight between entanglements, M_e, are relevant. Figure 4 shows that the molecular weight dependence extends far beyond the traditionally defined Kuhn segment length ($l_K \approx 7$ monomers, $M_n \approx 400$ for PIB; $l_K \approx 8-9$ monomers, $M_n \approx 800-900$ for PS).[21] It is approaching the infinite molecular weight limit in PIB at $M_n \approx 5000-10\,000$, which is close to the molecular weight between entanglements, $M_e \approx 6000$.[22] However, the molecular weight dependence in the case of PS continues even above M_e ($M_e \approx 15\,000$).[22] Thus, neither Kuhn segment length nor the molecular weight between entanglements appear to be the crucial parameters for the molecular weight dependence of the elastic constants and of the fast dynamics, at least in the case of PS.

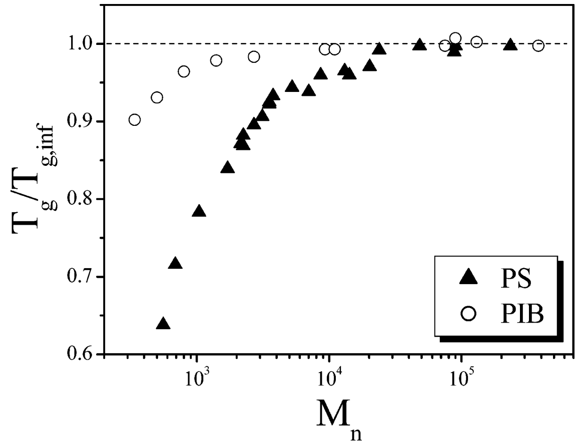

Figure 5. $T_g/T_{g,inf}$ as a function of molecular weight for PS (▲) and PIB (○). $T_{g\,inf}$ is the glass-transition temperature of the polymer with infinite molecular weight, 373 K for PS and 209.5 K for PIB.

Recent analysis presented in ref 5 demonstrates that the molecular weight dependence of T_g also appears to be insensitive to M_e and traditionally defined Kuhn segment length. Instead, it appears that T_g approaches its limiting value, $T_g(M_n = \infty)$, when the chain approaches Gaussian statistics.[5] The latter is different for different polymers. Figure 5 presents the molecular weight dependence of T_g in PS and in PIB. The dependence levels off at $M_n \approx 5000-10\,000$ for PIB,[23] while it extends up to $M_n \approx 100\,000$ in the case of PS[24] (Figure 5). In that respect, the molecular weight dependencies of the fast dynamics and elasticity (Figure 4) are similar to the dependencies of T_g. Apparently the same parameters that define molecular weight dependence of segmental relaxation and T_g appear to be important for the fast dynamics and elastic constants. It has been shown, for example, for PS and PDMS,[5] that chain statistics, i.e., the way a molecule approaches Gaussian coil, appears to be important for the molecular weight dependence of T_g. Following the idea presented in ref 5, we can speculate that chain statistics might be an important factor in molecular weight dependencies of the fast dynamics and glassy modulus of polymers. When the chain approaches the Gaussian coil behavior, the molecular weight dependence of many physical properties, including density and T_g,[5] fast dynamics and modulus (Figure 4) saturates.

Now we turn to the discussion of the opposite behavior observed between PS and PIB molecular weight dependence of the fast dynamics (Figures 1, 2, and 4). There are no systematic studies of the fast dynamics for other polymers, and it is not clear which tendency is more general for polymers. No significant molecular weight dependence has been observed for the fast dynamics in 1,4-polybutadiene down to $M_n \approx 2000$.[4] A comparison of neutron scattering spectra of propylene[25] to the spectra of atactic polypropylene (a-PP) [26] ($M_n \approx 1\,000\,000$) shows that ν_{BP} decreases from ~3 meV (~24 cm^{-1}) for monomer to ~1.3 meV (~10 cm^{-1}) for a-PP. Although it is known that the chemical structure of monomer bears little resemblance to the repeating unit of the polymers, still polypropylene seems to show a tendency similar to the one observed for PS (Figure 3). Various correlations of the boson peak frequency with molecular parameters have been proposed for polymers: (i) an inverse relationship between ν_{BP} and the molecular weight of the monomer has been proposed in ref 27; (ii)

