Determination of the Coupling Parameter of Local Segmental Motion in Poly(isobutylene) by Photon Correlation Spectroscopy

A. K. Rizos*

Department of Chemistry, University of Crete, Heraklion 71409, Crete, Greece, and Research Center of Crete, Heraklion 71110, Crete, Greece

T. Jian

Research Center of Crete, P.O. Box 1527, Heraklion 71110, Crete, Greece

K. L. Ngai

Naval Research Laboratory, Washington, D.C. 20375-5320

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ABSTRACT: Many workers in the past have found that poly(isobutylene) (PIB) exhibits viscoelastic properties distinct from other commonly known amorphous polymers. PIB has perhaps the most compact and symmetric monomer chemical structure among amorphous polymers, which leads to the expectation that it has a smaller capacity for intermolecular coupling and a lower degree of cooperativity of the local segmental motion. In the framework of the coupling model this expectation for PIB implies that it has a smaller coupling parameter which is sufficient to explain its various distinct viscoelastic properties as demonstrated in previous works. Up to now there is no direct determination of the coupling parameter for local segmental motion of PIB to confirm that it is indeed smaller compared with other amorphous polymers. Dielectric spectroscopy is inapplicable to PIB because the monomer has a negligible dipole moment. Mechanical spectroscopic measurements performed on PIB have not yielded unambiguous results because of the difficulty of isolating the contribution of the local segmental motion from the experimental data. In this work we have resorted to photon correlation spectroscopy and successfully obtained the correlation function of the local segmental motion of PIB which can be well fit by a Kohlrausch stretched exponential function. The stretch exponent, β, has the value of 0.56. The coupling parameter, given by $1 - \beta$, has the value of 0.44 for PIB which is indeed significantly smaller compared with other amorphous polymers and consistent with the value we deduced indirectly from other experiments.

Introduction

Throughout the history of the study of viscoelastic properties of polymers poly(isobutylene) (PIB) has continued to show distinct and sometimes even unique behaviors not found in other polymers. As early as 1953 Fitzgerald, Grandine, and Ferry[1,2] found from their complex shear compliance, $J^* = J' - iJ''$, measurement of PIB that it has a much broader dispersion in the glass–rubber transition region and a variation of compliance with frequency more gradual than has been found for other polymers. The distribution function of relaxation times of PIB conforms closely to the $\tau^{-1/2}$ predicted by the Rouse theory[3] which incidentally was proposed at approximately the same time, while in many other polymers, including polystyrene, the distribution function departs from the Rouse prediction. The frequency dependence of the loss tangent, J''/J', indicates the presence of a second, smaller maximum which did not appear in other polymers.[1,2] Tobolsky and co-workers[4,5] studied extensively the viscoelastic property of a high molecular weight PIB (National Bureau of Standards sample distributed by Marvin) and found that it corresponds very well to that predicted by his wedge-box distribution model which in the glass–rubber transition zone has characteristics very similar to that predicted by the Rouse model. The fact that PIB adheres to the Rouse model prediction while many other polymers do not has led Tobolsky[6] to generalize the Rouse model by his construction of two- and three-dimensional damped Debye oscillator models for other polymers. Aklonis and co-workers[7,8] used the index of steepness, defined as the absolute value of the maximum slope of a logarithmic plot of the stress relaxation function of time, to distinguish PIB which has the minimum value of 0.5 from other polymers.

More recently we have found[9,10] that among amorphous polymers PIB has the weakest temperature dependence of the local segmental relaxation time, τ^*, in a "cooperativity plot" which is a logarithmic plot of τ^* against T_g/T. Here T_g is the operationally defined glass temperature at which $\tau^*(T_g)$ reaches an arbitrarily chosen long time, say 100 s, which is then fixed for all polymers in making the comparison.[9,10] A recent creep and recoverable creep compliance measurement made on a high molecular weight entangled PIB[11] have found that the terminal and the local segmental relaxations of PIB have nearly the same temperature dependence, while in other high molecular weight polymers such as polystyrene the segmental relaxation time has a stronger temperature dependence than that of the terminal relaxation.[2,11–14] The same measurements performed on a lower molecular weight, unentangled PIB sample[15] show that the anomalous decrease of the steady-state recoverable compliance, J_e, with decreasing temperature which had been observed previously in other polymers[15–17] is drastically reduced in PIB.

