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Temperature Dependence of Segmental Motion in Polyisobutylene and Poly(vinylethylene)

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ABSTRACT: Solid-state ^{13}C NMR measurements carried out on poly(vinylethylene) (PVE) and polyisobutylene (PIB) demonstrate that the molecular motions underlying their respective segmental relaxations have vastly different temperature dependencies. These differences parallel the contrasting mechanical behavior exhibited by the two polymers in the vicinity of their glass transition temperature. It is suggested that greater temperature sensitivity reflects a more intermolecularly cooperative relaxation.

Introduction

During segmental relaxation, polymer chains in dense phase undergo correlated conformational transitions, with the correlations arising from both intramolecular (due to connectivity of the monomer units)[1,2] and intermolecular (due to the dense packing) cooperativity.[3,4] Nuclear magnetic resonance (NMR) provides a direct probe of molecular motions and hence can be employed to study the dynamics of the glass transition in polymers. The solid-state ^{13}C NMR technique used herein has previously been applied to measurements of local chain dynamics in pure polymers[5,8] and blends.[9,10]

This study focuses on the segmental dynamics of neat polyisobutylene and neat poly(vinylethylene), which represent extremes in segmental relaxation behavior. The mechanical spectrum of PVE has the broadest glass transition dispersion of any neat amorphous polymer (possibly excepting poly(vinyl chloride)[11]), and the measured relaxation time has a strong temperature dependence.[12] Contrarily, segmental relaxation of PIB is associated with a very narrow spectral dispersion[13] and relative insensitivity to temperature.[14] The consequences of these distinct behaviors on the solid-state ^{13}C NMR spectra obtained near the polymers' glass transition temperatures are described.

Experimental Section

The PVE was 97% 1,2-polybutadiene obtained from Firestone Tire and Rubber Co. It had a number-average molecular weight of 344 000 with a polydispersity equal to 1.2. The PIB was obtained from Aldrich Chemical Co. It had a broad molecular weight distribution, with an average molecular weight of about 840 000.

All NMR spectra were obtained on a Bruker MSL 300 spectrometer with a static magnetic field of 7.04 T (300.1-MHz ^{1}H and 75.5-MHz ^{13}C Larmor frequencies). A double-tuned multinuclear magic angle spinning (MAS) probe equipped for 7-mm-o.d. sample rotors was used to acquire all spectra. Probehead input impedance was readjusted after each temperature change prior to data acquisition. The Hartmann–Hahn cross polarization (CP) technique[15] was employed at temperatures where a sufficient static heteronuclear dipolar interaction was available for efficient cross polarization. At higher temperatures, a single carbon-13 $\pi/2$ pulse (5 μs) was used with high-power proton decoupling[16] during acquistion of the free induction decay. All spectra were obtained using magic angle spinning[17,18] maintained at 3.0 kHz ± 5 Hz. Observe (^{13}C) and decoupling (^{1}H) radio-frequency (rf) fields for cross polarization and one-pulse experiments were maintained at 50 kHz, a cross polarization contact time of 1 ms was used in all CP experiments, and a relaxation delay of 2 s was used for all spectra. No apodization of the free induction decay was employed in any of the experiments. The spin–spin relaxation time constant (T_2) of the methylene carbon of PIB was measured using the same rf field conditions and acquisition parameters as above; a standard Carr–Purcell spin–echo train[19] with proton decoupling was used (following cross polarization) with the refocusing pulses synchronized with the MAS rotor period (333 μs).

