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Complex Dynamics in Polyisobutylene Melts

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ABSTRACT: The dynamics of polyisobutylene at 407 K is investigated by means of quasi-elastic neutron scattering. By proper data reduction, data from two different instruments were combined to provide the incoherent intermediate scattering function, $I_s(Q,t)$, over 3 decades in time. The data were interpreted in terms of a superposition of exponentials with a distribution of characteristic times. The data provide an indication of the existence of three different relaxation processes in the time range between 0.1 and 1000 ps, thus confirming recent results from molecular dynamics simulations. The two fastest processes are spatially localized, while the slow one shows a momentum transfer dependence. Analysis in terms of the alternative phenomenological approach of stretched exponential is also discussed.

Introduction

Polymer dynamics is a complex issue: molecular motion in amorphous polymers occurs over many decades in time[1] and, due to the large size of macromolecular systems, extends over a wide spatial range. Despite continuous research efforts in this area, to date our understanding of the relationship between polymer structure and molecular motion is incomplete. However, because of advances in combining neutron scattering techniques with computer simulations,[2] there is now great potential for achieving a detailed knowledge of the fundamental dynamic processes in amorphous polymers.

In this respect, the case of polyisobutylene (PIB, monomer formula: $[-CH_2-C(CH_3)_2-]_n$) is highly representative. PIB is an important commercial elastomer used in a wide range of technological applications, but despite the industrial interest and the extensive research, some aspects of its microscopic dynamic behavior are yet to be clarified.

Recent studies on PIB have attempted to characterize the nature of the microscopic dynamic processes.[3−9] ^{13}C NMR[3] and electron spin resonance[4] measurements indicated that the temperature dependence of the segmental relaxation does not agree with the rheological behavior reported by Ferry[5] and the dielectric spectroscopy−neutron spin-echo (NSE) measurements of Richter et al.[6,7a]

The dielectric β process[7a] (we note by passing that only a careful set of measurements[7a] allowed the detection of the very weak dielectric response of PIB, due to its small dipole moment) was also investigated by means of high-resolution QENS in ref 7b. A detailed model accounting for a spatially resolved β process and incipient, diffusive relaxation was used to describe data above the glass transition temperature ($T_g + 20 < T < T_g + 80$).

Allen et al.,[9] on the basis of quasi-elastic neutron scattering measurements (QENS), attributed the PIB high local friction to the steric hindrance arising from the bulky double side groups. As a consequence, the potential barrier hindering the CH_3 reorientation in PIB is expected to be high. Contrary to other polymers, it has not been possible, using QENS, to characterize the methyl group dynamics in PIB. For example, fixed window scan measurements reported by Frick et al.[10] gave clear evidence of substantial superposition between the side group and skeletal relaxations. Such a superposition was also invoked in ref 7b to rationalize a variety of experimental findings in terms of “backbone” motions which induce, e.g. by steric effects, methyl group rotations.[7b] The role played by PIB compact and symmetric chemical architecture in determining its dynamic behavior, minimizing intermolecular coupling between neighbor chains, was also invoked by Ngai et al.[11a,b] to account for the unusually narrow breadth of the glass transition. Kanaya et al.[12] studied a number of polymer melts (including PIB), characterizing the existence of an elementary process associated with conformational transitions through torsional motions, whose spatial extent was consistent with a high degree of chain rigidity induced by the two side methyl groups.

All these investigations converge in highlighting the strong degree of coupling between methyl group motion and skeletal relaxation in PIB.

Considerable advances in the understanding of PIB melt dynamics have been recently made.[13−15] Using molecular dynamics (MD) simulations, Karatasos et al. investigated both skeletal[14] and side group[15] relaxation processes in PIB, above its glass transition ($T_g = 200$ K).

A careful analysis of memory functions led Karatasos et al.[14] to postulate the existence of two different skeletal processes occurring in the time range generally associated with the “segmental” motion. The two processes have been attributed to conformational trans ↔ gauche and trans ↔ trans jumps. The existence of a splitting of the trans conformation is characteristic of PIB, and the corresponding complexity of the relaxation is directly related to this conformational feature.