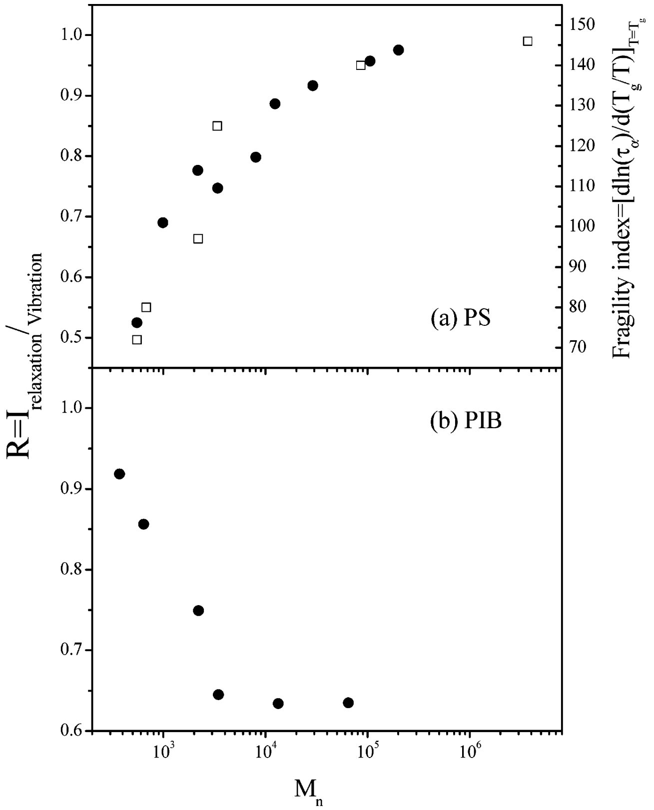

Figure 6. Relaxation-to-vibration ratio as a function of molecular weight for (a) PS and (b) PIB. The ratio is estimated from light scattering spectra for PS at $T = 80$ K (Figure 1b) and neutron scattering for PIB at $T = 100$ K (Figure 2). Also included in a is the fragility index m as a function of molecular weight for PS (data from ref 33).

an inverse correlation of ν_{BP} to the glass-transition temperature (higher T_g polymers should have lower boson peak frequency) has been proposed by Annis.[28] These correlations were deduced from analysis of polymers with different chemical structures. Our measurements offer a way to verify these correlations. The first relationship[27] is not supported by our results since the repeating unit remains the same for PS or PIB with different molecular weights, but ν_{BP} can vary in different directions between these two polymers. The second correlation also fails because T_g increases with molecular weight in both polymers while ν_{BP} shows opposite variations. Thus, it is not obvious which parameter of the polymer defines the direction of the molecular weight dependence.

Figures 1 and 2 show that the quasielastic intensity (contribution of the fast picosecond relaxation) also changes strongly with molecular weight. One would expect that chain ends have enhanced dynamics. As a result, shorter chains should have higher quasielastic scattering. This behavior is observed for PIB (Figure 2), but the reverse behavior is observed for PS chains: the lower M_n is for PS (larger contribution of chain ends), the lower the quasielastic intensity (Figure 1). Thus, this simple explanation based on chain ends fails in the case of PS.

