Segmental Relaxation and Molecular Structure in Polybutadienes and Polyisoprene

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ABSTRACT: The glass transition dispersion in the mechanical spectrum was measured for polybutadienes of various vinyl content and for polyisoprene. The breadths of spectra were found to parallel the concentration of pendant vinyl groups on the main chain. Consistent with results on many other materials, the shape of the spectra were well described by the Kohlrausch-Williams-Watts function; consequently, the segmental relaxation behavior can be specified by the dependence of the fractional exponent on molecular structure. It was determined that the spectral shapes correlate with the temperature dependence of the time-temperature shift factors. Specifically, segmental relaxations that are more intermolecularly cooperative exhibit larger shift factors, indicating a relationship between time and temperature dependencies. The spectral bandwidths were not associated with structural diversity within the polymer backbone. The behavior can be interpreted using the coupling model of relaxation. This model identifies the origin of the Kohlrausch form for the spectral dispersion and provides a plausible physical picture. The model's prediction of a correspondence between the spectral shape and the temperature dependence of the shift factors is corroborated.

Introduction

Near their glass transition temperature, polymers exhibit a dispersion in their mechanical response. Independently of the nature of the experiment used to measure local segmental relaxations in polymers, these cannot be represented as a single Debye process; that is, the relaxation functions are invariably nonexponential.[1] The origin of this behavior is uncertain. Obviously the nature of the relaxation, and hence the shape and temperature dependence of the relaxation function, is governed by the molecular structure and its effect on the local chain dynamics. However, systematic information, and hence even a qualitative understanding, concerning the relationship between molecular relaxation near the glass transition and the structure of the polymers is scarce.

Changes in the tacticity of poly(methyl methacrylate) were found to have no influence on the width of the relaxation function in the vicinity of the glass transition.[2] Similarly, poly(1-vinylnaphthalene), poly(2-vinylnaphthalene), and poly(vinylbiphenyl) reportedly all exhibit similar segmental relaxation.[3] Hydrogenation was shown to effect a small decrease in the segmental relaxation rate of polystyrene.[4] The effect was ascribed to a reduction in the degree of cooperativity of the molecular relaxation due to the increased bulkiness of the pendant group.

Tobolsky, Aklonis, and co-workers proposed an empirical lattice model comprised of damped Debye oscillators to describe the relaxation behavior in the glass transition zone.[5,6] "Dimensionalities" of the elastic constants of the lattice were invoked to account for the various time dependencies of the generalized Rouse relaxation exhibited by different polymers in the transition zone. When a connection is drawn between the dimensionality of the damped lattice and the severity of the intra- and interchain interactions of the elastic oscillators, the model was applied with some success to the effect of plasticizers on the slope of the stress relaxation curve in the transition zone.[7-11] Notwithstanding this success, experimental analysis of the mechanisms underlying the viscoelastic spectrum indicates that, in the vicinity of the transition zone, the shorter time behavior is dominated by segmental relaxation.[12] At least for the polymers studied therein,[12] the motion of the Rouse modes contributed to the response in the transition zone only at longer times.

In an attempt to relate transition zone behavior to chemical structure, an empirical correlation was suggested for the time dependence of segmental relaxation and a polymer's cohesive energy density, flexibility, and available free volume.[13,14] Some success in rationalizing the behavior of various polymers, particularly polyacrylates, was reported; however, the correlation for polymer chains containing bulky side groups is deficient.[14]

Recently it has been shown from an analysis of the local segmental dynamics of a number of polymers that a correlation exists between the shape of the relaxation function and the temperature dependence of the time-temperature shift factors.[15] This temperature dependence is expressed in terms of the normalized temperature variable $(T - T_g)/T_g$ or the inverse temperature variable T_g/T, where T_g is the glass transition temperature. The observed correlation is consistent with a prediction of the coupling model of relaxation,[16-18] which relates the degree of nonexponentiality of the segmental relaxation to the extent of intermolecular coupling between the local conformational transitions.

In this paper dynamic mechanical measurements in the glass transition region for various polybutadienes and polyisoprene are reported. The influence of chemical structure on the shape of the glass transition dispersion and the temperature dependence of the shift factors are investigated. Efforts to interpret the results in terms of the degree of cooperativity of the segmental dynamics are described.

