

Breadth of the α -Relaxation Function in 1,4-Polybutadiene

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ABSTRACT: Mechanical and dielectric spectroscopy studies of local segmental motion (α -relaxation) in polybutadienes are reviewed and new results presented. Previous mechanical spectra for 1,4-polybutadiene relied on time–temperature superpositioning, leading to discrepancies regarding the breadth of the relaxation function. By measuring over a wide range of actual frequencies, we show that the mechanical dispersion is narrow, relative to 1,2-polybutadiene. The disagreement among published dielectric α -relaxation results is shown to be a consequence of the intrusion of the secondary relaxation for temperatures near the glass transition. The actual breadth of the relaxation function can be gleaned from analysis of the temperature dependence of the α -relaxation time and is consistent with the determination from mechanical spectroscopy (i.e., a narrow dispersion). Thus, decreasing vinyl content is associated with a narrower segmental relaxation function, whereby the correlation of chemical structure with both the breadth of the relaxation function and its temperature dependence holds for polybutadiene. This is in accord with an interpretation of the segmental dynamics based on steric interactions involving the pendant vinyl group enhancing intermolecular cooperativity. The T_g -normalized temperature dependences for 1,2- and 1,4-polybutadiene are also consistent with the respective energy barriers between conformational states of their backbones.

Introduction

The manner in which chemical structure governs relaxation associated with the glass transition (the α -relaxation) is the starting point to a fundamental understanding of the physical properties of polymers. For a wide range of materials, both the time and temperature dependences of the α -relaxation have been shown to be correlated with the degree to which local structure enhances intermolecular cooperativity.^{1–8} For polymers with smooth, flexible, compact, symmetrical chain backbones, the segmental relaxation function is relatively narrow, and the relaxation times depend weakly (more nearly Arrhenius) on temperature; this represents behavior associated with relatively unconstrained structural relaxation. Polymers having less flexible backbones, sterically hindering pendant groups, or polar interactions among chains usually exhibit broader segmental dispersions and enhanced temperature dependencies (i.e., more “fragile” behavior^{9,10}), reflecting segmental relaxation that is strongly intermolecularly cooperative.

Structure–property relationships of this sort are most persuasive when a single molecular feature can be systematically varied. Popular in this regard is polybutadiene, whose vinyl content (1,2-addition product) can range from essentially zero to nearly 100%, corresponding to a 100 deg change in the glass transition temperature. The low- T_g 1,4-polybutadiene (1,4-PB) has a smooth and symmetric backbone, which intuitively is expected to be less intermolecularly cooperative than 1,2-PB. The presence of the pendant, inflexible vinyl moiety in the latter causes a larger volume to be swept out during backbone conformational transitions, effecting greater steric hindrance. Experimentalists, using various techniques, have examined the α -relaxation in polybutadienes. This work is reviewed herein, along with some new experimental data, to reconcile discrepancies among different findings, particularly concerning the breadth of the α -relaxation function in 1,4-PB.

Background

Mechanical Spectroscopy. Several years ago in our laboratory, dynamic mechanical measurements were carried out on local segmental relaxation in polybutadienes of varying 1,2-content.¹ The breadths of spectra were found to parallel the concentration of pendant vinyl groups. In the vicinity of the maximum in the loss modulus, G'' , the shape could be described by the Laplace transform of the Kohlrausch–Williams–Watts function¹¹

$$\phi_{\alpha}(t) = \exp\left(-\left(\frac{t}{\tau_{\alpha}}\right)^{\beta}\right) \quad (1)$$

where τ_{α} is the relaxation time and β the Kohlrausch exponent for the α -process. It was determined¹ that the broader relaxation spectra of higher vinyl content PB were accompanied by a more marked T_g -normalized temperature dependence (more fragile behavior) of the average (or most probable) relaxation time.