Dependence of Fragility on Molecular Weight in Different Polymers. One of the most intriguing features of the fast dynamics is its correlation to the fragility of glass-forming systems, m.[29,30] m is usually defined as[31]

$$m = \left.\frac{\partial \log \tau(T)}{\partial (T_g/T)}\right|_{T=T_g} \quad (3)$$

Here τ is the α relaxation time. It has been shown that the ratio of the fast relaxation contribution (quasielastic scattering) to the boson peak contribution (intensity), $R = I_{QES}/I_{BP}$, correlates to the fragility of various materials,[29] including polymers.[32] The higher the ratio, the more fragile is the system. The nature of this correlation still remains a puzzle. However, it apparently works for PS: Figure 6a presents a comparison of the ratio R, defined as proposed in ref 29, to the fragility of PS defined by dielectric spectroscopy.[33] Clear correlations between variations of both parameters are observed. Moreover, their molecular weight dependencies seem to saturate at similar M_n.

The molecular weight dependence of the ratio R in PIB is also opposite to the one observed in PS (Figure 6). This behavior of the fast dynamics suggests that the fragility of PIB might decrease with an increase in molecular weight. Unfortunately, there are no data for the molecular weight dependence of fragility in PIB. However, calorimetric measurements[20] for two samples, $M_n = 640$ and 200 000, provide qualitative information. The data present two estimates of T_g: (1) using the onset of the transition in DSC, which corresponds to a relaxation time $\tau \approx 200$ s, $T_{g200}(M_n = 640) = 192$ K and $T_{g200}(200\,000) = 204$ K; (2) using adiabatic calorimetry, which probes T_g at $\tau \approx 1000$ s, $T_{g1000}(640) = 190$ K and $T_{g1000}(200\,000) = 200$ K. Using eq 3 we estimate the fragility of PIB as $m \approx 67$ for chains with $M_n = 640$ and $m \approx 36$ for chains with $M_n = 200\,000$. Thus, calorimetric results and the behavior of the fast dynamics indicate an increase of fragility with a decrease of the molecular weight of PIB chains. Direct measurements of fragility are required to verify these indications.

There have been only a few studies of the influence of molecular weight on the fragility of polymers. A significant increase in fragility with an increase in molecular weight has been reported for PS,[24,33] while no change in fragility has been observed for polydimethyl siloxane (PDMS).[34] Roland et al. also found no significant difference in the fragility of polyvinyl acetate (PVAc) samples with two different molecular weights, $M_n \approx 15\,000$ and 170 000.[35] However, M_n of the polymers studied might be too high to display any molecular weight dependence. We found dielectric relaxation data for PMMA oligomer with $M_n \approx 375$[36] and light scattering data for relaxation in PMMA with two different molecular weights, $M_n \approx 3900$ and 10 000 000.[37] Also, recent analysis of dielectric relaxation in methyl-group-terminated PPG presented in ref 6 allows comparison of the fragility for molecules with different M_n. Figure 7 presents the segmental relaxation data from these two systems in the well-known Angell plot. It is clear that the fragility of both PMMA and methyl-group-terminated PPG increases with an increase in molecular weight. Thus, this tendency appears to be common for PS, PMMA, and PPG with methyl end groups.

Figure 8 summarizes the molecular weight dependencies of fragility for a few polymers. We assume that most of the monomers and/or oligomers should have similar fragility, $m \approx 60-90$ (range of fragilities for most of van der Waals liquids).[38] One would expect that short isobutylene oligomers also have fragility in this range. In that case the fragility of PIB should decrease with