Experimental Section

The high polymers used and their sources are listed in Table I, with the chemical structures depicted in Figure 1. For testing the rubbers were molded under pressure at 140 °C into 0.15-cm-thick sheets. The dimensional stability of the test specimens was enhanced by incorporation of a few hundred ppm of dicumyl peroxide prior to molding. The level of the peroxide was adjusted for each polymer in order to obtain a cross-link density only slightly greater than that at the gel point. It was determined that these changes in polymer macrostructure exert no significant influence on mechanical behavior in the glass transition region.

Dynamic mechanical testing was conducted in uniaxial extension with an Imass Corp. Dynastat Mark II instrument. Measurements were averaged over a minimum of seven cycles at various frequencies ranging from 0.01 to 100 s^{-1}. The experiments

Table I
Polymer Samples

designation	microstructure
97% 1,2-PBD	atactic 97% 1,2-polybutadiene[b]
83% 1,2-PBD[a]	atactic 83% 1,2-polybutadiene[b]
50% 1,2-PBD[a]	atactic 50% 1,2-polybutadiene[b]
20% 1,2-PBD[c]	80% 1,4-polybutadiene (mixed cis and trans)
1,4-PIP[d]	*cis*-1,4-polyisoprene (SMR-L type Hevea Brasiliensis)

[a] Firestone/Bridgestone Co. [b] The remaining chain units were 1,4-butadiene. [c] Aldrich Chemical Co. [d] Ore and Chemical Corp.

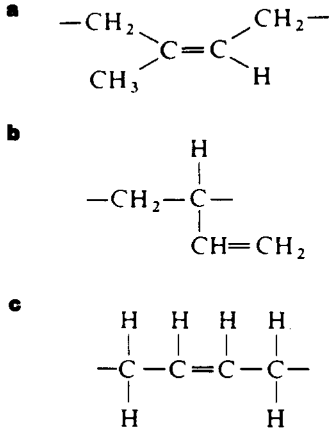

Figure 1. Chemical structure of the chain units of (a) 1,4-polyisoprene, (b) 1,2-polybutadiene, and (c) 1,4-polybutadiene. In the text the term "vinyl content" refers to the concentration of chain units having the 1,2-addition product depicted in b.

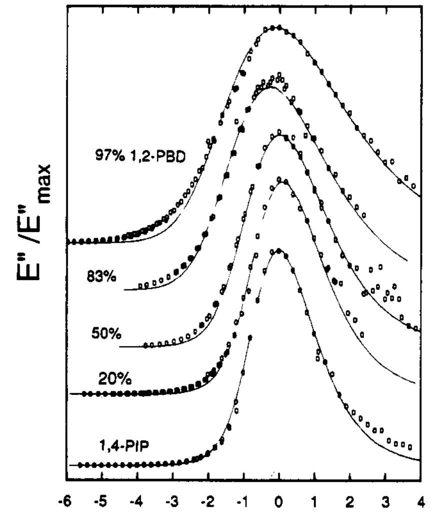

Figure 2. Superpositioned loss moduli spectra measured for the polymers in the vicinity of their glass transition temperature, along with the best fit curve calculated using eqs 1 and 2. Semilogarithmic plotting emphasizes the contribution of the segmental motion and deemphasizes the Rouse modes.

were done at several temperatures encompassing the glass transition region. The shift factors used to construct master curves were obtained by empirically time–temperature superpositioning the loss tangent data to an arbitrary reference temperature.

Results

Relaxation Behavior. The superpositioned mechanical loss modulus spectra for the polymers in the glass transition zone are shown in Figure 2. The reference temperature, T_{ref}, for each master curve is listed in Table II. Conspicuous in these results is the systematic increase in the breadth of the loss modulus peak with an increase in the vinyl content (1,2-addition product) of the polymer. The data were analyzed with the intent of quantifying this effect. As alluded to above, the band shapes are not Lorentzian; however, it is well established that relaxation data in the glass transition zone can be represented by the Kohlrausch–Williams–Watts function[19,20]

$$E(t) = E(0) \exp\left[-\left(\frac{t}{\tau^*}\right)^{1-n}\right] \qquad (1)$$

where τ^* is a temperature-dependent apparent relaxation time and $0 \leq n \leq 1$. While it is often employed as an empirical fitting function, eq 1 in fact has been deduced from a coupling model of relaxation.[16-18] Discussion of this is deferred.

