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Distinctive Manifestations of Segmental Motion in Amorphous Poly(tetrahydrofuran) and Polyisobutylene

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Received October 6, 1992; Revised Manuscript Received March 2, 1993

ABSTRACT: Polyisobutylene (PIB) and poly(tetrahydrofuran) (PTHF) exhibit segmental relaxation behavior that is distinctly different from that found for other amorphous polymers. These unusual properties include a segmental relaxation dispersion that is much broader when measured mechanically than as seen by other spectroscopic techniques, a relative insensitivity of the segmental relaxation time to temperature, a small "steepness index", and an absence of encroachment of the segmental modes in time scale toward the Rouse region as temperature is lowered. It is proposed herein that these phenomena are the result of the very low extent to which segmental relaxation in PIB and PTHF is constrained by nonbonded neighboring segments. This weak intermolecular coupling, deduced from quasi-elastic neutron scattering measurements, solid-state NMR spectroscopy, and the temperature dependence of the segmental relaxation time, arises from the smooth, symmetric, and flexible structure of the two polymers.

Introduction

Polymer chains undergo numerous modes of motion, involving a broad range of times and length scales. Segmental relaxation, associated with the glass to liquid transition, primarily involves correlated local motion of only a few backbone bonds.[1,2] The contribution of segmental relaxation to the viscoelastic response of polymers is emphasized when experimental data (e.g., dynamic mechanical loss modulus) are displayed semilogarithmically with a linear ordinate scale. Usually the shape of the segmental relaxation dispersion reflects the intermolecular cooperativity associated with molecular motion in the dense phase.[3,4] The dynamical constraints of nonbonded neighboring segments (from different chains and from the same chain but separated by many bonds) retard the conformational transitions, slowing down the relaxation.

In general, motions over longer length scales than segmental relaxation are expected to occur at longer times. The dynamics of chain segments containing on the order of 50 or more chain atoms,[5] and hence having a Gaussian distribution of vectors, are described by the Rouse theory. While Rouse modes of motion occur at longer times and over greater length scales than segmental relaxation, conceivably, modes involving on the order of 10 backbone bonds may occur simultaneously with, albeit as a result of, segmental motion. These modes we designate as "sub-Rouse modes" to convey that the motion involves segments, while larger than the couple of conformers involved in local segmental relaxation, which contain fewer chain units than the shortest of the Gaussian submolecules described by the Rouse model. The intramolecularly correlated and intermolecularly coupled conformational transitions comprising the glass transition permit relaxation to proceed beyond the locally relaxing segments themselves. When the rate of segmental relaxation approaches that of the sub-Rouse motion, the former will be manifested over a length scale larger than the few conformers associated with the glass transition.

An indication of the concurrent nature of segmental and sub-Rouse dynamics is seen in the overlapping of *distortional* (involving alterations in bond angles and lengths) and orientational (Rouse modes) processes in the glass transition region of polymers, as brought out in measurements of strain-optical coefficients in polymers.[6,7] In the following sections, additional evidence will be given

why most amorphous polymers tend to have virtually simultaneous contributions from their segmental and sub-Rouse modes. Of course, not all motions are necessarily manifested in a given experimental measurement. Dielectric relaxation, photon correlation spectroscopy, and quasi-elastic neutron scattering usually probe only the local segmental motion; the sub-Rouse modes are not observed. Contrarily, all modes are expected to contribute to the relaxation of stress and hence be reflected in mechanical spectra. In the usual circumstance, in which the segmental relaxation is simultaneous with, if in effect the cause of, the sub-Rouse motion, experiments that probe only the former yield similar experimental spectra as mechanical measurements.[8] Particularly when a linear ordinate scale is employed, as customary for dielectric relaxation and photon correlation spectroscopies, the contribution of the sub-Rouse modes is subsumed by the segmental dynamics.

If the conformational transitions comprising segmental relaxation occur sufficiently fast, motion of the sub-Rouse modes may only transpire subsequent to, and thus be separated in time from, segmental relaxation. This would truncate the length scale of the glass transition normally associated with the local segmental relaxation; in this circumstance, the contribution of the sub-Rouse motions may be resolvable in the viscoelastic spectrum. Such a situation is anticipated whenever segmental relaxation is only weakly impeded by intermolecular cooperativity and will be apparent in measurements made with experimental probes sensitive to all modes of motion. We will elaborate on this phenomenon and its consequences in a later section.