Results

Displayed in Figure 1 are the ^{13}C NMR spectra of PVE obtained at a series of temperatures encompassing the glass transition zone of the viscoelastic spectrum. Narrow resonant line widths can be obtained in the solid state because magic angle spinning (MAS) of the sample averages the chemical shift to its isotropic value and radiofrequency irradiation modulates the heteronuclear dipolar interaction of the protons with the ^{13}C nuclei. However, when molecular motion produces magnetic fields fluctuating at frequencies close to the MAS rate (3 kHz) or the frequency of the rf decoupling field (50 kHz), the modulation of chemical shift anisotropy and dipolar interactions is diminished.[20-22] This interference by the molecular motions with the line-narrowing methods broadens the NMR resonances. At higher (lower) temperatures the molecular motions are too fast (slow) to interfere with MAS or rf decoupling, and narrower lines are observed in the spectrum. The temperature dependence of the NMR line widths thus yields a "transition" corresponding to the temperature range over which molecular motion produces fluctuations in local magnetic fields at a particular range of frequencies (i.e., 3–50 kHz). In principle, molecular motions in the frequency range of the proton decoupling field (50 kHz) could also be probed by characterizing the rotating frame spin–lattice relaxation time constant, $T_{1\rho}$, of the carbons. A minimum in the proton $T_{1\rho}$ is expected when the molecular correlation times are on the order of the inverse spin lock field. The technique of observing variations in line width used in this investigation offers the advantage of probing motions over a wide frequency range (several to tens of kilohertz) in a single experiment.

In PVE, the resonances are broad over a temperature range of about 20 K, although the maximum broadening is seen in Figure 1 to occur at slightly different temperatures for the vinyl (downfield) as opposed to the aliphatic (upfield) carbons. This is unsurprising given the different positions of the nuclei relative to the chain axis and consequent differences in their local dynamics. In Table I the temperature of maximum peak breadth is compared to the glass transition temperature determined from volumetric measurements on PVE. The latter, sensitive to slower motions than the NMR experiment (i.e., ca. 10^{-4}–10^{-6} kHz[12,23] versus 3–50 kHz for NMR), yield a lower glass transition temperature.

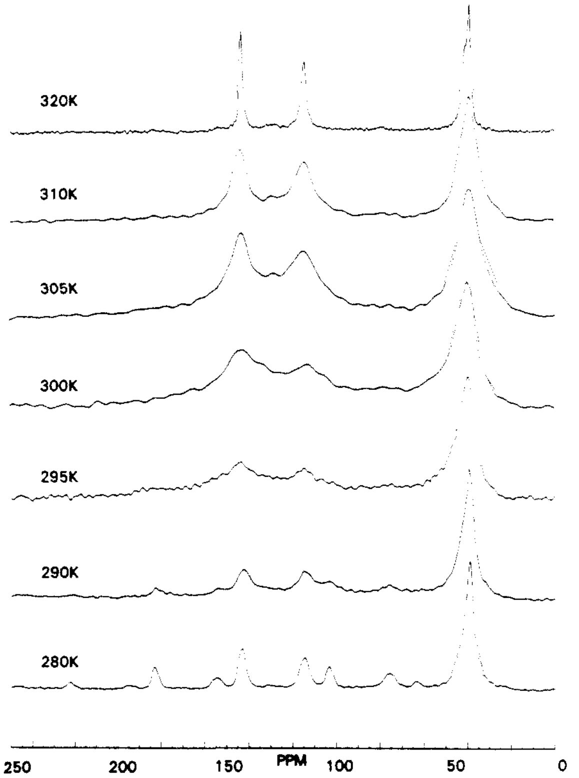

Figure 1. Carbon-13 NMR spectra of neat PVE obtained with magic angle spinning (3 kHz) and high-power proton decoupling (50-kHz field). The peak at $\delta = 39$ corresponds to the two backbone carbons, while the peaks at $\delta = 115$ and 143 correspond to the pendant vinyl carbons. The spectra from 280 to 300 K were acquired using cross polarization, while spectra from 305 to 320 K were obtained using a single $\pi/2$ carbon pulse. At low temperatures (<295 K) spinning sidebands displaced 3 kHz downfield from the vinyl resonances appear, as a result of incomplete averaging of the chemical shift anisotropy due to anisotropic motion of the polymers. Note that the vinyl resonances exhibit extreme broadening in the temperature range 290–310 K.

Table I
Glass Transition Temperatures

	$T_g{}^a$ (K)	$T_g{}^b$ (K)	NMR transition temp^c (K)
PVE	261	272	300
PIB	205	201	~220

[a] From volumetric measurements.[30] [b] Temperature at which $\tau^* = 100$ s. [c] Midpoint of temperature range over which ^{13}C NMR resonance is broad (see Figure 1).