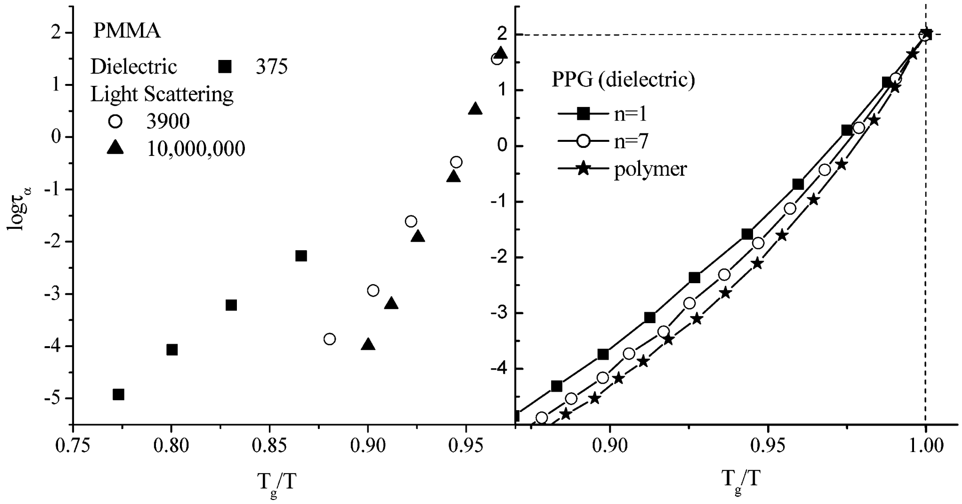

Figure 7. Temperature dependence of segmental relaxation time for different molecular weight (a) PMMA (data from refs 36 and 37) and (b) methyl-group-terminated polypropylene glycol (data from ref 6).

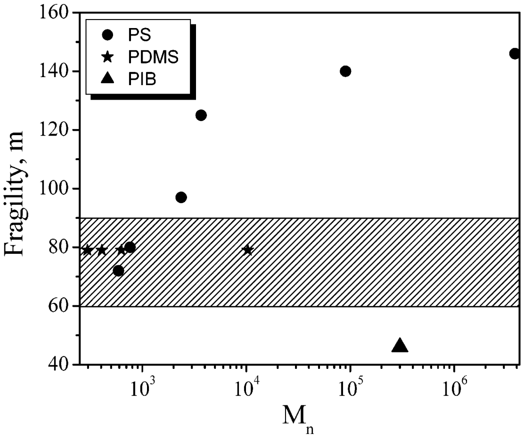

Figure 8. Molecular weight dependence of fragility index m for PS (●), PDMS (★), and PIB (▲). Shaded area marks the fragility range expected for monomers and oligomers.

an increase in molecular weight (Figure 8), approaching the value $m \approx 46$ at high M_n. This idea is consistent with the thermodynamic analysis presented in ref 20 and with our analysis of the fast dynamics in PIB (Figure 6), where a decrease of the ratio R suggests a decrease in fragility with molecular weight. Figure 8 also provides an idea of why fragility of PDMS is essentially independent of molecular weight: the fragility of the polymer appears in the range of fragility expected for monomers.

The above speculations, however, do not explain different behavior of fragility in different polymers. It is not clear why starting from rather similar fragility of the monomers an increase of chain length increases the fragility of PS and PMMA but apparently leads to a decrease in PIB. The difference of the molecular weight dependence of fragility between PDMS and PS has been ascribed to the difference in the flexibility of the chains.[24,33,34] Obviously the PDMS backbone is more flexible than that of PS. However, it is difficult to see how this idea could explain the observed difference between PIB and PS, which both have a C−C backbone with more or less bulky side groups. It is well known that PIB and PS represent two types of polymeric systems in terms of fragility. PIB is one of the strongest polymers, while PS is one of the most fragile polymers. PDMS is an intermediate case. Ngai and Roland[39] proposed that the symmetry of the monomer might affect the fragility of polymers. They speculate that the chemical structure of monomers affects intermolecular coupling: polymers with symmetric structural units have lower intermolecular coupling than polymers with asymmetric units. According to the coupling model,[39] it means that a symmetric structural unit leads to a stronger polymer while an asymmetric unit leads to a more fragile polymer. In that respect, PIB has a symmetric unit with two methyl groups symmetrically substituted on the backbone while PS has an asymmetric unit with one bulky phenyl ring.