It is hard to find amorphous polymers that exhibit weak intermolecular coupling of their segmental relaxation. As will be described below, one example is polyisobutylene. Intuitively, from the compact, symmetric repeat unit, we anticipate that PIB has weak intermolecular coupling. There are other polymers that similarly have simple, flexible-chain structures. Unfortunately, these polymers are usually semicrystalline. Crystallization broadens the segmental dispersion and shifts it to lower frequencies.[9-13] Evidently the motion of amorphous chain segments near crystallites is resctricted, such that their relaxation time is longer than τ^* for the amorphous phase, although it has been established that the temperature dependence of τ^* is still largely governed by a polymer's degree of intermolecular cooperativity.[14] It is desirable to identify

another amorphous polymer with weak intermolecular coupling in order to corroborate any trends seen in the behavior of PIB. When cross-linked, PTHF has a sufficiently slow crystallization rate that it can be quenched into a completely amorphous state. The repeat unit in PTHF, consisting of four methylene groups with an ether linkage, is expected to have weak intermolecular coupling. We shall show that various viscoelastic properties of amorphous PTHF and PIB are similar but distinct from those observed for most other polymers. The latter comprise the majority class of amorphous polymers, whose segmental relaxation is strongly intermolecularly coupled.

Independent of the nature of the experiment used to measure local segmental motion in polymers, the relaxation functions are invariably nonexponential. According to the coupling model of relaxation,[3,4] the degree of nonexponentiality of the segmental relaxation of amorphous polymers reflects the extent of intermolecular coupling between the local conformational transitions. The relaxation of macroscopic variables proceeds in accord with the Kohlrausch–Williams–Watts (KWW) stretched exponential function[15,16]

$$E(t) = \exp[-(t/\tau^*)^{1-n}] \qquad (1)$$

Although the KWW form was originally derived and is still sometimes employed as an empirical fitting function, in the coupling model the degree of nonexponentiality, as captured by the parameter n, provides a measure of the degree of intermolecular coupling. According to the model, stronger cooperativity broadens the dispersion, while a narrow dispersion implies less intermolecular coupling. The segmental relaxation time, τ^*, depends on both the coupling parameter and τ° (the longer of the two relaxation times in the Hall–Helfand relaxation function describing segmental relaxation of an isolated chain)[4]

$$\tau^* = [(1 - n)\omega_c^{\,n}\, \tau^\circ]^{1/(1-n)} \qquad (2)$$

where $1/\omega_c$ defines a characteristic time for the onset of intermolecular coupling (for polymers ω_c is typically on the order of 10^{11}–10^{12} s^{-1} [3]). On rewriting eq 2 as

$$\tau^* = (1 - n)^{1/(1-n)}(\omega_c\tau^\circ)^{n/(1-n)}\tau^\circ \qquad (3)$$

and recognizing the fact that the condition $\omega_c\tau^\circ \gg 1$ holds under the usual experimental conditions, we can see that τ^* increases rapidly with increasing coupling parameter.

In this paper measurements of segmental relaxation of two amorphous polymers, polyisobutylene and poly-(tetrahydrofuran), are analyzed. In both cases, weak intermolecular coupling of the segmental motions results in segmental relaxation less constrained by other segments in the local environment. The consequences of this on the length scale of segmental relaxation are examined.

Experimental Section

Dynamic mechanical spectra in the vicinity of the glass transition were obtained in tension with an Imass Corp. Dynastat Mark II instrument. Sample dimensions were typically 5 × 14 × 1 mm. Measurements were averaged over five cycles at various frequencies ranging from 0.01 to 100 s^{-1}. Temperature control was usually better than ±0.1 °C.

The PIB was obtained from Aldrich Chemical Co. It had a broad molecular weight distribution, with an average molecular weight of about 840 000. The poly(tetrahydrofuran) elastomer was prepared and characterized by Prof. R. S. Stein and Dr. L. Jong of the University of Massachusetts. An allyl-terminated linear polymer (M_n = 2000) was cross-linked with a stoichiometric amount of pentaerythritol tetrakis(3-mercaptopropionate), yielding an end-linked PTHF network of polydispersity less than 1.3.[17] End linking gives the greatest suppression of crystallization per

cross-link[18] and so is the preferred method to minimize chemical alteration of the polymer.