The distinctive viscoelastic properties of PIB listed above has been rationalized or explained in the framework of the coupling model.[18] These explanations[9,10,18,19] are based on the premise that, among the better known amorphous polymers, PIB has the most symmetric and compact monomer structure which minimizes the intermolecular interactions or the degree of cooperativity between the monomers. In the coupling model the degree of intermolecular cooperativity of the local

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segmental (α) relaxation is specified by the coupling parameter, n_α, which determines the dispersion of the relaxation through its correlation function being given by the Kohlrausch stretched exponential,

$$C_\alpha(t) = \exp[-(t/\tau^*)^{1-n_\alpha}] \tag{1}$$

The temperature dependence of τ^* is also determined and is given by the relation

$$\tau^* \propto [\zeta_0(T)]^{1/(1-n_\alpha)} \tag{2}$$

where $\zeta_0(T)$ is the friction factor before the effect of intermolecular coupling on the relaxation process is considered.

As have been shown in previous works,[9,10,11,15] the manifestly distinct viscoelastic properties of PIB can be explained quantitatively, provided that indeed PIB among amorphous polymers has a smaller value of n_α as expected also by the coupling model based on a comparison of the chemical structure of PIB with those of other amorphous polymers. Thus a burning question is the exact value of n_α or interchangeably the stretch exponent, $\beta \equiv 1 - n_\alpha$, in eq 1, of PIB. Normally for many amorphous polymers the coupling parameter can be obtained directly from the stretched exponential form of the correlation function which can be deduced from dielectric[19-22] and mechanical[23] measurements. First, PIB is not dielectrically active which rules out dielectric measurements. Of course deliberate contamination of PIB will introduce electric dipoles into the polymer chain which can be used to monitor the segmental motion.[24] The dielectric spectrum will necessarily be further broadened by inhomogeneities and randomness introduced in the contamination process, rendering it useless to deduce the exact value of n_α for PIB. Second, the distinct character of the viscoelastic spectrum of PIB having a much broader dispersion in the glass–rubber transition region made it difficult if not impossible to isolate the local segmental relaxation contribution from mechanical relaxation or compliance measurements. ^{13}C nuclear magnetic resonance (NMR) measurement is sensitive only to the local segmental motion. Application of such a NMR technique to PIB[25] has enabled its segmental dynamics to be monitored and the weak temperature dependence of its τ^* to be verified. Unfortunately this NMR technique cannot provide a quantitative estimate of n_α.

In spite of the fact that PIB plays an important and unique role in the study of viscoelasticity of polymers, direct experimental data that give information of the stretch exponent, $\beta \equiv 1 - n_\alpha$, for the local segmental motion in PIB have so far been nonexistent. Photon correlation spectroscopy (PCS) has proven to be useful to characterize the local segmental dynamics of amorphous polymers near and above T_g.[17,21,26-30] The technique requires a sample of good optical quality, and thus it is not immediately applicable to any amorphous polymer. Fortunately this is not the case for PIB. Patterson[26,31,32] has demonstrated that one can obtain Brillouin scattering data at high frequency on PIB. However, as far as we know, PCS has remained unexplored as an option to determine the correlation function of segmental motion in PIB. This state of affair is probably due to the fact that it is relatively difficult to obtain dynamic light scattering data of PIB near and above T_g and the concern of possible complications caused by the slight tendency of PIB to crystallize. In this paper we report PCS measurements performed on a sample of PIB. The experimental results and the coupling parameter n_α deduced from the data will be discussed in connection with the distinct viscoelastic properties of PIB.