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These findings[14] provide an interpretation for the apparent inconsistency between the weak temperature dependence observed by ^{13}C NMR measurements and the more pronounced one followed by rheological as well as NSE and dielectric data.

On the basis of their MD simulation, Karatasos et al.[15] provided an explanation for the observation of the weak dielectric signal as due to a small intrinsic dipole moment in PIB. In fact, they showed that, "due to the symmetry of the CH_3 group, a simple methyl rotation would not change the reorientation of the dipole, rendering this motion invisible to dielectric spectroscopy. However, a correlated motion arising from the *combination* of the two methyl groups attached to the same carbon, which could be equivalently described by reorientation of a resultant dipole moment, may be dielectrically active. Such a motion could be facilitated to a lesser extent by the relative reorientation of the two $C-CH_3$ bonds and to a larger extent by backbone motion which would involve the concurrent movement of the two CH_3 groups".[15]

Accordingly, the fast, highly localized skeletal motion is strongly coupled to the methyl side group reorientation, these two processes falling in almost the same time window.

To investigate the complex dynamic behavior of polyisobutylene, we performed QENS measurements on two spectrometers with different resolutions and energy ranges. In the following we focus on the analysis of the intermediate scattering functions obtained by overlapping time-of-flight (TOF) and backscattering (BS) data at $T = 407$ K. Our aim is to illustrate an alternative route to the analysis of the intermediate scattering function, as compared to the widely used, empirical Kohlrausch−Williams−Watts (KWW) function. We therefore restrict data analysis to one temperature and investigate the Q dependence at 407 K.

Experimental Section

The polyisobutylene (PIB) sample was obtained from Aldrich, who quote a (number-average) molar mass of 2.0×10^5 g mol^{-1} and a polydispersity of 2.5. As our experiments probe the local dynamics in PIB ($r < 5$ Å), such a polydispersity is not expected to affect the highly localized polymer segmental motions (and thus our results and conclusion). The glass transition, T_g (from differential scanning calorimetry), occurs at 200 K.

QENS measurements were carried out at 407 K on the backscattering spectrometer IRIS[16a] at ISIS (Rutherford Appleton Laboratory, UK) using the PG(002) analyzer (offset), giving an energy range of −0.2 to 1.0 meV, with a resolution of 15 μeV (measured as full width at half-height). The Q range used varied from 0.50 to 1.96 Å^{-1}.

Measurements were also performed on the time-of-flight instrument NEAT (HMI, Berlin),[16b] using a wavelength of 5.1 Å, corresponding to a resolution of 100 μeV, Q range between 1.1 and 2.0 Å^{-1} and, for reasons of resolution and statistical accuracy, energy window between −2 and 10 meV. The sample thickness was 0.2 mm, so chosen to achieve a transmission close to 90% in order to minimize multiple scattering events.

Data were corrected for transmission and absorption using software available at the neutron facilities.

To combine data from the IRIS and NEAT spectrometers without having to make use of models, it is convenient to transform the $S(Q,\omega)$ data into the time domain, i.e., to obtain the incoherent intermediate scattering function, $I_s(Q,t)$. After conventional data reduction (i.e., empty can subtraction, transmission and absorption corrections, vanadium normalization), the time-of-flight data were converted from $S(\theta,\omega)$ to $S(Q,\omega)$ by means of an interpolation procedure over the angle−energy space. Because of the wide energy range accessible on NEAT, this correction is necessary to properly combine the NEAT and IRIS data sets. The $I_s(Q,t)$ data were obtained using FURY,[17] after dividing the Fourier transform of the experimental data by the Fourier transform of the resolution, obtained from a vanadium slab. Generally, Fourier transformation of QENS data is affected by scatter and cutoff effects; however, the extremely good degree of superposition (vide infra) between the Fourier transforms of the two complementary data sets from NEAT and IRIS makes us confident that, in the present case, such errors can be considered inside the statistical error bars.