Because these initial experiments were done in tension, modest peroxide cross-linking of the samples was used to minimize creep deformation. However, free radical cross-linking of 1,2-PB is accompanied by chain propagation, leading to a high concentration of high functionality cross-links, even for low levels of peroxide. Consequently, the segmental relaxation behavior for the highest vinyl polybutadienes was influenced by the network structure. Various studies^{12–15} have demonstrated that cross-linking per se broadens the relaxation function and increases the observed fragility. Nevertheless, this initial study¹ demonstrated that β_{mech} decreased and fragility increased with increasing vinyl content, notwithstanding the contribution from the cross-links. For the cross-linked polybutadiene with 20% vinyl units, $\beta_{\text{mech}} = 0.45$. The lowest vinyl polymer, which actually was the structurally very similar 1,4-poly(methylbutadiene) (or polyisoprene, 1,4-PI), had a significantly larger Kohlrausch exponent, $\beta_{\text{mech}} = 0.5$ (see Table 1).

Table 1. Mechanical Results for Kohlrausch Exponent

	β_{mech}	
	1,2-PB	1,4-PB
Roland & Ngai (1991) ¹	> 0.26 ^a	$\geq 0.50^b$
Colmenero et al. (1994) ¹⁶	0.39	
Roland (1995) ¹⁷	0.39 ^c	
Zorn et al. (1995) ⁸	0.41	0.49
Palade et al. (1995) ¹⁸		0.40
this work		0.52

^a Cross-linked sample. ^b 1,4-Poly(methylbutadiene). ^c $M_w = 20$ kg/mol.

Table 2. Dielectric Results for Kohlrausch Exponent

	β_{diel}	
	1,2-PB	1,4-PB
Roland (1994) ¹²	0.41	
Colmenero et al. (1994) ¹⁶	0.41	
Roland (1995) ¹⁷	0.39 ^a	
Arbe et al. (1996) ³⁰		0.41 ^b
Hofmann et al. (1996) ¹⁹	0.43 [‡]	0.41, ^b 0.50 ^c
this work		≥ 0.5

^a $M_w = 20\,000$ g/mol. ^b As reported by authors from shape of dielectric loss peak. ^c Using eq 9.

Subsequently, Colmenero et al.¹⁶ measured the mechanical α -process of 1,2-PB over a range of temperatures. The peak breadth increased somewhat as temperature was reduced toward the glass transition, with $\beta_{\text{mech}} = 0.39$ in the vicinity of the T_g . This same value of the Kohlrausch exponent was obtained for 1,2-PB of relatively low molecular weight (2 kg/mol).¹⁷ Both studies are consistent with the earlier mechanical results on cross-linked 1,2-PB.¹

Zorn and co-workers⁸ carried out mechanical measurements on PB of varying vinyl content. Their results were in accord with the earlier findings¹ that β_{mech} decreased and fragility increased with increasing 1,2-content of the polybutadiene. Because of the limited range of their mechanical spectrometer, however, Zorn et al.⁸ employed time-temperature superpositioning to obtain modulus spectra. This procedure introduces some uncertainty into the analysis, particularly given the vertical scaling required to obtain master curves. Indeed, almost simultaneously, Palade et al.¹⁸ reported dynamic mechanical results on 1,4-PB, also relying on time-temperature superpositioning. Their fit of eq 1 to the modulus master curve yielded $\beta_{\text{mech}} = 0.40$ (Table 1). This is substantially smaller than the determinations of the two other groups.^{1,8} From all these results, collected in Table 1, we can conclude that while the situation for 1,2-PB is clear, there is some ambiguity regarding the shape of the mechanical spectrum for local segmental motion in 1,4-PB.

Dielectric Spectroscopy. There have been various studies of dielectric relaxation in 1,2-PB, including the effect of cross-link density¹² and temperature¹⁶ on the local segmental dynamics. For linear 1,2-PB near the glass temperature, $\beta_{\text{diel}} = 0.41$ (Table 2). This result, corroborated by subsequent work,¹⁹ agrees with the value determined mechanically. Dielectric and mechanical spectroscopy on a low molecular weight 1,2-PB (ca. 2 kg/mol) also yielded identical values for the Kohlrausch exponent.¹⁷ Absent bulky or polar side groups, it is usual for the segmental relaxation function to have a similar shape as measured by mechanical and dielectric spectroscopies.^{16,20–22}