Experimental Section

A. Samples. The poly(isobutylene) (PIB) samples studied in this work were purchased from Polysciences. The glass transition temperature (T_g) was measured by differential scanning calorimetry with a DSC Mettler instrument at a scan rate of 10 °C/min. Gel permeation chromatographic results in THF at 30 °C on the low molecular weight sample show that it is quite polydisperse with $M_n = 2530$ and $M_w = 9800$. The higher molecular weight sample has $M_w = 160\ 000$ and is quite monodisperse with $M_w/M_n = 1.05$.

B. Photon Correlation Spectroscopy (PCS). The autocorrelation function $G_{vv}(q,t)$ of the polarized light scattering intensity was measured at a scattering angle of 90° at different temperatures, where $q = (4\pi n/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector at scattering angle θ, λ is the wavelength, and n is the refractive index. The light source was an Ar$^+$ laser (Spectra-Physics 2020) operating at $\lambda = 488$ nm with a power of 100 mW. The incident beam was polarized vertically (V) with respect to the scattering plane using a Glan polarizer. The vertical (V) polarized scattered light was measured using a Glan–Thomson polarizer (Halle-Berlin). The function $G_{vv}(t)$ was measured with an ALV-5000 digital correlator that covered a broad dynamic range of about 10 decades. The desired correlation function $g(q,t)$ is given by $g(q,t) = [(G_{vv}(q,t) - 1)/f]^{1/2}$ where f is the instrument factor that can be calculated by means of a standard.

Results

The measured intensity autocorrelation functions of the PIB sample with $M_w = 9800$ are clearly bimodal and, in this respect, very similar to what has been seen before in plasticized polydisperse poly(cyclohexyl methacrylate) (PCHMA)[29] and PMMA.[30] In all these cases the polarized correlation functions reveal clearly two steps or two processes. The fast process is due to density fluctuations (which will later be identified with the local segmental or α relaxation), and the slow process is due to concentration fluctuations. Density and concentration fluctuations were observed together by PCS for the first time in polydisperse low molecular weight poly(methylphenylsiloxane) (PMPS).[28] The similarity of the PIB data to these previously published results suggests a similar interpretation of the measured photon correlation function. It has been repeatedly found in many amorphous polymers that the correlation function of the fast process caused by local segmental motion is well represented by the Kohlrausch stretched exponential function.[21,26-30] Also theoretically the coupling model has suggested the correlation function of local segmental motion should have the stretched exponential form. We follow this empirically established fact and theoretical suggestion in using the stretched exponential function to represent the correlation function of the fast process. There is no theoretical guidance to what the correlation of the slow process should be. Experimentally the correlation function of the slow process has been observed to be slightly broader than an exponential function and can be fit by a stretched exponential, with the stretch exponent having a value close to 1.[17,28-30] Thus we represent the measured correlation function of the two well-separated processes at temperatures above T_g by the sum of two

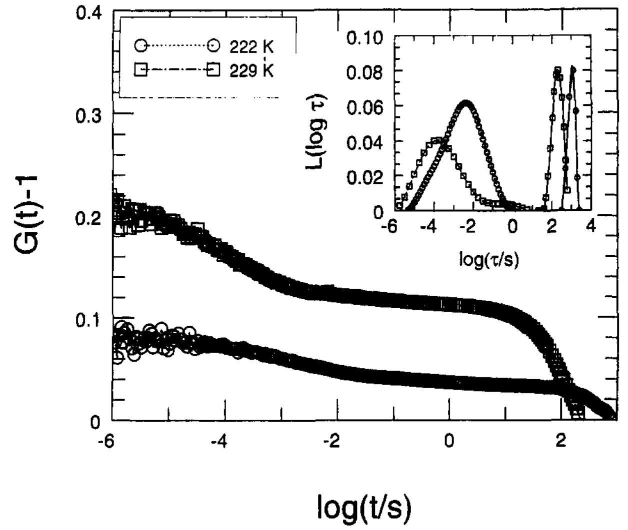

Figure 1. Measured correlation function for the 9800 molecular weight PIB at 222 and 229 K. The corresponding retardation time spectra, $L(\log\tau)$, obtained by inverse Laplace transform are also shown as a function of log τ in the inset.