In order to obtain measurements on amorphous PTHF, the environmental chamber of the Dynastat was modified so that liquid nitrogen could be introduced directly onto the surface of the test sample. Chamber cooling rates of better than 4 °C/s from room temperature to –120 °C were achieved; the sample was quenched faster. The crystallization rate of the cross-linked PTHF was determined to be sufficiently slow that the quenching resulted in a completely amorphous sample. The dynamic mechanical measurements were then made on the quenched, amorphous PTHF after warming to ca. T_g, the glass transition temperature.

Results

A. Polyisobutylene. A means to assess the strength of intermolecular coupling is from the temperature dependence of the segmental relaxation time. The latter is predicted by the coupling model to be correlated with the breadth of the segmental relaxation dispersion.[19,20] Specifically, the measured time–temperature shift factors, defined by

$$a_T = \frac{\tau^*(T)}{\tau^*(T_0)} \qquad (4)$$

where T_0 is a reference temperature, are seen from eq 2 to be related to the shift factors describing the relaxation in the absence of intermolecular coupling by

$$[a_T(\tau^*)]^{1-n} = a_T(\tau_0) \qquad (5)$$

The observed temperature dependence of τ^*, the experimental observable, is expected from eq 5 to parallel the magnitude of the coupling parameter. Since temperature dependencies are almost always non-Arrhenius, however, some normalization scheme must be employed in order to compare data from polymers having different glass transition temperatures. Angell[21–23] suggested plots of log a_T versus inverse temperature normalized by T_g. The validity of this approach has recently been demonstrated[24] by comparisons of polymers differing only in molecular weight (and hence having different T_g's but equivalent segmental dynamics).

Various experimental studies on pure polymers[14,20,25,26] as well as on blends[27–29] have confirmed the correlation between the breadth of the T_g dispersion and the change in τ^* with temperature. This connection between time and temperature dependencies enables one to use the temperature dependence of the shift factors to deduce n. Applying this method to the data in Figure 1 (obtained from creep measurements on PIB[20]), a value of n = 0.38 was deduced. This weak temperature dependence of the segmental relaxation time (indicative of weak intermolecular coupling) was also observed in solid-state ^{13}C NMR experiments on the same polymer.[30]

A well-known distinctive feature of the viscoelastic properties of PIB, which also reflects its weak intermolecular coupling, is its small (=0.65) "steepness index" (defined as d log $E(t)$ vs d log t in the middle of the glass–rubber transition region).[31,32] (This steepness index is to be distinguished from the same term sometimes used to describe the normalized temperature dependence of segmental relaxation times.[20]) A small steepness index is attributed to the prominence of the Rouse mode contribution, a consequence of the persistence of the sub-Rouse modes, which have not been subsumed by the segmental
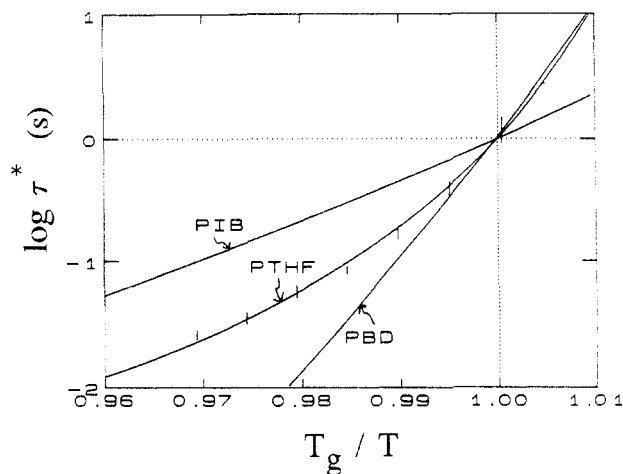
Figure 1. Temperature dependence of the segmental relaxation times expressed in the T_g-normalized Arrhenius form, where the glass transition is operationally defined to be the temperature at which $\tau^* = 1$ s. Both PIB and PTHF exhibit a weak temperature sensitivity, consistent with weak intermolecular cooperativity. The mechanical T_g dispersion of the 86% 1,2-polybutadiene can be fitted with eq 1 using a coupling parameter equal to the apparent n for PTHF (Figure 2); however, in the case of PBD the peak is not inhomogeneously broadened by the contribution of the sub-Rouse modes. The broadening in PBD denotes strong intermolecular coupling and consequently the more marked temperature dependence of the segmental relaxation time.