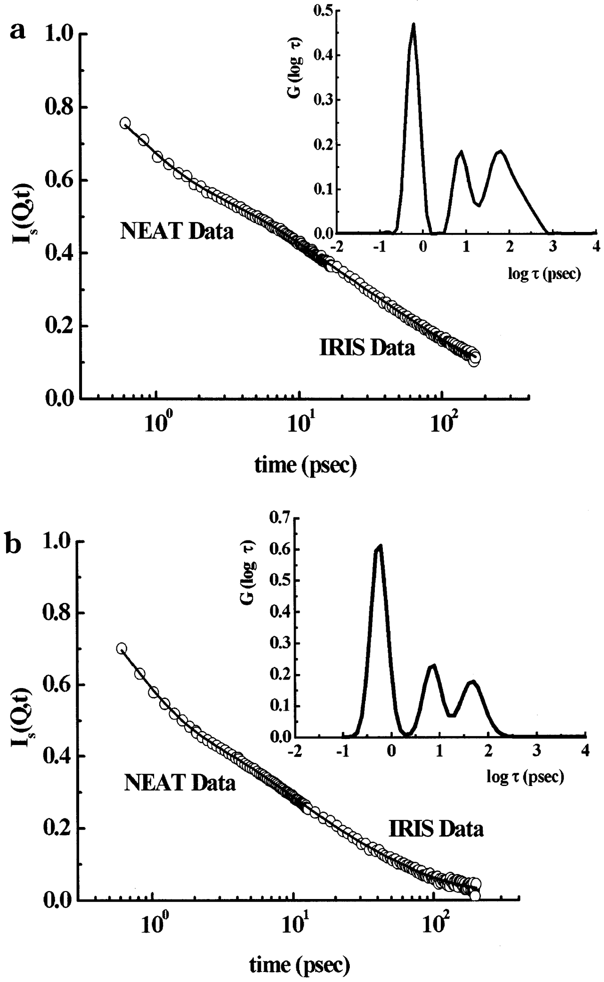

Figure 1. Incoherent intermediate scattering function, $I_s(Q,t)$, for polyisobutylene at $T = 407$ K and (a) $Q = 1.31$ Å^{-1} and (b) $Q = 1.80$ Å^{-1}. Combined data from NEAT and IRIS are reported after Fourier transformation. The lines correspond to a fit of the experimental data with a superposition of simple exponentials whose distribution of characteristic times, $G(\log \tau)$, is reported in the insets.

Results and Discussion

In parts a and b of Figure 1 the intermediate scattering functions, $I_s(Q,t)$, computed from the NEAT and IRIS data at $T = 407$ K are reported for $Q = 1.31$ Å^{-1} and $Q = 1.80$ Å^{-1}, respectively. We note that the overlap between the two data sets is excellent and similar in quality at all Q values. The experimental $I_s(Q,t)$ data clearly indicate, at all Q's, the existence of a fast process occurring on a time scale of 0.5 ps. For example, at $Q = 1.31$ Å^{-1} (Figure 1a) this process leads to a loss of correlation corresponding to ca. 30−40%. A slower, distinctly nonexponential process follows the initial fast decay. The origin of this slow process is the main focus of the present work.

A number of approaches have been used to describe the dynamic behavior of amorphous polymers at temperatures far above the glass transition. Polymer melt relaxation functions are generally characterized by a distinctly non-Debye decay: the deviations from a Debye behavior have been rationalized in terms of the degree of intermolecular coupling[18a] and of intramolecular cooperativity.[18b] The origin of the nonexponential decay has been discussed in the literature (see e.g. refs 19–21). Both homogeneous (all elementary relaxations occurring in an identical, nonexponential way) and heterogeneous (all relaxation processes are represented by exponential decays but there is a distribution of relaxation times leading to the resultant nonexponential behavior) scenarios have been invoked. While recent QENS measurements on polymer melts appear to support the homogeneous scenario,[19] other studies indicate the alternative behavior as more realistic.[20,21] Incidentally, we note that a recent report[2d] comparing MD and QENS results on a glass-forming polymer provides a possible way of rationalizing this apparent contradiction.