Loss modulus spectra were calculated from eq 1 using[21]

$$E''(\omega) = \omega \int_0^\infty E(t) \cos(\omega t)\, \mathrm{d}t \qquad (2)$$

The results are displayed in Figure 2, where it is seen that agreement with the experimental data is satisfactory. The best fit values for the adjustable parameters $E(0)$, $\tau^*(T_{ref})$, and n are listed in Table II. The $\tau^*(T_{ref})$ represent the apparent relaxation times at the particular reference temperature and thus reflect the difference between T_{ref} and the glass transition temperature, T_g, for the polymers.

The parameter n provides a measure of the breadth of the glass transition peak. The dependence of n on the vinyl content of the polymers is displayed in Figure 3. Also included in the figure and in Table II are the results of ultrasonic absorption measurements that have been reported for a 71% 1,2-polybutadiene.[22] Insight into the origin of the evident relationship of n to molecular structure requires interpretation of the physical significance of the parameter n. A value of $n = 0$ connotes exponential relaxation. The deviation in Figure 2 from simple Debye-type behavior might result from a distribution of relaxation times, for example, due to a distribution of free volume[1,23-25] or relaxation mechanisms.[1,21,26,27] The latter implies

$$\exp\left[-\left(\frac{t}{\tau^*}\right)^{1-n}\right] = \int_0^\infty p(\tau) \exp\left(-\frac{t}{\tau}\right) \mathrm{d}\tau \qquad (3)$$

where $p(\tau)$ is the relaxation time distribution function. The explicit form of this Kohlrausch distribution function has been calculated.[28] The function has the necessary asymmetry, while n describes the spread. A larger n (broader spectrum) is associated with a broader distribution of relaxation times.

Interpretation of the present results (Figure 2) simply in terms of a relaxation time distribution is problematic. For random copolymers, the structural diversity among the segments of a chain might be expected to engender a distribution of relaxation times; however, no maximum exists in the curve of Figure 3. The breadth of the loss modulus peak increases with vinyl content, up through the 97% 1,2-polybutadiene. Evidently dispersion in the chain microstructure of these polymers is not the primary source of the breadth of the spectral dispersion.

Notwithstanding any difficulty in reconciling the spectra in Figure 2 with a distribution of relaxation times, local segmental relaxations measured herein, as well as by diverse techniques on numerous other polymers, invariably exhibit the Kohlrausch form (eq 1). This relaxation function is obtained directly by the coupling model of relaxation, which has been applied extensively to polymeric materials.[1,15,17,29,31] In this model the fundamental relaxation mode, in the absence of intermolecular interactions, is represented as a Debye-type process ($n = 0$) or

Table II
Glass Transition Results

sample	T_{ref}, K	$E(0)^a$	$\tau^*(T_{ref})^a$	n^a	$-\log(\tau_\infty)^b$	B^b	T_∞,^{b} K	T_g,^{e} K
97% 1,2-PBD	278	1650	1.3×10^{-1}	0.74	12.6	824	247	272
83% 1,2-PBD	253	1363	1.2×10^{0}	0.68	18.7	2009	207	249
71% 1,2-PBD^d	293^d			0.65^d	12.4^d	845^d	200^d	226
50% 1,2-PBD	208	1360	6.6×10^{-2}	0.61	25.5	4064	135	200
20% 1,2-PBD	178	1330	9.0×10^{-2}	0.55	8.2	266	162	173
1,4-PIP	213	1820	1.5×10^{-2}	0.50	14.8	1700	156	200

[a] Equations 1 and 2. [b] Equation 6. [c] Temperature at which $\tau^* = 100$ s (using eq 6). [d] Reference 22.