The dielectric α -relaxation times and their temperature dependence for polybutadienes of varying vinyl

content were shown to be the same as measured by dynamic light scattering.²³ Moreover, the Kohlrausch exponent for 1,2-PB was substantially less than the value for 1,4-PB.²³ Such equivalence of time and temperature dependences is not true for all spectroscopies, which may involve different correlators, as well as a momentum transfer dependence.^{24–28} However, since the respective Kohlrausch exponents are equal for 1,2-PB, we expect that in the case of 1,4-PB, which lacks pendant groups, β_{mech} and β_{diel} should equal one another. Consistent with this expectation, Zorn and co-workers²⁹ determined that the temperature dependence of the dielectric α -relaxation in polybutadienes of various vinyl content was equivalent to the corresponding temperature dependence measured mechanically.

Dielectric measurements of the α -relaxation in 1,4-PB were carried out by Hofmann et al.¹⁹ They found that the secondary relaxation in 1,4-PB (i.e., the β -peak) had substantial dielectric strength. Unfortunately, at temperatures for which the α -dispersion of 1,4-PB fell within the experimentally accessible frequencies, it overlapped the neighboring β -relaxation. From fitting the α -relaxation, Hofmann et al.¹⁹ deduced a Kohlrausch exponent of $\beta_{\text{diel}} = 0.42$, which is significantly lower than β_{mech} .^{1,8} However, the dielectric result is open to question, since the partially overlapping secondary relaxation in 1,4-PB was unaccounted for.¹⁹

Another measurement of β_{diel} for 1,4-PB was subsequently carried out by this same group.³⁰ In these experiments, the authors attempted to correct for the presence in the spectrum of the secondary relaxation by assuming

$$\phi(t) = f_{\alpha}\phi_{\alpha}(t) + (1 - f_{\alpha})\phi_{\beta}(t) \quad (2)$$

where f_{α} is the relaxation strength of the α -relaxation, and $\phi_{\beta}(t)$ refers to the secondary, or β -relaxation, function. Equation 2 is an approximation of a previously proposed correlation function³¹

$$\phi(t) = f_{\alpha}\phi_{\alpha}(t) + (1 - f_{\alpha})\phi_{\alpha}(t)\phi_{\beta}(t) \quad (3)$$

However, this evaluation method has been criticized as being insensitive to the shape and position of the relaxation functions.³² There is no consensus on the correct manner to separate overlapping α - and β -relaxations. For example, Donth and co-workers^{33,34} suggested the two processes superimpose in the frequency regime

$$\phi^*(\omega) = \phi_{\alpha}^*(\omega) + \phi_{\beta}^*(\omega) \quad (4)$$

where ω is the angular frequency and the functions are complex. Removal of the β -process according to this prescription results in a different form for the α -relaxation function than that obtained from eq 2. Without a molecular level identification of the β -process and the manner in which it is related to the α -relaxation,^{30,35–40} determination of the Kohlrausch exponent by fitting convoluted or overlapping spectra is a questionable procedure. Certainly the reported value of $\beta_{\text{diel}} = 0.41$ ^{19,30} is anomalously low both in comparison to that determined mechanically and given the expected correspondence between the mechanical and dielectric values of β in 1,4-PB.

Experimental Section

The 1,4-PB was a lithium-catalyzed polybutadiene, obtained from Goodyear Tire & Rubber Co., courtesy of A. F. Halasa.