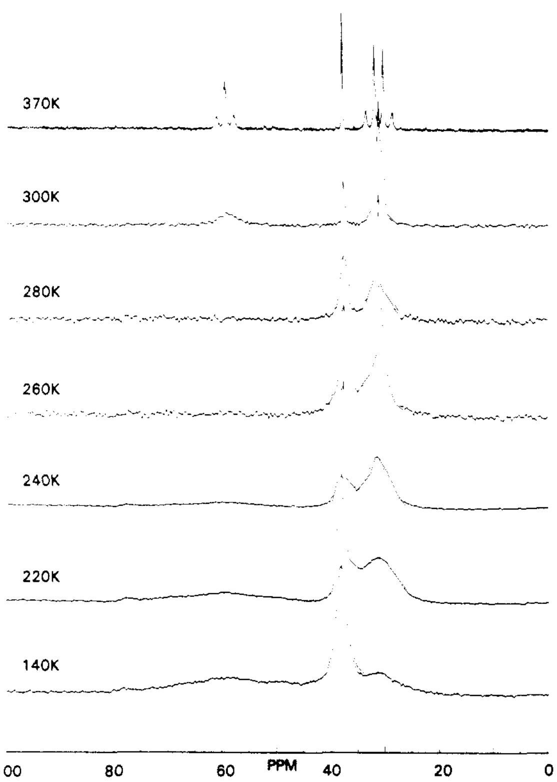

Figure 2. Carbon-13 NMR spectra of PIB obtained over the temperature range 140–370 K ($\delta = 31$, 40, and 60 ppm for the methyl, quaternary, and methylene carbons, respectively). All spectra were obtained using cross polarization, magic angle spinning (3 kHz), and high-power proton decoupling (50-kHz field), except the spectrum at 370 K. This spectrum, which enables identification of the resonances, was obtained using a single $\pi/2$ carbon pulse with no proton decoupling. Note that the methylene resonance remains extremely broad over the entire temperature range of the cross polarization experiments (>140 K).

The NMR results obtained for PIB (Figure 2) are quite different from the data in Figure 1. Although the temperature dependence of the line widths is not exactly equivalent for the various resonances in PVE, it is very similar, and in particular the spectral broadening persists over ca. a 20 K range for each resonance. In PIB, however, each of the three carbons exhibits a qualitatively distinct response to temperature changes.

The resonance at $\delta = 40$ (Figure 2) arising from PIB's quaternary carbon broadens around 260 K, a temperature equal to the bulk T_g plus roughly 50 K (Table I). This correspondence between these two "transitions" is in accord with the results for PVE. Actually, close inspection of Figure 2 revels that, within the temperature range for which the quaternary carbon resonance exhibits this broadening, there is a temperature (ca. 240 K) at which the peak narrows slightly relative to the breadth at lower and higher temperatures. We speculate that this transient decrease in relative line width is due to a somewhat reduced spectral density at 3 kHz and at 50 kHz when the temperature is 240 K. Above (below) this temperature molecular motions at 50 kHz (3 kHz) intensify and hence interfere with the rf decoupling (MAS spinning). In any case the magnitude of the peak broadening is never very large for the PIB quaternary carbon. Lacking directly bonded protons, it has on average fewer protons in spatial proximity; its consequently weaker heteronuclear dipolar coupling is in part responsible for the modest extent of the observed line broadening. Quaternary carbons in general exhibit longer cross relaxation time constants due to the latter's dependence on the inverse sixth power of the distance separating the ^{1}H and ^{13}C spins.[24] In addition, quaternary carbons are associated with smaller chemical shift anisotropies than seen, for example, for unsaturated carbons. This will minimize any broadening due to interference with MAS.

The PIB resonance furthest upfield in Figure 2 corresponds to the methyl carbon nucleus ($\delta = 31$). It is well-known that this moiety continues to undergo rotation about its C3 symmetry axis at temperatures well below the bulk glass transition.[8,25] The spinning motion of the methyl group sweeps out a negligible volume and therefore persists at temperatures for which main-chain segmental motions are "frozen out" by steric constraints. This spinning motion underlies the very gradual onset of broadening of the methyl's NMR resonance as the temperature is lowered to 140 K (Figure 2).