In general, any monotonic function can be described as the superposition of exponential decays, weighted by a distribution of relaxation times (DRT), $G(\log \tau)$:[22,23]

$$\phi(t) = \int_{-\infty}^{\infty} G(\log \tau) e^{-t/\tau} \, d(\log \tau) \tag{1}$$

Equation 1 has been extensively used for example in light scattering to determine the distribution of relaxation times using a CONTIN analysis[23] but, to our knowledge, has never been used to describe experimental neutron scattering data. This is certainly to be ascribed to the limited energy range that is accessible on QENS spectrometers, leading to lack of information at either short or long times. In this work, this problem is partly overcome by overlapping data from two different spectrometers.

Analysis of the intermediate scattering function $I_s(Q,t)$ in terms of a distribution of relaxation times as defined by eq 1 should provide a model-independent phenomenological description of the underlying polymer dynamics. We note that the widely used KWW function

$$\phi(t) = \exp(-t/\tau)^{\beta} \tag{2}$$

where τ is the characteristic time for the relaxation and β ($0 < \beta \leq 1$) is a shape parameter indicating deviations from a Debye-like process, can be expressed in terms of eq 1, i.e., as a superposition of exponential decays (see e.g. ref 22). This implies that the distribution of relaxation times associated with the set of functions defined by eq 2 (for the different β values) forms a subset of the $G(\log \tau)$ functions given by eq 1.[22] Thus, data analysis in terms of eq 1 offers an unbiased approach to the characterization of relaxation processes in terms of a DRT.[23]

The results of the MD analysis made by Karatasos et al. suggest that different processes may contribute to the decay of $I_s(Q,t)$ in PIB melts and may be observable within the large time window that is covered by the superposition of the NEAT and IRIS data. As will be shown later, while use of a KWW function (eq 2) may lead to a satisfactory fit at $t > 1$ ps, the corresponding parameters cannot be simply interpreted in terms of a single but distributed relaxation. On the contrary, they point to the coexistence of two relaxation processes. In the following, we will compare the two different approaches to data analysis (i) based on eq 1 and (ii) using the KWW function.

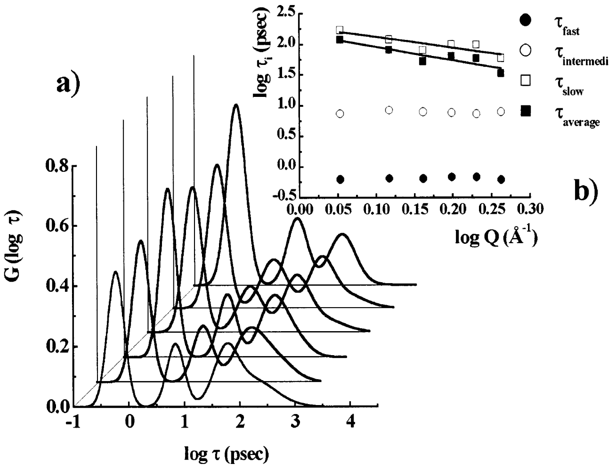

Figure 2. (a) Momentum transfer dependence ($1.13 < Q$ (Å^{-1}) < 1.80) of the distributions of characteristic times, $G(\log \tau)$, for polyisobutylene at 407 K, as obtained from the fit of combined data from IRIS and NEAT. (b) Momentum transfer dependence of the characteristic times, τ_i (see the text for an explanation of the different parameters). The lines through the τ_{slow} and τ_{average} points correspond to power law fits.

The fits shown in parts a and b of Figure 1 for $Q = 1.31$ Å^{-1} and $Q = 1.80$ Å^{-1}, respectively, were generated using a superposition of exponentials (eq 1). Initially, no assumption was made on the nature of the distribution of relaxation times, $G(\log \tau)$. The corresponding DRT's are characterized by three distinct peaks, the one at long relaxation times being asymmetric. On the basis of this initial result, to decrease the number of degrees of freedom associated with eq 1, we have subsequently repeated the fits using eq 1 but fixing the number of peaks in the DRT. In doing this, we have assumed that the resulting $G(\log \tau)$ could be described by a combination of four log-Gaussian functions. As will be shown later, this is equivalent to three distinct processes, the slowest, asymmetric one being described by two log-Gaussians. The resulting fits and the corresponding DRT's are reported in Figure 1a,b.