Figure 2. Semilogarithmic plots of the dynamic loss modulus measured for amorphous PIB at -67 °C (O) and for quenched, amorphous PTHF at -78 °C (+), along with the best fits of eqs 1 and 6.

relaxation. The decrease in the modulus over time is more gentle due to the separation in the time scales of these different viscoelastic mechanisms and, as a consequence, the more significant contribution of the Rouse modes in this region of the viscoelastic spectrum. As is well-known, the Rouse relaxation mechanism itself exhibits a small steepness index of one-half,[31,32] near to the value for PIB.

Quasi-elastic incoherent neutron scattering[33] can be used to selectively probe segmental dynamics by making measurements at scattering angles corresponding to the length scale, Q^{-1}, appropriate for local chain motions (e.g., $1 \leq Q^{-1} \leq 15$ Å). The quasi-elastic neutron scattering function has the KWW form (eq 1), with the angle dependence of the scattering providing a measure of the coupling parameter. The coupling model relates the exponent κ in the observed Q^κ dependence of τ^* to the coupling parameter, $\kappa = 2/(1 - n)$. From scattering data on PIB it was determined that $n < 0.4$,[34] a result in accord with the value ($n = 0.38$) deduced from the temperature dependence of the creep compliance. It is worth noting that most other polymers have significantly larger values of n.[14,20,25,26] Preliminary photon correlation spectroscopy results on PIB are also consistent with a small value of the coupling parameter.[35]

The mechanical loss modulus measured for PIB at -67 °C is shown in Figure 2, along with a calculated curve representing the transform of eq 1

$$E''(\omega) = \omega \int_0^\infty E(t) \cos(\omega t) \, dt \qquad (6)$$

With semilogarithmic plotting used to emphasize the contribution of segmental motion, the KWW function is seen to represent the data well. The best-fit value for n is 0.67, ostensibly indicating strong intermolecular coupling.

The fitting of the mechanical loss peak of PIB (Figure 2) thus yields a value for the coupling parameter that is larger than can be reconciled with either the neutron scattering data or the weak temperature dependence
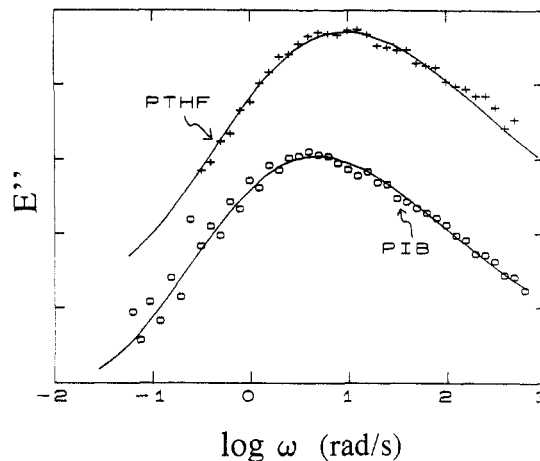
observed by creep and NMR. The latter techniques unambiguously show that PIB is associated with weak intermolecular cooperativity. We propose that the greater breadth of the mechanical dispersion is a consequence of inhomogeneous broadening; this is, the observed dispersion includes contributions from a distribution of relaxation modes, each associated with somewhat different relaxation times. The disparate contributions from the sub-Rouse modes and segmental relaxation arise as a result of the latter being relatively unconstrained by intermolecular coupling ($n < 0.4$). Hence, τ^* is not large (see discussion of dependence of τ^* on n following eq 2), allowing PIB's segmental relaxation to occur significantly faster than the transition rate of the sub-Rouse modes. The latter make their contribution to the mechanical relaxation only at longer times. The sub-Rouse relaxation is not simultaneous with nor subsumed by the segmental relaxation and thereby broadens the mechanical dispersion. The temperature dependence of the mechanical response, particularly as determined from the shift of the E'' peak, is still governed by segmental relaxation; thus, the temperature dependence extracted from the creep data is consistent with the small n obtained from neutron scattering. This is analogous to the results on semicrystalline polymers, in which crystallinity broadens the dispersion but the temperature dependence of the relaxation time or peak frequency remains essentially unchanged from that of the amorphous polymer.[14]