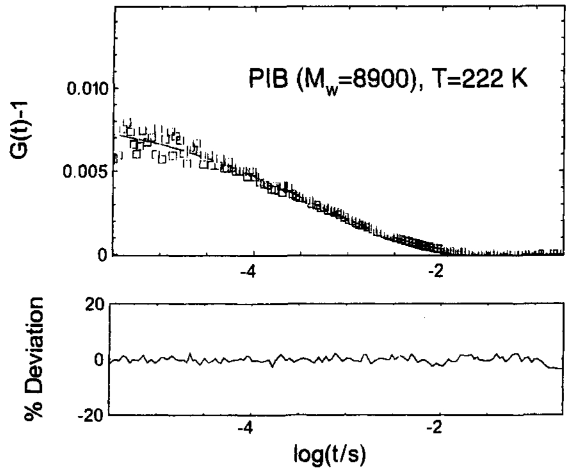

Figure 2. Correlation function of the local segmental motion obtained by subtracting the slow process from the experimental data. Shown also is the Kohlrausch stretched exponential fit to the data with $\beta_f = 0.56$. The quality of the fit is indicated by the percentage of deviation (lower part).

KWW functions:

$$g(t) = \alpha_f \exp[-(t/\tau_f^*)^{\beta_f}] + \alpha_s \exp[-(t/\tau_s^*)^{\beta_s}] \quad (3)$$

where α_f, α_s, τ_f, and τ_s and the β's are treated as adjustable parameters. Figure 1 shows the correlation function for the lower molecular weight PIB at 222 and 229 K. The KWW fit to the experimental spectra gave $\beta_f = 0.59 \pm 0.05$. The fast-decaying portion of the bimodal correlation function, identified with density fluctuation, was obtained by subtraction of the slow component. This was accomplished by first making an inverse Laplace transform (ILT) analysis[33] and subsequently deleting the contributions from the slow process in the data file. The residual correlation function was then analyzed using a single KWW fit to obtain the relaxation time and the stretch exponent of the fast process. The inset of Figure 1 shows the retardation spectrum, $L(\ln\tau)$, has two peaks corresponding to the two processes at two temperatures. The temperature shift factors of the most probable retardation times of the two processes as defined by the positions of the peaks of the L's are not the same. The fast process (which we shall identify with the local segmental motion below) has a slightly larger shift factor. This moderate breakdown of thermorheological simplicity is consistent with what has been seen before by creep compliance measurements in another sample of PIB with M_w = 10 700.[15] The degree of thermorheological complexity found in PIB is considerably less than that exhibited by PMPS,[28] PCHMA,[29] and PMMA[30] in similar experiments and by polystyrene in a different experiment.[15,16,34]

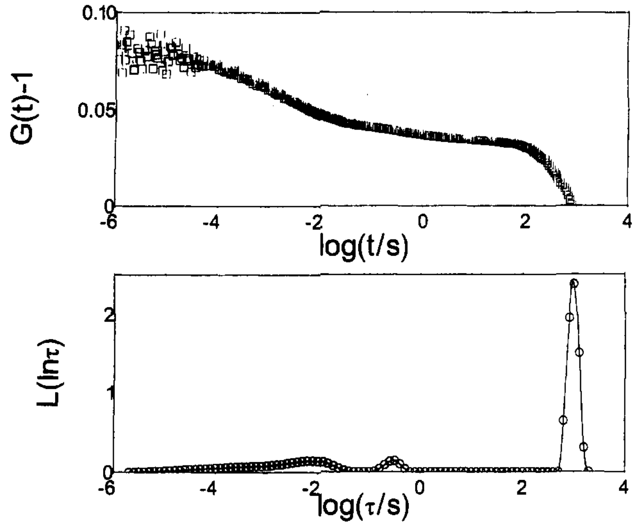

Figure 3. Result of the inverse Laplace transform (lower part) of the measured correlation function (upper part) of the 9800 molecular weight PIB at 222 K.