To verify whether this difference might be key to polymer fragility, we divided polymers with known fragility[38,40,41] and simple backbones into two groups (Table 3): Group I includes asymmetrically substituted polymers, while Group II includes symmetrically substituted or nonsubstituted polymers. It appears that polymers in Group I are fragile and those in Group II are relatively strong. In most cases the fragility of polymers from Group I is higher while the fragility of polymers from Group II is lower than the expected fragility of their monomers. Thus, the opposite molecular weight dependence of fragility in polymers might be related to the difference in the symmetry of monomers between these two groups. This idea is supported by the observation that PS, PMMA, and methyl-terminated PPG, polymers that show an increase in fragility with molecular weight, all appear in the same group. However, the idea of intermolecular coupling does not explain why fragility increases with molecular weight in PS but seems to decrease in PIB.

A direct consequence of an asymmetric substitution is the irregularity of the structure due to two reasons: (i) the way of connecting repeating units (head-to-head or head-to-tail) and (ii) stereoregularity (tacticity). The first effect on fast dynamics and fragility has been studied by Annis[28] for the case of polypropylene. The head-to-head-connected polymer (hhPP) appears to be stronger than the atactic PP. This effect can still be minimized due to the more favorable head-to-tail connection for most asymmetric repeating units. However, the second effect, i.e., the tacticity, determined by relative positions of the side groups of the neighboring repeating units, exists for all polymers with asymmetric units. Let us consider the example of a PS chain where a pair of neighboring repeating units named a dyad is usually used for description of tacticity. A dyad is called

Table 3. Fragility Indexes for Different Polymers[a]

	group I		group II	
	polymer	fragility	polymer	fragility
C−C backbone	poly(vinyl chloride)	191 (N/A)	polyethylene	46 (N/A)
	poly(methyl methacrylate)	145 (6.0×10^4)	polyisobutylene	46 (1.4×10^6)
	polystyrene	139 (6.0×10^5)		
	PVE(1,2 PBD)	156 (N/A)		
	polypropylene	137 (6.0×10^4)		
	poly(methyl acrylate)	102 (9.0×10^4)		
	poly(vinyl acetate)	95 (6.5×10^4)		
	poly(vinylmethyl ether)	75 (6.6×10^3)		
Si−O backbone	poly(methylphenylsiloxane)	86 (8.3×10^5)	poly(dimethylsiloxane)	79 (1.0×10^4)
	poly(methyltolylsiloxane)	85 (3.5×10^4)		
C−O backbone	poly(propylene oxide)	74 (9.5×10^5)	poly(ethylene oxide)	23 (531)
			poly(tetramethylene oxide)	34 (N/A)

[a] Data are from refs 38, 40, and 41. The number in parentheses is the number-average molecular weight M_n of the polymers reported in the original article. N/A means M_n is not available.

"meso" when the configurations of the two repeating units are identical or "racemic" when they are reverse to each other. Chains with all meso dyads are isotactic, and with all racemic ones they are syndiotactic. A random sequence of dyads forms atactic chains.[42] This sequence is a feature of the structure and is invariant with the conformational change of the chain. The conformational energy of a dyad is usually described in terms of the energy associated with various bond rotations or combinations of such rotations calculated using rotation isomeric state theory.[43] It has been shown that meso and racemic dyads in PS have a different number and different energy of conformational states.[44] The energy of these conformational states controls the selection of rotational isomeric states at or around the energy minima for a particular chain.

The number of different configurations strongly increases with molecular weight for atactic polymers (Group I) due to both the composition and the sequence of the dyads. In particular, the number of combinations of meso and racemic dyads for one single chain increases dramatically with chain length. For example, a dyad (dimer) has only two possible combinations (*m* or *r*), while for a pentad there are 10 different combinations (*mmmm*, *rrrr*, *mmmr*, *mmrr*, *mrrr*, *mrmr*, *mrrm*, *rmmr*, *mmrm, rrmr*).[42] Each combination has its own distribution of conformational states. For each molecule the configuration is fixed during the polymerization. However, different atactic chains with the same molecular weight have a variety of configurations that also increase with M_n. As a consequence, the distribution of conformational energy minima in an ensemble of atactic chains changes drastically with the change of molecular weight. It is known from the energy landscape approach that a broad distribution of energy minima corresponds to a fragile behavior.[45,46] Therefore, an increase of molecular weight for polymers in Group I should lead to an increase of fragility.