Since the segmental dispersion in the dynamic mechanical spectrum of PIB is broadened by the contribution from other modes, the magnitude of the best fit n in Figure 2 does not reflect intermolecular cooperativity. The fact that the peak in $E''(\omega)$ can still be described by the KWW function (Figure 2) demonstrates only that eq 1 has sufficient functionality to fit the data, at least over the limited range of frequencies displayed in this semilogarithmic plot. In Figure 3 the relaxation modulus, $E(t)$, measured for PIB in a transient experiment,[5] is plotted logarithmically versus time. The deviation of the data from the best fit of eq 1 becomes significant after $E(t)$ has decreased by only 1.3 decades. Similar fitting of transient data to other, more strongly coupled, polymers typically yields agreement over at least 2 decades of time. The point herein is that in the case of an inhomogeneously broadened dispersion conformance to the KWW function is not guaranteed, even with an exaggerated n, although as seen for PIB such agreement may occur over a limited range.
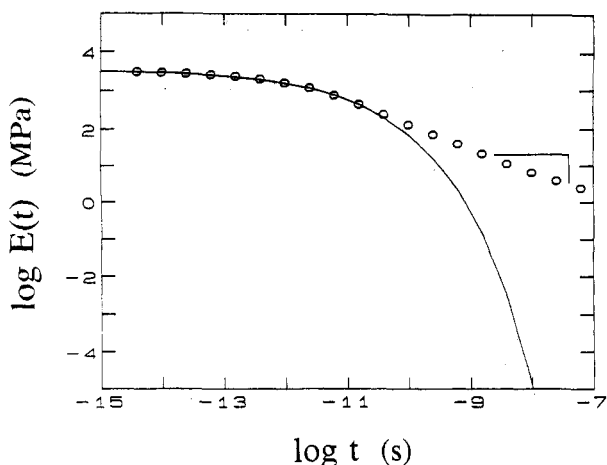
Figure 3. Relaxation modulus[5] measured in a transient experiment for PIB, along with eq 1 using the value of n determined by fitting the loss modulus (Figure 2). The steepness index denoted at longer times equals 0.65.
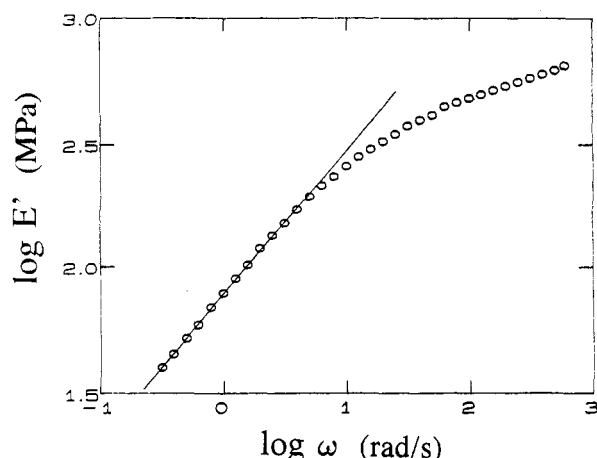

Figure 4. Storage modulus of amorphous, quenched PTHF measured at -80 °C displayed in double-logarithmic form. The fit to the low-frequency data yields a steepness index = 0.58.

B. Poly(tetrahydrofuran). Analysis of quasi-elastic neutron scattering from PTHF in a manner similar to that used above for PIB and as in ref 34 yields $n = 0.44$. This indicates weak intermolecular coupling, similar to PIB. As described above, investigation of segmental dynamics unencumbered by crystallinity required measurements on quenched PTHF networks. The dynamic mechanical spectrum was obtained at a series of temperatures in the vicinity of the glass transition temperature. The τ^* obtained from these measurements is displayed in Figure 1 (in the T_g-scaled Arrhenius form) and is congruent with the small value of the coupling parameter determined by neutron scattering. The steepness index of PTHF, obtained from the slope of the storage modulus (Figure 4), equals 0.58. Similar to PIB, this is unusually small compared to most other polymers, reflecting the greater prominence of the Rouse mode contribution for the weakly coupled polymer.