In order to present that part of the correlation function due to the segmental relaxation in a clear manner, we show in Figure 2 the residual correlation function obtained after subtraction of the slow process. The full line is the single KWW fit with $\beta_f = 0.56 \pm 0.08$. The shape parameter or the stretch exponent, β_s, for the slow process is close to 1. The separation in time scales of the fast and slow processes measured by the difference between $\log(\tau_f^*)$ and $\log(\tau_s^*)$ is about 5–6 decades (see also the separation of the peaks of the retardation spectrum in Figure 3, upper part). This separation is almost the same as the width of the glass–rubber transition zone of a nearly monodisperse PIB sample I-7 which has molecular weight M_w = 10 700[15] comparable to that of our present low molecular weight sample. The width of the glass–rubber transition zone can be readily obtained from the plot of $\log(J_r(t))$ against log t, where $J_r(t)$ is the recoverable creep compliance (see Figure 2 of 15). Such a good correspondence between the difference, $\log(\tau_s^*) - \log(\tau_f^*)$, from our PCS measurement and the width of the glass–rubber transition zone from creep compliance measurement supports the identification of the fast process as density fluctuation caused by the local segmental motion and the slow process as concentration fluctuation caused by the Rouse diffusional mode in our low molecular weight PIB sample. Moreover, the recoverable compliance data of PIB I-7 published in ref 15 have enabled us to determine approximately the retardation time of local segmental motion. We find at T = 222.9 K the retardation time of PIB I-7 is approximately 10^{-2} s which is nearly the same as the retardation time at the position of the peak of L obtained from the PCS data of our 9800 molecular weight sample at 222 K. This comparison of the local segmental retardation times obtained by PCS with that determined by another technique on samples with similar molecular weights helps to confirm the identification of the fast process with the local segmental motion in PIB.

A similar interpretation has been given for the dynamic light scattering data of PMPS,[17] plasticized PCHMA,[29] and PMMA.[30] Creep compliance data of PMPS and PMMA are available from Plazek and coworkers[17,35] and can be used to estimate the difference of the time scales of the fast (local segmental) process and the slow (the end of the glass–rubber softening dispersion indicated by the position of the first peak of the retardation spectrum[12,13]) process. Like in the present case of PIB, there is also good correspondence between the estimate of the separation between the two processes from compliance data and dynamic light scattering data in PMPS and PMMA. On comparing the separation in time scales of the fast and slow processes of PIB seen by dynamic light scattering with that of other polymers,[17,29,30,35] we can attest to the known fact that PIB has a much broader glass–rubber transition zone than other amorphous polymers.[1,2,4,5]

An alternative approach to eq 3 is to express $g(t)$ in terms of a continuous distribution of relaxation times, by making use of the inverse Laplace transform of the time-correlation function using the CONTIN algorithm:[33]

$$g(t) = \int_{-\infty}^{+\infty} \exp(-t/\tau)L(\ln \tau)\, \mathrm{d} \ln \tau \qquad (4)$$

with $L(\ln \tau)$ being the distribution of retardation times. Figure 3 shows an experimental correlation function taken at 222 K together with the result of the CONTIN analysis. A two-peak structure is clearly evident in the short time portion, $-6 < \log(\tau/\mathrm{s}) < 0$, of the correlator time window. Guided by the creep compliance data[15] in the manner as discussed before, the faster and more prominent peak is identified with the local segmental relaxation. The broad shoulder on the short time side seems to indicate the presence of secondary β-relaxation as well, although the quality of the data is not good enough for us to make a definitive statement at this time. The other peak of the pair located at about 2 decades longer may correspond to motions (sub-Rouse modes) that involve a length scale intermediate between that of the local segmental motion and the Gaussian submolecule for Rouse modes. The slow process located nearly at the long time limit of the correlator window exhibits a sharp peak which naturally is contributed by the diffusional mode that gives rise to concentration fluctuation in the low molecular weight polydisperse sample.