We speculate that the symmetry of the chemical structure in Group II polymers results in a distribution of configurational energies being rather independent of chain length.[47] Moreover, it is known from the analysis of *n*-alkanes that the C−C rotational energy barrier increases slightly with the increase of the chain length from 3.0 kcal/mol in ethane to 3.6 kcal/mol in butane due to the short-range interactions.[47] A similar increase of the rotational barrier with chain length can be expected in PIB.[47] This increase of the rotational barrier with an increase in chain length can decrease the fragility if the distribution of energy minima remains the same.

The above prediction also can be reached in a different manner using the Vogel−Fulcher−Tamman (VFT) ansatz for the viscosity or structural relaxation time, $\tau = \tau_0 \exp(B/(T - T_0))$. Through this equation fragility, defined as in eq 3, can be expressed via T_0 and T_g as

$$m = \frac{16}{(1 - T_0/T_g)} \tag{4}$$

Normally, T_0 is equivalent to the Kauzman temperature T_K, which is defined by the Adam−Gibbs model ($\tau = \tau_0 \exp(E/TS_c(T))$) at the condition that configurational entropy goes to zero ($S_c(T_K) = 0$), although some exceptions exist. In the case of polymers with symmetric structures such as PIB, adding new molecular units does not introduce new internal configurations for the chain. In addition, the dependence of the configurational entropy of a chain on the number of the monomers N can be simply approximated by $S_c(T,N) \propto NS_c(T)$. Thus, T_0 basically does not depend on the molecular weight in the approximation that only intrachain configurations are accounted for by S_c. In this case, according to eq 4, the dependence of fragility on M_n is determined by the variation of T_g; since T_g increases with M_n, fragility of PIB should decrease accordingly.

However, the situation is different in the case of PS. Asymmetrical substitution leads to two different possible states of each dyad, *m* and *r*, as mentioned above. Thus, contrary to symmetric polymers, various possible distributions of *m* and *r* dyads at a fixed chain length N contribute to the configurational entropy of a chain. As a result, S_c is expected to rise drastically with N instead of being simply proportional to N. The complexity of the energy landscape increases and, as it was argued above, the fragility increases with M_n.

PDMS does not show any significant dependence of fragility down to ~8 repeating units (Figure 8).[34] Moreover, all the polymers with a Si−O backbone presented in Table 3 have similar fragility regardless of the molecular weight and symmetry of their structural units. We speculate that an extremely low rotational energy barrier, characteristic of the Si−O backbone, might be the reason for this behavior. A C−O backbone has a rotational energy barrier lower than a C−C chain but significantly higher than a Si−O chain. As a result, the difference in the fragility of C−O-based polymers with symmetric and asymmetric structural units is still obvious (Table 3).

On the basis of the above analysis, we speculate that polymers with asymmetric or single substituted units should show an increase of fragility with molecular weight. The extent of the fragility variations depends on the difference in the conformational energies between meso and racemic dyads and on changes of composition and sequence of dyads with chain length. Of course, the asymmetry of the monomer is not the only important parameter. Group I includes extremely fragile polymers such as PS and PMMA and less fragile examples such as PVME ($m \approx 75$). Apparently the size and flexibility of the side groups are also important factors. We speculate that bulky side group such as the phenyl ring in PS will make the polymer more fragile, while the flexible oxygen bridge that connects the methyl group to the backbone in PVME makes this polymer closer to symmetric.