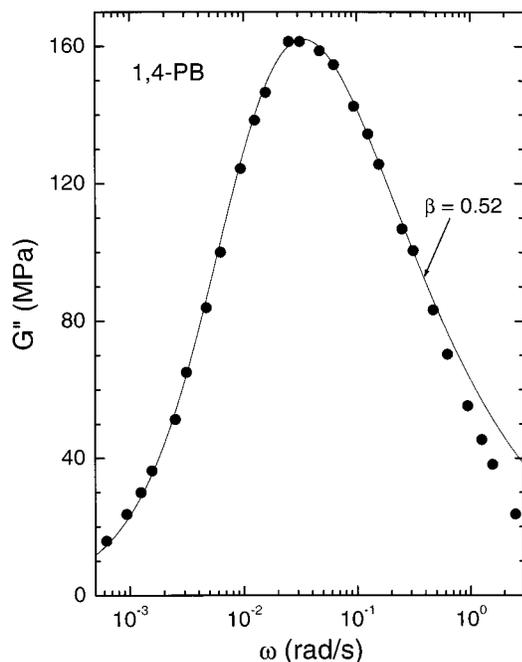


Figure 1. Dispersion in the loss modulus measured for 1,4-PB, along with the fit (solid line) to eq 1 with a value of 0.52 for the Kohlrausch exponent.

The polymer was reported to be 8% vinyl, although the exact 1,2-content varies somewhat according to the method of analysis.

Dynamic mechanical spectra were obtained with a Bohlin VOR rheometer, using a parallel plate geometry (sample diameter and gap equal to 3.2 and 1.3 mm, respectively). The shear modulus was measured isothermally at temperatures just above the glass temperature, over the frequency range $6 \times 10^{-4} \leq \omega \leq 10^1$ rad/s, at strains from 0.1 to 2%.

Isothermal dielectric measurements were obtained using a time domain spectrometer (Imass Inc.) having a frequency range $-3.2 < \log \omega$ (rad/s) < 4.8 . A 25 mm parallel plate geometry was employed, with a guard ring on the detector side. Samples were about 0.1 mm thick. A Delta Design model 9023 oven provided temperature control to ± 0.1 K.

Results

In Figure 1 is displayed the loss modulus for 1,4-PB, measured at -96 °C. The abscissa is the actual frequency, sans time-temperature superpositioning. The fit to the transform of the Kohlrausch function (eq 1) with an exponent = 0.52 is seen to describe the data well over most of the peak. The dielectric spectrum of 1,4-PB was measured over a range of temperatures, just above the glass temperature. The α -relaxation dispersion is shown in Figure 2, with the data shifted to superimpose the peaks. Particularly as temperature is increased, a contribution to the dielectric loss from the secondary relaxation is observed, especially toward higher frequencies. The consequent overlap of the two dispersions causes a broadening with increasing temperature. Note that while most marked toward higher frequencies, there is also slight broadening on the low-frequency side. This has been seen previously, but only in polybutadiene of very low vinyl content,²⁹ and presumably reflects intensity from the secondary relaxation. The width of the α -peak at the half-intensity points is plotted versus temperature in the inset to Figure 2.

The α -relaxation times determined by Hofmann et al.¹⁹ from their dielectric measurements were fitted to

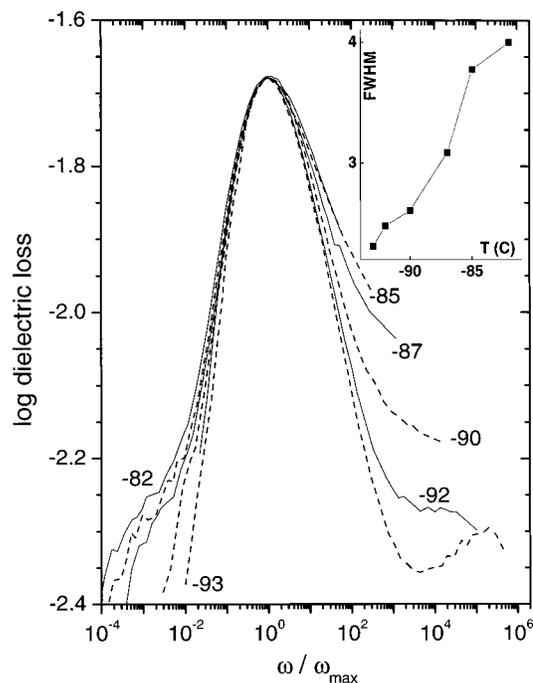


Figure 2. Dispersion in the dielectric loss of 1,4-PB measured at the indicated temperatures. The data have been superimposed to show the systematic broadening with increasing temperature. The spectral width at the half-intensity points are plotted in the inset.

the Vogel-Fulcher equation⁴¹

$$\tau_{\alpha} = A \exp\left(\frac{B}{T - T_0}\right) \quad (5)$$

Using the parameters A , B , and T_0 they reported,¹⁹ we can operationally define T_g as the temperature at which $\tau_{\alpha} = 1$ s; thus, $T_g = 272$ and 174 K for 1,2- and 1,4-PB, respectively. We then calculate the T_g -normalized Arrhenius plots of the relaxation times ("fragility curves"^{9,10}) for polybutadiene shown in Figure 3.