We stress that the $G(\log \tau)$ that we derived is defined over more than 3 decades in time, due to the simultaneous fit of experimental data over a broad temporal range. Any attempt to describe the data from a single instrument (either NEAT or IRIS) led to unsatisfactory results (data not shown): the reason is that NEAT data are far from being fully relaxed at the longest times, while IRIS data are already substantially relaxed even at the shortest times covered by the instrument.

The Q dependence of the DRT is reported in Figure 2a: at all Q values ($1.13 < Q$ (Å^{-1}) < 1.80), three distinct processes are observed at $T = 407$ K. While the DRT's associated with the two fastest processes are Gaussian, this is not the case for the slowest one which, particularly at the lowest Q values, appears to have an asymmetric non-Gaussian shape. (As mentioned earlier, this asymmetry was modeled by a combination of two log-Gaussian functions.)

The fastest process centered at ca. $\log \tau = -0.25$ ($\tau = 0.5$ ps) is believed to be related to skeletal dihedral angle oscillations within the torsional wells.[14] Similar processes have been observed in other polymers, such as polyethylene,[24] polybutadiene,[25] polyisoprene,[26] and polypropylene.[27] Their interpretation in terms of damped vibrational motions or diffusion on a sphere was presented previously.[24,25] More recently, this process has been associated with the softening of the vibrational boson peak with increasing temperature.[26]

After 1 decade in time, a second process is detected which accounts for ca. 20% of the relaxation at $Q = 1.31$ Å^{-1}. This process falls within the time range of the intermediate skeletal process reported by Karatasos et al.[14] We note that the position of this peak is almost Q independent, and only a change in amplitude is observed with increasing Q: the motion corresponds to a fast ($\log \langle\tau_{\text{intermediate}}\rangle = 0.8$, $\langle\tau_{\text{intermediate}}\rangle = 6$ ps), highly localized process.

Recently, Karatasos et al.[15] carried out MD simulations to investigate the methyl group dynamics in PIB. Using a procedure similar to that described in ref 14, these authors reported that three distinct processes take place in PIB. Methyl group motion in PIB was found to occur in the same time scale (ca. 10 ps) as the intermediate process of the chain backbone atoms; i.e., there is considerable coupling between the two motions.

Our findings are consistent with MD results for both skeletal and side-group motions. Since our sample is fully hydrogenated, we cannot separate between skeletal and side-group processes: both hydrogen atoms in the backbone and in the methyl side groups will contribute to the decay of $I_s(Q,t)$. Accordingly, we are presently not able to discern the nature of this intermediate peak; on the other hand, as six out of eight of the hydrogen atoms in the PIB monomer belong to methyl groups, we might expect a substantial contribution from these H atoms.

Finally, on a time scale of ca. $\log \langle\tau_{\text{slow}}\rangle = 1.8$ ($\langle\tau_{\text{slow}}\rangle = 60$ ps) a third relaxation process is detected, leading to the remaining loss of correlation of ca. 35%. The shape of the corresponding DRT appears of a complex nature, and two log-Gaussian functions were necessary to satisfactorily fit the time decay. At present it is not possible to conclude if the observed behavior corresponds either to the existence of two distinct, though similar, processes or to a single process whose shape is non-log-Gaussian. Measurements at higher resolution (e.g., by higher resolution backscattering or by neutron spin echo) and at lower temperature are required to clarify this point. However, the DRT relative to the slowest relaxation process is Q-dependent.