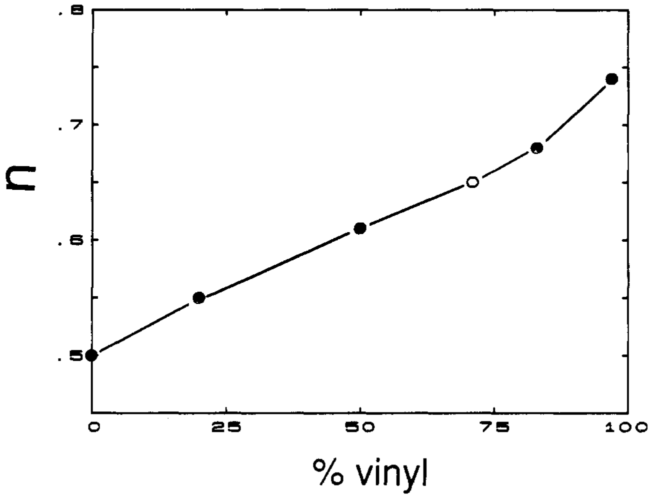

Figure 3. Dependence of the spectral breadth, as measured by the parameter n, on the concentration of vinyl (1,2-addition product) chain units in the polymer. The filled circles are the data obtained in this study, and the hollow point was taken from ref 22.

more appropriate for segmental motions of polymers a Hall–Helfand type of intrachain conformational transition.[34] In a densely packed polymer, each segment tries to relax with a Hall–Helfand rate, W_{HH}. However, intermolecular couplings among the segments cause some of these attempts to fail. When averaged over the segments this effect can be viewed as a slowing down (reduction) of W_{HH} for all segments. Actually, from a microscopic viewpoint, the segments are not all coherently delayed in identical fashion; some relax sooner and others later. The averaging over all segments appropriate for consideration of the relaxation of macroscopic variables such as the modulus leads to an effective description of the dynamics in terms of the product $W_{HH}(\omega_c t)^{-n}$ ($\equiv W(t)$). This time-dependent relaxation rate governs the relaxation of $E(t)$ according to $dE/dt = -W(t)E$. Solution of this equation yields eq 1,[18] as well as a relation between τ^* and one of the relaxation times in the Hall–Helfand function. It is important to note that in the coupling model motions of individual segments, though slowed down, are not identical at any given time. On the molecular level a "distribution of relaxation times", heterogeneous on the time scale of τ^*, exists. The distribution reflects stochastic variations as dictated by cooperativity in the success rate for conformational transitions by the segments. This feature of the coupling model is consistent with the recent experimental findings of Spiess et al.[32] for segmental relaxation in poly(vinyl acetate). Of course, the depiction of relaxation in a multibodied system in the language of single-body dynamics, as we are doing here, must be applied with caution. A portrayal of relaxation in terms of the success rate for conformational changes might suggest a waiting time distribution of primitive relaxation modes as an approach to segmental relaxation. However, recent simulations of another correlated system[33,34] demonstrate that the observed behavior cannot be described by a distribution of correlation times. The observation of a Kohlrausch relaxation function is a consequence of the cooperative nature of the relaxation. The coupling parameter, n, captures the strength of the intermolecular interaction, thus providing a measure of the degree of cooperativity associated with the relaxation process.

Although the experimental data follow the Kohlrausch form derivable from the coupling model (Figure 2), assessment of the model's merits herein depends on the extent to which its application yields a physically plausible description of the observed behavior. An increasing magnitude of the coupling parameter with 1,2-content (Figure 3) would suggest that the vinyl groups enhance the cooperativity of the segmental relaxation process. Certainly in comparison to a methyl group or protons, pendant vinyl moieties, with the relatively inflexible carbon–carbon double bond projecting over 3 Å from the chain backbone, sweep out a larger volume during the course of conformational changes. Encounters of the vinyl groups, mutually and with the backbone, become more probable with an increase in their concentration. The supposition is that this promotes steric interferences among or couplings between the locally rearranging chain segments. To the extent that segmental motions are more strongly resisted intermolecularly by the medium, retardation of the primitive relaxation is promoted, and hence n increases. This interpretation is consistent with the trend in Figure 3. This physical picture was actually suggested by earlier work;[35] the present experiments were undertaken to confirm inferences therefrom.