Immediately apparent is the steeper slope (more fragile behavior) of 1,2-PB. The fragility, or "steepness index", is commonly defined as the slope at T_g of the fragility curve

$$m = \left. \frac{d \log(\tau)}{d(T_g/T)} \right|_{T=T_g} \quad (6)$$

This yields $m = 97$ and 155 for 1,4-PB and 1,2-PB, respectively.

Discussion

Segmental Relaxation Dispersion. The first mechanical data¹ on polybutadiene indicated an increasing Kohlrausch exponent with decreasing vinyl content of the polybutadiene. For 1,4-PI (zero vinyl groups), $\beta_{\text{mech}} = 0.5$.¹ Since the methyl group in 1,4-PI is known to hinder conformational rearrangements of the backbone,⁴² this value of 0.5 provides a lower limit on β_{mech} for 1,4-PB.

Herein (Figure 1) we find that the mechanical dispersion of 1,4-PB with ca. 8% vinyl corresponds to $\beta_{\text{mech}} = 0.52$. This agrees with earlier determinations^{1,8} and is also consistent with a systematic variation of β_{mech} with chemical structure¹ (Table 1). In obtaining the spectrum herein, the time-temperature superpositioning used in

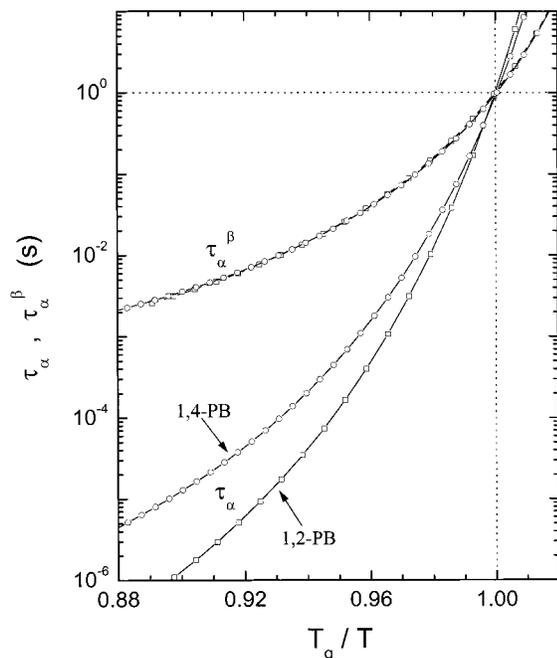


Figure 3. α -Relaxation times measured by dielectric spectroscopy¹⁹ for the two polybutadienes, displayed as fragility plots with $\tau_\alpha(T_g) = 1$ s. The upper curves are these same data raised to the power of their Kohlrausch exponents, $\beta_{\text{diel}} = 0.42$ and 0.50 for 1,2- and 1,4-PB, respectively. For the latter, β_{diel} is deduced from the requirement that the curves superpose.

earlier studies^{8,18} was avoided. We believe the substantially smaller β_{mech} reported by Palade et al.¹⁸ was in error due to reliance on master curves, with both vertical and horizontal shifting of the data.