Figure 4 displays a typical autocorrelation function for the higher M_w and nearly monodisperse PIB sample at 222 K. In this sample the slow process of concentration fluctuation is not seen. The reason for its absence is a combination of near monodispersity which suppresses concentration fluctuation and high molecular weight which shifts the time scale of the slow process beyond the correlator time window. The KWW fit to the experimental spectrum gave $\beta_f = 0.55 \pm 0.08$ which is close to the value determined in the lower molecular weight sample. The intensity of the scattered light remains constant as a function of time as shown by the inset of Figure 4, which indicates that crystallization is not a concern over the temperature range of the present investigation. However, below −60 °C the scattered light intensity increased rapidly with time, indicating the onset of crystallization.

The high and low molecular weight data at 222 K are compared in Figure 5. The retardation spectrum of the fast process of 9800 PIB is very similar in shape to that of the 160 000 PIB. The similarity of the shape of L indicates that the stretched exponent β_f is about the same for the two samples, which reaffirms the interpretation of the fast process as due to local segmental motion. This is because for local segmental motion its stretch exponent is independent of the molecular weight and polydispersity of the sample. The most probable retardation times defined by the positions of the peaks of L of the two samples differ by approximately 2 decades, with that of the low molecular weight PIB being naturally shorter.

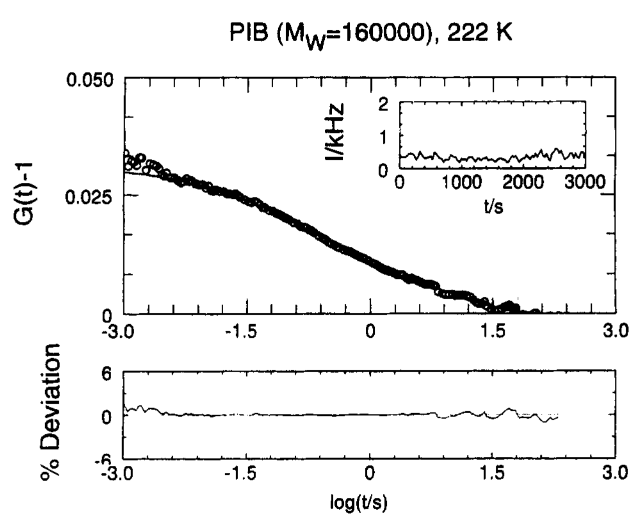

Figure 4. Measured correlation function of local segmental motion in 160 000 molecular weight PIB at 222 K. Shown also is the Kohlrausch stretched exponential fit to the correlation function with $\beta_f = 0.55$. The quality of the fit is shown by the percentage of deviation (lower part). The inset in the upper part shows constancy of the scattered light intensity as a function of time in the course of the experiment.

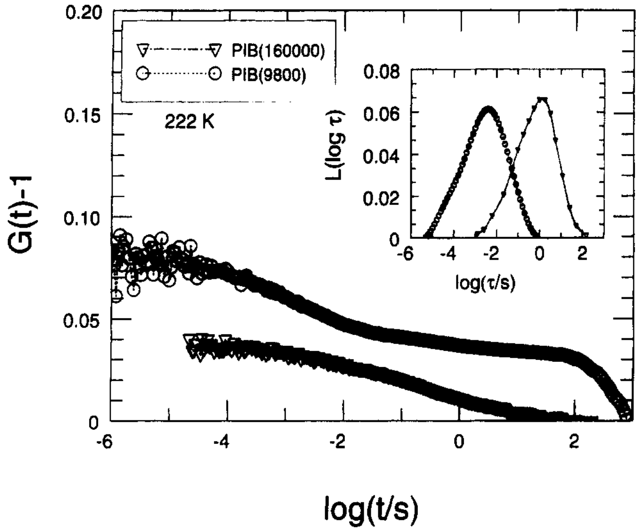

Figure 5. Comparison of the measured correlation functions and calculated retardation spectra of the two samples of PIB.