There have recently appeared simulations (based on a collective motion algorithm) of both the structure and dynamics in dense systems of complex molecules.[36] The calculated time dependence of the monomer displacements is comprised of a short-time regime, where only local oscillations are possible, and a long-time regime associated with translational diffusion. The correspondence of these regimes to the glass–liquid relaxation is obvious. Of interest herein is the transition zone connecting the short- and long-time behaviors, which is predicted by the simulation to broaden as the structural irregularity[37] of the relaxing elements is increased. Structural irregularities of the molecules enhance interparticle interactions. This implies that the onset of liquidlike mobility becomes more gradual (is broadened) as intermolecular couplings are promoted by a less compact or more irregular structure. The results of this simulation can only be used as a guide to segmental relaxation in polymers. Nonetheless, it is tempting to infer a corroboration that steric hindrances arising from pendant vinyl groups in polybutadiene increase the cooperativity of the segmental motions therein.

Fragility of the Liquid State. The glass transition does not correspond to a change in state, since the molecular configurations are unchanged. The change in density, however, does alter the relaxation time and its (putative) distribution. The temperature dependence of the relaxation time for a primitive relaxation process (one uncoupled intermolecularly) is governed by a shift factor, $a_T{}^0$. This fundamental shift factor is related to the observed (apparent) shift factor as[16,17,38]

$$\log a_T{}^0 = (1 - n) \log a_T \qquad (4)$$

This relationship suggests that segmental relaxation that is more cooperative will exhibit larger apparent shift factors.

Small-molecule liquids have been classified as strong or fragile, depending on the rapidity with which their "structure", or actually the properties associated with the glassy state, are lost, modified, or degraded as the temperature is increased through the glass transition region.[39] These alterations manifest themselves in the enormous reduction in relaxation times over this temperature range. The relative magnitudes of the respective relaxation times for different temperatures can be expressed by the time–temperature shift factor[21]

$$a_{T_1} = \tau^*(T_1)/\tau^*(T_0) \qquad (5)$$

Hence, the change of a_T with temperature provides a measure of the fragility of a liquid. More fragile liquids have a larger apparent activation energy near T_g, and hence their shift factors will exhibit in the vicinity of T_g a more marked dependence on temperature. Angell[40] was the first to suggest the extension of the fragility plot concept to segmental relaxation in polymers. His results and conclusions can be found in a forthcoming paper.[41]

For macromolecules, there is no obvious modification of structure with temperature variation, so that the use of the term "fragility" may not be appropriate. The alternative terminology "cooperativity plot" may better convey the physics in the polymer case. In any event the temperature dependence of the shift factors can be depicted by Arrhenius plots of a_T versus the normalized temperature, T_g/T, in the manner suggested by previous workers.[39,42]

A glass transition temperature for the polymers was defined as the temperature at which the apparent relaxation time (τ^* in eq 1) equals 100 s. This T_g was extracted from the mechanical spectra by fitting the VFTH equation[21]

$$\tau^* = \tau_\infty \exp\left(\frac{B}{T - T_\infty}\right) \qquad (6)$$

to the measured temperature dependence of τ^*. The application of eq 6 to the data is displayed in Figure 4, with the results tabulated in Table II. Also included are the VFTH parameters reported previously for a 71% 1,2-polybutadiene.[22]

Using the T_g obtained by this procedure, fragility (cooperativity) plots were constructed (Figure 5). It is seen that the rank ordering of the fragility curves for the polymers parallels the magnitude of their coupling parameters. This agrees with the prediction of the coupling model (eq 4) that more fragile liquids are those whose segmental relaxation is more cooperative (i.e., larger n). If both the activation energy and n were constant with temperature, the relationship given by eq 4 further suggests that the fragility plots should superimpose when scaled by the quantity $(1 - n)$.[15] Although there is some experimental scatter in the data when such a superposition is attempted with the present data, Figure 5 is consistent with the approach embodied by eq 4.