The dielectric α -relaxation dispersion of 1,4-PB is seen in Figure 2 to broaden with increasing temperature. This is contrary to the expected behavior of the α -relaxation, as seen, for example, in mechanical and dielectric spectroscopy on 1,2-PB,¹⁶ as well as for polyisoprene,²² wherein peak broadening is associated with decreasing temperature. The reason for the difference, of course, is that the broadening herein is due to greater overlap with the secondary relaxation at higher temperatures. As reported previously by others,^{19,30} the secondary relaxation in 1,4-PB encroaches upon the primary α -peak, to an increasing degree as temperature is increased. At sufficiently high temperature (ca. -63 °C) the two dispersions will merge.³⁸

Direct fitting of the overlapping dispersions would be misleading. However, absent a reliable, established procedure for deconvolution of the α - and β -peaks, the Kohlrausch exponent can only be estimated from the data in Figure 2. At the lowest measurement temperature (least overlap), the width of the peak at the half-intensity points is 2.3 decades. This corresponds to a Kohlrausch exponent of one-half, so that we can conclude $\beta_{\text{diel}} \geq 0.5$.

Fragility. The published determinations of β_{diel} for 1,4-PB^{19,30} can be subjected to a simple test. The breadth of the α -relaxation function should correlate with the degree to which the temperature dependence deviates from Arrhenius behavior. This correlation holds generally for polymers and small molecule glass-formers^{2-8,10} and has even been expressed mathematically⁴³

$$m = 250(\pm 30) - 320\beta \quad (7)$$

Although exceptions to the correlation between fragility

and peak breadth are known, they are usually associated with heterogeneity of the structure, as found in copolymers,^{44,45} blends,^{5,6} or semicrystalline polymers.⁴⁶

Specifically for polybutadiene, it has been demonstrated that m increases, concomitant with a decrease in β_{mech} , with increasing vinyl content of the polymer.^{1,8} Moreover, the temperature dependence of 1,4-PB measured dielectrically was shown to be equivalent to the temperature dependence measured mechanically,²⁹ which implies a correspondence between β_{mech} and β_{diel} . Thus, the fragility plot of the α -relaxation times reported by Hofmann et al.¹⁹ should be consistent with the value of β_{diel} . Note that the peak of the dispersion is negligibly affected by the overlap toward higher frequencies with the secondary relaxation; thus, the τ_α should be fairly accurate.

Figure 3 shows clearly that 1,2-PB is more fragile than 1,4-PB. This fact is at odds with the suggestion^{19,30} that the β_{diel} are equivalent for the two polybutadienes. Using eq 7, we can obtain crude estimates of $\beta_{\text{diel}} = 0.48$ and 0.42 for 1,4-PB and 1,2-PB, respectively.

We can also make use of a relation from the coupling model of relaxation⁴⁷ to extract a value of β_{diel} for 1,4-PB from the data in Figure 3. This model relates the observed relaxation time, τ_α , to the intermolecularly uncorrelated relaxation time, τ_0 ; the latter can be identified with a Hall-Helfand relaxation time.⁴⁸ The relation is given by⁴⁷

$$\tau_0(T) = t_c^{1-\beta} \tau_\alpha(T)^\beta \quad (8)$$

where the crossover time of the model, t_c (\sim picoseconds⁴⁹), is essentially a constant, so that

$$\tau_0(T) \propto \tau_\alpha(T)^\beta \quad (9)$$

These expressions of the coupling model have been given experimental verification from quasi-elastic neutron scattering experiments on polymers,⁵⁰ including specifically 1,4-PB.⁵¹ Equations 8 and 9 indicate that any temperature dependence of τ_0 , involving conformational transition rates of isolated chains, will be amplified due to intermolecular cooperativity by the $1/\beta$ power.

The τ_α data for 1,2-PB in Figure 3 are scaled by the exponent $\beta_{\text{diel}} = 0.43$ (i.e., the Kohlrausch parameter reported by Hofmann et al.¹⁹), to yield the curve for τ_0 . For 1,4-PB, we determine β_{diel} from the requirement that the fragilities for the respective τ_0 of the two polybutadienes superimpose. As shown in the Figure 3, such superposition is obtained for $\beta_{\text{diel}} = 0.50$. This value is consistent with the β_{mech} for 1,4-PB determined from the shape of the loss modulus, previously^{1,8} and herein (Figure 1). All results for the Kohlrausch exponent from dielectric spectroscopy are collected in Table 2.