Discussion

PIB occupies a unique position among amorphous polymers in the development of the field of viscoelasticity of polymers. As enumerated in the Introduction, there are several viscoelastic properties found in PIB which are not shared by other commonly known amorphous polymers. The important question of why PIB has such unique properties has been addressed in the literature by many authors.[2-8] An explanation of the distinct viscoelastic manifestation of PIB[2-11,15] is certainly very desirable. A different angle of approach to viscoelasticity has been introduced by the coupling model,[18] which emphasizes the importance of the inclusion in the consideration of dynamic constraints or "cooperativity" between molecular moieties when describing their motions in dense-packed systems. We still have to first consider the mobility or the friction factor, $\zeta_0(T)$, which governs initially at sufficiently short times the independent relaxation rate, $\tau_0^{-1} \propto \zeta_0(T)$, of motion of molecules. $\zeta_0(T)$ is determined by some static "mean-field" consideration of the dense-packed systems which may very well be approximated by free volume[2] or configurational entropy[36] considerations. However, once the molecular moieties are set in motion and the corresponding relaxation process is underway, the dynamic constraints or many-body correlations after a time, t_c, characteristic of the molecular interaction Hamiltonian will take over to determine ultimately the effective relaxation rate. Based on theoretical considerations,[37,38] the coupling model proposes that t_c is temperature insensitive and the effect of the dynamic constraints can be represented as a rate slowing down to give rise to the stretched exponential given by eq 1, with the effective relaxation time, τ^*, given in terms of the independent relaxation time τ_0 and crossover time t_c by the second relation:

$$\tau^* = (t_c^{-n}\tau_0)^{1/(1-n)} \qquad (5)$$

Recently a quasielastic neutron scattering experiment[39] has given direct confirmation of these principal results. Such a simple relation given by eq 5 has led to many predictions which have been verified by applications to experiments.[18] Examples related to PIB can be found in refs 11 and 15.

Applying to local segmental motion, the coupling model expects a chemical structural dependence of the coupling parameter, n_α. Intuitively as well as theoretically from the dependence of n_α on the interaction Hamiltonian,[37,38] PIB having the most symmetric and compact monomer structure among amorphous polymers is expected to have a smaller n_α compared with that of other vinyl polymers such as polystyrene which has $n_\alpha = 0.65$. An indirect determination of an approximate value of $n_\alpha = 0.4$ for PIB was made possible by comparing the measured momentum transfer, Q, dependence of the segmental relaxation times obtained by quasielastic neutron scattering with the coupling model predicted dependence of $Q^{2/(1-n_\alpha)}$.[18,40] Another indirect determination of n_α can be obtained from the empirically found correlation between the temperature sensitivity, $S = \mathrm{d}\log(\tau^*)/\mathrm{d}(T_g/T)$ determined at T_g which is operationally defined as the temperature as which $\tau^*(T_g) = 100$ s, with n_α.[9,10] An extrapolation of this correlation between S and n_α defined by other amorphous polymers to PIB (see Figure 2 of ref 9) suggests its coupling parameter has a value of $n_\alpha \simeq 0.45$. These two estimates of n_α we deduced indirectly from other experimental data are consistent with its value that we now obtain directly by photon correlation spectroscopy. This value of n_α is indeed smaller than other commonly known amorphous polymers and can explain quantitatively some of the differences in viscoelastic properties between PIB and other amorphous polymers.[9,11,15,41] In the future we shall further exploit the information obtained in this work on the local segmental motion of PIB to explain other distinct viscoelastic properties of PIB.

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