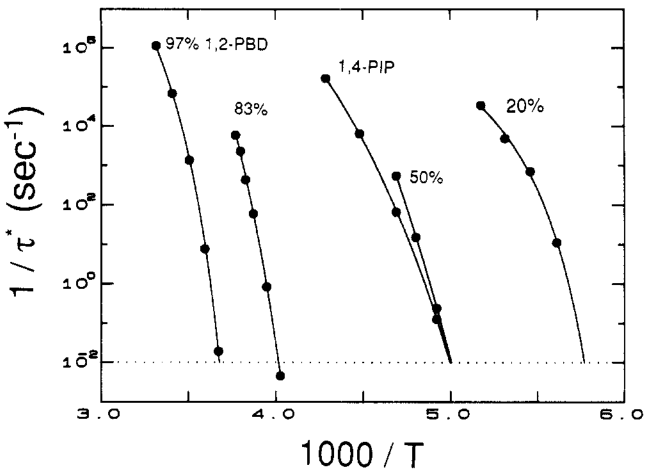

Figure 4. Arrhenius plots of the inverse of the apparent relaxation time for the various polymers, obtained by fitting eq 1 to the loss moduli spectra and using the empirically determined a_T. The solid curves represent the results of fitting eq 6 to the experimental data. The extrapolation to $\tau^* = 100$ s provided a measure of the glass transition temperature.

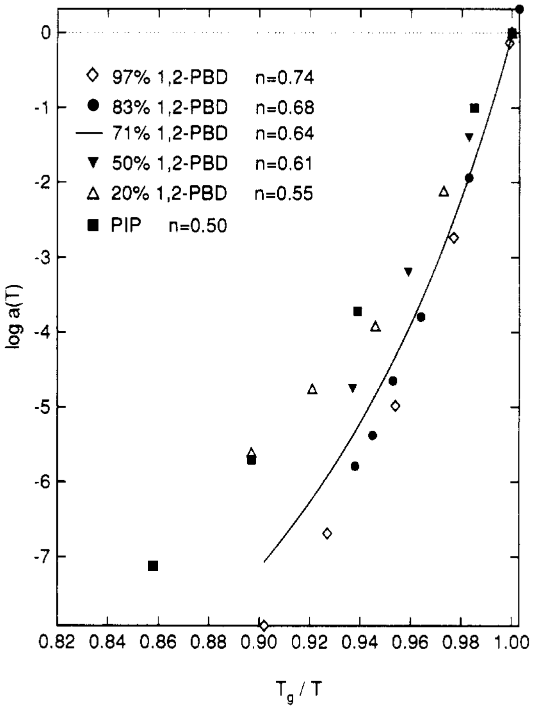

Figure 5. Shift factors used to construct the master curves of Figure 2 displayed as a function of the inverse temperature, normalized by $T_g{}^{-1}$. The glass transition temperatures were obtained from the data in Figure 3 and correspond to the temperature at which the apparent relaxation time equaled 100 s. Also included in this figure are data taken from ref 22.

The change in heat capacity at T_g has been proposed as a measure of fragility. It is noted in passing that preliminary calorimetry measurements on the polymers in the present work gave no evidence of a correlation between this change in heat capacity and the breadth of the transitions seen in Figure 2. This concurs with earlier conclusions drawn from work with other polymers.[41]

Summary

An absence was found herein of any correlation between the breadth of the spectral dispersion and the structural diversity of the polymer segments. The coupling model offers a plausible explanation for the dependence of the spectral breadths on molecular structure. The theory also correctly predicts the existence of a relationship between the shape of the spectral dispersion and the temperature dependence of the shift factors.

It should be borne in mind that the emphasis herein has been only on the segmental relaxation behavior. A prominent contribution of the Rouse modes to the mechanical response can effect a broad spectrum (as is seen, for example, in polyisobutylene[43]), particularly when the spectrum is displayed on a logarithmic scale. Although the present findings for polybutadienes and polyisoprene were predicted by the coupling model, it has not been established that these experimental results cannot be rationalized using other approaches to segmental relaxation in polymers. Certainly further experiments are necessary to allow critical assessment of all models for describing molecular motions and the glass transition.

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Registry No. 1,2-Polybutadiene (homopolymer), 9003-17-2.