The peak furthest downfield ($\delta = 60$) in the PIB spectra corresponds to the backbone methylene carbon. It might be expected that the motional behavior of this nucleus would be comparable to that of the PVE main-chain carbon resonances. However, unlike the range of the spectral

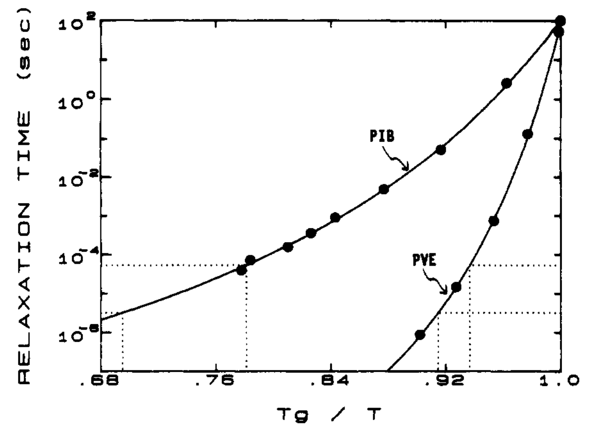

Figure 3. Arrhenius plots of the relaxation time determined mechanically for PVE[12] and PIB.[13,14] The temperature has been normalized by the respective glass transition temperature of the polymer, determined as the temperature at which $\tau^* = 100$ s. The solid curves represent the results of fitting the Vogel equation[30] to the data. The characteristic time scales associated with the MAS frequency (3 kHz) and the rf decoupling field (50 kHz) are indicated by the dotted lines, whose intersection with the Vogel curves provides a rough measure of the temperature range over which molecular motions will interfere with the MAS and rf irradiation.

broadening seen for PVE (Figure 1), which is limited to roughly 20 K, the PIB methylene carbon exhibits a very broad resonance, extending beyond the range of the experimental measurements (a 140 K span).

This insensitivity of the spectrum to temperature could result from a broad distribution of isotropic chemical shifts. If the methylene carbons were associated with a distribution of chemical environments giving rise to a distribution in isotropic chemical shifts, inhomogeneous broadening of the methylene line would result. It is expected that such broadening would be relatively independent of temperature. To examine this possibility, the spin-spin relaxation time, T_2, of the methylene resonance was measured at 173 K. At this temperature, the intensity of the methylene peak is sufficiently strong to allow accurate T_2 measurements. Its contribution to the spectral breadth is estimated as

$$\Delta\nu_{1/2} = (\pi T_2)^{-1} \tag{1}$$

The result, $T_2 = 0.86$ ms, yielding $\Delta\nu_{1/2} = 368$ Hz, is not inconsistent with the experimentally observed line width of 536 Hz. Clearly, a broad distribution of isotropic chemical shifts having this T_2 value would yield a much broader line width than is observed in FIgure 2. This indicates that the breadth cannot be attributed to a distribution of isotropic chemical shifts. The T_2 result suggests that the PIB backbone motions per se are unusually insensitive to temperature; that is, significant motion transpires in the critical 3–50-kHz frequency range over a very broad range of temperatures (>100 K).

Discussion

In Figure 3 the temperature dependence of the segmental relaxation time, τ^*, determined for PIB by creep experiments[26] and for PVE from dynamic mechanical measurements[12] is displayed in the form of fragility plots,[27,28] that is, Arrhenius plots with the temperature normalized by the respective T_g of each polymer. The validity of this approach to comparing temperature dependencies of different polymers has recently been demonstrated.[29] From the fragility plot for PVE it is seen that its segmental relaxation time is much more sensitive to temperature than that of PIB. In the parlance of small-molecule liquids,[27,28] PVE is "fragile" in that a temperature increase through T_g markedly decreases the relaxation time. Since polymers experience no actual structural change as their glass transition temperature is traversed, the term "fragility" may be inaccurate in this context. "Cooperativity plot" has been suggested as more appropriate terminology for polymers.[12] In comparison to PVE, the relaxation time of PIB is much less affected by temperature changes (Figure 3); hence, it is a "strong" (less cooperative) liquid.