The dynamic mechanical loss modulus measured at -78 °C for the amorphous PTHF is shown in Figure 2, along with the best fit of eqs 1 and 4. The magnitude of the coupling parameter deduced from the fitting ($n = 0.67$) denotes a broad dispersion; again, however, this value is not related to the strength of the intermolecular coupling. As in the case of PIB, the dispersion is inhomogeneously broadened by virtue of the sub-Rouse modes' contribution to the relaxation. This mechanism is operative because of the weak intermolecular cooperativity associated with segmental relaxation of these two polymers.

In Figure 1, along with the data for PIB and PTHF, are results for a polybutadiene (PBD) polymer (14% 1,4-microstructure), whose n for segmental relaxation (=0.68) is equivalent to that determined by fitting the PTHF mechanical loss modulus. The relaxation time of the PBD changes more with temperature, because its segmental relaxation is strongly coupled.[24] It is this strong coupling which is the source of the breadth of the dispersion, unlike PTHF, whose dispersion is inhomogeneously broadened by the contribution of the sub-Rouse modes to the relaxation.

Discussion and Summary

The degree to which a polymer's segmental relaxation is constrained by intermolecular cooperativity must be governed to a significant extent by chemical structure. Segmental relaxation in chain backbones comprised of flexible skeletal bonds or segments which are smooth and symmetric is anticipated to be less sterically impeded by nonbonded neighboring chain units. Examples of this relationship between monomeric molecular structure and the degree of intermolecular coupling have previously been reported.[14,25,26] The weak coupling of segmental relaxation in both PIB and PTHF (ca. $n = 0.4$) can be rationalized in terms of their local structure. PIB is nonpolar and has a symmetric skeletal structure, with only hydrogen and the methyl groups on alternate carbons projecting from the backbone. Consequently, there is negligible potential for polar or strong steric interactions between chains. In PTHF, which is also nonpolar, the methylene groups are interrupted at every fourth carbon by an ether linkage. Freedom of rotation about the C–O bond increases the flexibility of the chain, thus diminishing the effectiveness of steric constraints from nonbonded neighboring segments. Although the chain dynamics in dense phase are too complex to allow a priori predictions concerning intermolecular cooperativity, we can at least say that the relatively unconstrained segmental relaxation found for these two polymers is unsurprising.

While intermolecular coupling of segmental relaxation will broaden the dispersion in the viscoelastic spectrum, in both PIB and PTHF the narrow peak expected for a weakly coupled relaxation is not observed in mechanical measurements due to inhomogeneous broadening. For most polymers, measured in the usual experimental range of frequencies or time, the consequences of segmental relaxation are manifested over a longer length scale than a few backbone bonds because segmental relaxation subsumes motion of the sub-Rouse modes. This phenomenon can be referred to as encroachment in time of segmental dynamics on the longer length scale relaxation processes. In PIB and PTHF, segmental relaxation is retarded to a lesser degree because of the weak intermolecular coupling. There is less encroachment of the different modes of motion, allowing contributions to the dispersion from more than one mechanism to be separated in time and thereby become directly apparent in the measured spectrum. The resolution in time of the segmental and sub-Rouse modes will smear out the glass transition dispersion whenever it is measured by a technique sensitive to all motions. We expect this effect to be evident in the dynamic mechanical spectrum of all small n polymers, provided they are amorphous. Unfortunately, the latter proviso restricts the amount of available data.

In closing let us summarize the various viscoelastic properties of amorphous polymers having weak intermolecular coupling, as exemplified by PIB and PTHF, and

contrast them with those of polymers that are strongly intermolecularly coupled. Some of these properties are drawn from investigations reported elsewhere. The combination of these with the data reported herein brings out clearly the difference between weakly and strongly coupled segmental relaxation.

(i) The segmental relaxation time, τ^*, of either PIB or PTHF has a much weaker dependence on normalized temperature, T/T_g, than other polymers. From the expected correlation between the normalized temperature dependence and the coupling parameter[19,20] (see eq 5 herein), this feature implies that PIB and PTHF have small segmental coupling parameters (weak intermolecular coupling).

(ii) The exponent κ of PIB and PTHF in the observed Q^κ dependence of τ^* by quasi-elastic neutron scattering has the smallest value among amorphous polymers,[33,34] indicating that the n values for PIB and PTHF are among the smallest of any polymers.