The analysis of the data in Figure 3 based on the coupling model assumes comparable fragilities for 1,2-PB and 1,4-PB in the absence of intermolecular cooperativity. The accuracy of this assumption is not easily judged. Energy barriers between conformational states have been reported for the two polybutadienes from NMR measurements on dilute solutions. The obtained values vary with solvent and for 1,4-PB depend as well on the backbone carbon being measured. The bond activation energies fall in the range from 12 to 17 kJ/mol for 1,2-PB⁵² and 6 to 10 kJ/mol for 1,4-PB.⁵³ The latter agree with values used by Gee and Boyd in simulations on 1,4-PB.⁵⁴ Although these energy barriers

Table 3. Apparent Activation Energies

	E_a (kJ/mol)	
	1,2-PB	1,4-PB
conformational barrier	14 ^a	8 ^b
τ_0 (eq 9) ^c	250	160
τ_α ^c	600	320

^a Reference 52. ^b Reference 53. ^c Measured at the temperature at which $\tau_\alpha = 1$ s.

between conformational states are related to the intermolecularly noncooperative relaxation time of the chain, they cannot be identified with the temperature dependence of τ_0 . The dynamics underlying τ_0 involve correlated motions of a few backbone bonds, along with contributions from librational motions⁵⁵ and back-transitions between rotameric states.⁵⁶ Thus, the apparent activation energy of τ_0 in Figure 3 (i.e., the slope at T_g) is a factor of 20 larger than the bond rotational barriers determined from NMR. It is noteworthy, however, that the apparent activation energies for τ_0 of each polymer are in proportion to the respective energy barriers between conformational states (Table 3). This is consistent with the notion that the latter govern the temperature dependence of the (intermolecularly) noncooperative relaxation time and gives credence to the value of β_{diel} (=0.50) for 1,4-PB deduced using eq 9.

Summary

Mechanical spectroscopy data for polybutadienes show a clear trend that increasing vinyl content broadens the segmental relaxation function and increases the T_g -normalized temperature dependence. Agreement between mechanical and dielectric results is seen in 1,2-PB and is expected for 1,4-PB, given the absence of side groups on the backbone of the latter polymer. The dielectric α -dispersion observed for 1,4-PB is anomalously broad; however, as shown herein, this is an artifact of overlapping at higher frequencies with the secondary relaxation at temperatures near T_g .

Notwithstanding this convolution of the α - and β -processes, the Kohlrausch exponent for the α -peak was deduced by scaling the fragility curves for polybutadiene, using a relation from the coupling model. In this manner, we show that the α -relaxation measured dielectrically for 1,4-PB is narrow ($\beta_{\text{diel}} = 0.5$) and in accord with the mechanical data. Thus, the breadths of the spectra parallel the concentration of pendant vinyl groups on the polybutadiene backbone. The obvious interpretation is that pendant groups promote steric interactions, leading to enhanced intermolecular cooperativity. The latter is manifested as a broadened spectrum and a more fragile temperature dependence.

The shape of the α -relaxation spectrum for polybutadiene has significant implications for structure–property relationships in polymers. If the Kohlrausch exponent were invariant to chemical structure, it would mean that local segmental relaxation is unaffected by either the intrinsic structure (including backbone rotational potentials and the volume swept out by side groups) or its interaction with the local environment (intermolecular cooperativity). Moreover, leaving aside 1,4-PB homopolymer, there is a well-established correlation from mechanical measurements of both the Kohlrausch exponent and the fragility with the vinyl content of polybutadiene.^{1,8} An abrupt discontinuity when the vinyl level goes toward zero is contrary to intuition.

It is of some interest that the β -process, which occurs generally in glass-formers of diverse chemical structures, tends to overlap with the α -relaxation for glass-formers lacking side groups,^{57,58} a category including 1,4-PB. Moreover, it was recently demonstrated that there is a relationship between the magnitude of the β -relaxation and the Kohlrausch exponent for the α -relaxation function.^{36,37} This relation appears to be borne out by polybutadiene: to wit, the observed overlapping of these two processes in 1,4-PB and the absence of same for polybutadienes of higher vinyl content.

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