In the NMR experiment the observation of a broad resonance for the methylene carbon of PIB over a wider range of temperatures than for the PVE carbons can be ascribed at least in part to the weaker dependence on temperature of the segmental relaxation time of PIB than PVE. A crude of estimate of the predicted temperature range over which the NMR resonance will be broadened can be gleaned from the mechanical data in Figure 3. It is estimated that the relaxation time of PVE will lie within the characteristic time scale defined by the MAS and rf field frequencies (3 and 50 kHz, respectively) over a 7 K range of temperatures. For PIP, however, this temperature range is determined to be about 32 K. Although these numbers cannot be expected to correspond exactly to the range of temperatures over which the NMR resonances are broadened, it is seen that the temperature dependencies of the mechanical relaxation times for these polymers are consistent with the NMR results.

A possible origin of their different temperature dependencies can be found from consideration of the polymers' segmental relaxation dynamics. The latter reflect the intermolecularly coupled and intramolecular correlated conformational transitions associated with the glass transition relaxation. In dense phase the breadth of the segmental relaxation dispersion reflects the strength of the intermolecular couplings.[3,4] Moreover, the temperature dependence of the relaxation time is governed by the temperature dependence of this intermolecular cooperativity.[14] Specifically, broad dispersions (corresponding to strong intermolecular cooperativity) exhibit relaxation times which are more sensitive to temperature.

The breadth of the glass transition dispersion measured mechanically for PVE is greater than that of almost any amorphous polymer.[12] This breadth reflects enhanced intermolecular cooperativity arising from steric interferences among the vinyl groups pendant to the main chain. Contrarily, segmental relaxation in PIB is associated with an unusually narrow dispersion.[13] In comparison to vinyl moieties, a methyl group is evidently less effective in promoting intersegment coupling, in addition to which their presence at every other backbone carbon in PIB may exclude significant penetration by neighboring chains. The result is weaker intermolecular cooperativity and a narrow dispersion. The behavior seen in Figure 3 is a consequence of the different degree of intermolecular cooperativity for segmental relaxation in PIB versus PVE. The weaker intermolecular coupling of PIB implies a consequently smaller dependence of the measured relaxation time on temperature. This means that for the same change in temperature the time scale or the frequency of segmental relaxation will not change as much for PIB in comparison to PVE.

This analysis suggests an origin of the NMR results in Figures 1 and 2. As the glass transition temperature is traversed in PVE, segmental motion commences and the corresponding motions of the nuclei are reflected in the NMR line broadening. As the temperature is further changed, substantial molecular motions no longer occur within the characteristic frequency range between 3 (MAS) and 50 kHz (rf irradiation), whereby narrow spectral lines are measured. In PIB, however, motion at these frequencies persists over a much broader range of temperatures, extending the range over which the methylene carbon exhibits substantial breadth. The difference in the NMR results for the two polymers is attributed primarily to differences in the temperature dependencies of their segmental relaxation.

In addition to segmental relaxation, there can be motions occurring at different times and/or over different length scales which also modulate the local magnetic interactions and thus influence the measured NMR spectrum. In the vicinity of T_g, contributions to the relaxation spectrum may arise from these other motions. As the temperature is altered from T_g, a broader relaxation spectrum per se could cause spectral density to continue to exist within the critical frequency range over which the present NMR experiment senses motion. From a comparison of their glass transition dispersions, a broader relaxation spectrum is expected for PVE (broad dispersion) than for PIB (narrow dispersion); however, consideration of only the breadth of the relaxation spectrum would lead to an argument contradicting the results in Figures 1 and 2.

The main conclusion of the present investigation is that the temperature dependence of the NMR line broadening reflects the degree of intermolecular cooperativity of the segmental relaxation. Currently, the NMR study is being extended to other amorphous polymers to assess the correlation of temperature dependencies with the relaxation dynamics and molecular structure.

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References and Notes

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Registry No. PIB (homopolymer), 9003-27-4; polybutadiene (homopolymer), 9003-17-2.