(iii) Direct measurements of the coupling parameter can be made using techniques, such as dielectric relaxation (if the material is dielectrically active) or photon correlation spectroscopy, that are sensitive to only the local segmental motion. When fitted to the stretched exponential function, the dispersion gives n directly. For weakly coupled polymers such as PIB and amorphous PTHF, a narrow dispersion will be observed. The value of n so determined is small, in agreement with deductions from i and ii. On the other hand, mechanical relaxation measurements are sensitive to local segmental motion, the sub-Rouse modes, and the Rouse modes. The resolved contribution of the longer length scale modes inhomogeneously broadens the mechanical dispersion; the breadth is greater than that observed by other (local segmental motion specific) spectroscopies. In spite of the difference in the measured dispersion, the normalized temperature dependence of τ^* remains weak and essentially the same for different experimental techniques.

By contrast, in strongly coupled polymers in which, for example, the dielectric activity (i.e., dipole moment) is associated with the main chain, both the breadth of the dispersion and the normalized temperature dependence of τ^* are the same for the two types of spectroscopies.[36] This provides evidence that the local segmental relaxation and the sub-Rouse modes are contributing together, collectively, in these strongly coupled polymers.

(iv) If we broaden our focus to include the Rouse modes (if the polymer is unentangled) and the terminal relaxation (for entangled polymers), then another difference exists between a weakly coupled polymer like PIB and strongly coupled polymers such as polystyrene (PS) and poly(vinyl acetate) (PVAc). It has long been established that the latter class of polymers exhibit a temperature dependence of their segmental relaxation that is much stronger than the Rouse or terminal modes. As temperature is lowered toward T_g, this breakdown of thermorheological simplicity[37-39] means that the separation in time scale between τ^* and the Rouse modes is shrunk. A consequence of this is that the local segmental motion encroaches into the time scale of the sub-Rouse modes. Naturally this provides the mechanism for the merging and simultaneous relaxation of the segmental and sub-Rouse motions in strongly coupled polymers. On the other hand, in a weakly coupled polymer, the temperature dependence of τ^* is more like that of the terminal relaxation and the Rouse modes. Thus, the local segmental mode is separated in time and at all temperatures remains distinct from the sub-Rouse modes. It is worthwhile to point out here that the coupling model

has explained encroachment and its manifestations in strongly coupled polymers by their large coupling parameters[40,41] and the absence of encroachment in weakly coupled polymers by their small n.[42,43]

(v) PIB and PTHF both have small steepness indices. A small steepness index (close to $1/2$) is attributed to the Rouse mode contribution, transpiring in PIB and PTHF because of the persistence (resolution in time) of the sub-Rouse modes. This guarantees the integrity of the Rouse modes; that is, their contribution is well resolved. Much of the relaxation strength can also be accounted for by the sub-Rouse and Rouse modes. The relaxation strength of the segmental motion, when it can be separated out in weakly coupled polymers like PIB and PTHF, is reduced, reflecting the short length scale of their segmental relaxation. Contrarily, the sub-Rouse modes of strongly coupled polymers have been subsumed into the segmental motion and in the process make the steepness index much larger, as well as increasing the relaxation strength. These trends are consistent with the longer length scales for segmental relaxation in strongly coupled polymers.

The segmental relaxation properties of PIB and PTHF are decidedly different from those of other amorphous polymers. This summary relates the new data presented in this paper to previously known facts. The various viscoelastic properties of PIB and PTHF are ultimately a reflection of the monomeric structure of these polymers. Their different manifestations of segmental motion can be ascribed to the weak intermolecular coupling therein, resulting from the rather compact, smooth, and symmetric repeat unit structures of PIB and PTHF.

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(36) Depending, for example, on the location of the dipole moment governing the dielectric response, it is possible that in some strongly coupled polymers both n and the normalized temperature dependence may vary as measured dielectrically versus by some other type of spectroscopy. However, in such a circumstance the variations will be correlated. A larger observed n is associated with a corresponding increase in the normalized temperature dependence. This correlation is to be contrasted with the lack of it in weakly coupled polymers such as PIB and PTHF, in which divergence of the apparent n deduced from the mechanical spectrum with the n otherwise obtained is not simply a manifestation of the probe dependence of segmental dynamics.

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