Another direct prediction of the above analysis is that atactic polymers should be more fragile than chemically identical isotactic and syndiotactic polymers. The influence of tacticity on segmental relaxation in PMMA has been analyzed in ref 48. It shows that a decrease in the concentration of the isotatctic dyads leads to an increase of an apparent activation energy of the segmental relaxation at T close to T_g.[48] It suggests that fragility in PMMA increases with an increase of randomness in tacticity, in agreement with our speculations. Unfortunately, we were not able to find more data on the effect of stereoregularity on polymer dynamics. Therefore, this prediction has to be tested in the future.

These arguments, however, do not predict which molecular weight parameter is important for the variation of fragility with M_n. Experimental results for PS[33] show (Figure 6a) that the molecular weight of fragility extends far beyond a single Kuhn segment length ($M \approx 800-900$) and even beyond M_e ($\sim$15 000) and seems to saturate at the same chain length as T_g (Figure 5) and the fast dynamics (Figure 4). Following the idea proposed in ref 5, we speculate that approaching a Gaussian coil can be also important for statistics of chain conformation and the fragility of the polymer.

We want to emphasize that the purely intrachain consideration presented above may not be the only explanation for the different behavior observed for polymers with symmetric and asymmetric monomers. Disorder in tacticity may also lead to an increased disorder in the packing of chains and in this way affect fragility and the fast dynamics of polymers. The energy landscape arguments given above might therefore be amplified by such packing effects. A weighting of the relative importance of the intra- or interchain disorder effects for the diverse experimental quantities discussed above is out of the scope of this paper. It remains also unclear why the fast dynamics shows opposite dependence on molecular weight in the case of PS and PIB. It might be related to the same argument of chain packing. Furthermore, for PIB we cannot exclude that the methyl group dynamics are influenced by possible changes of packing.

V. Conclusions

The presented analysis shows that neither traditionally defined Kuhn segment length nor molecular weight between entanglements appear to be crucial parameters for the molecular weight dependence of the fast dynamics, elasticity, and fragility of polymers. Surprisingly, all these parameters that characterize different physical properties show rather similar molecular weight dependencies that approach infinitely high molecular weight limits at nearly the same M_n. Moreover, they seem to follow the molecular weight dependence of T_g. It has been proposed recently[5] that the molecular weight dependence of T_g follows chain statistics: It approaches an infinitely high molecular weight asymptotic limit when the chain approaches Gaussian statistics. We speculate that approaching a Gaussian coil levels off the molecular weight dependence of density, T_g, elasticity, fragility, and many other physical properties of polymers.

The most interesting observation is that variations of the fast dynamics, elasticity, and fragility with molecular weight have different directions depending on polymer, while T_g always increases with an increase of the chain length (for chains without functional ends). We speculate that the opposite behavior observed for the molecular weight dependencies in PS and PIB can be ascribed to the difference in symmetry of their monomers. More specifically, polymers with symmetric structural units appear to be less fragile than polymers with asymmetric monomers. We found that this simple argument works astonishingly well for many polymers analyzed. We speculate that most of the monomers and short oligomers should have similar fragility, $m \approx 60-90$, that is characteristic of low molecular weight van der Waals liquids. However, the increase of the chain length will affect a distribution of conformational states in different ways depending on the monomer's symmetry. We try to rationalize this observation by using statistical arguments suggesting that asymmetric monomers lead to strong broadening of the distribution. As a result, fragility should increase with molecular weight in polymers with asymmetric structural units. Moreover, the same idea predicts the influence of tacticity on the fragility of polymers. Systematic studies are required for verification of these predictions

It remains, however, unclear why the fast dynamics and elasticity of PS and PIB also show opposite molecular weight dependencies. It is known that fragility correlates to the fast dynamics.[28,29] This subject has attracted more attention recently[49,50] but still remains a puzzle. It is not clear for us whether the symmetry of monomers is also a reason for the opposite behavior of the fast dynamics and elasticity. This question requires more systematic analysis of the fast dynamics in polymers with various microstructures and tacticity.

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