In Figure 2b, the Q dependence of the average times, $\langle\tau_i\rangle$, of the ith processes is also reported. The average times, $\langle\tau_i\rangle$, are defined by the following relationship:

$$\langle\tau_i\rangle = \frac{\int_{\Delta\tau_i} \tau G(\log \tau)\, \mathrm{d}(\log \tau)}{\int_{\Delta\tau_i} G(\log \tau)\, \mathrm{d}(\log \tau)} \tag{3}$$

where $\Delta\tau_i$ is the time interval over which the ith process is active. It is clear from the data reported in Figure 2b that the characteristic times of the fast and intermediate processes are Q-independent. Values of $\langle\tau_i\rangle$ for the slow process show a power law Q dependence, i.e., $\langle\tau_{\text{slow}}\rangle(Q) = \tau_0 Q^n$, with $n = -1.8$.

Following the procedure adopted by Karatasos et al.,[14] we also report in Figure 2b the Q dependence of τ_{average}, defined as the characteristic time associated with the *two* slowest processes (i.e., in eq 3 the time interval $\Delta\tau_\iota$ was chosen in order to cover both the intermediate and slow processes). Since τ_{average} includes both intermediate and slow processes, for the purpose of our discussion, this quantity has no physical meaning. However, any data analysis describing the "slow" decay of the intermediate scattering function in the time range $1 < \tau$ (ps) $< 10^3$ using a single process would lead to an apparent τ value corresponding to τ_{average}. The corresponding power law is described by an exponent $n = -2.2$ (see Figure 2b).

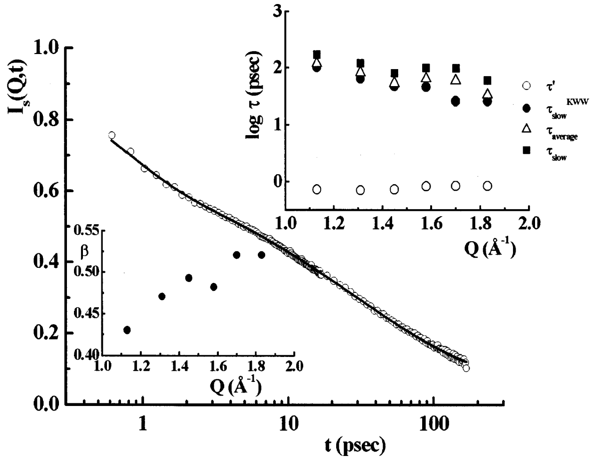

Figure 3. Incoherent intermediate scattering function, $I_s(Q,t)$, for polyisobutylene at $T = 407$ K and $Q = 1.31$ Å^{-1}. Combined data from NEAT and IRIS are reported after Fourier transformation. The line corresponds to a fit of the experimental data with the model of eq 4, where a simple exponential and a stretched exponential term are properly combined (see the text). In the upper inset a comparison of the characteristic times for the corresponding two processes (τ' and $\tau_{\text{slow}}^{\text{KWW}}$, see eq 4), and the characteristic times derived by the DRT approach is presented. The Q dependence of the shape parameter, β, is also reported in the lower inset. (Note that in previous QENS studies on the α relaxation in PIB a value of $\beta = 0.55$ had been assumed.[7b,19])

The aim of this paper is to show the limitations of using empirical model functions such as the KWW function in the analysis of experimental $I(Q,t)$ data. We therefore compare the results of the DRT analysis with those of fits carried out using the following expression:

$$I(Q,t) = [A + (1 - A)\mathrm{e}^{-t/\tau'}]\exp(-t/\tau_{\text{slow}}^{\text{KWW}})^{\beta} + B \tag{4}$$

Two relaxation processes are considered in eq 4: a fast, exponential decay with characteristic time τ' and a slower process which we modeled using a stretched exponential function, with characteristic time $\tau_{\text{slow}}^{\text{KWW}}$. Furthermore, a constant term, B, has been added to account for any unresolved dynamics as this slightly improves the quality of the fits. We note, however, that the fitting value for this parameter is of the order of a few percent.

As shown in Figure 3 for the case of $T = 407$ K and $Q = 1.31$ Å^{-1}, this model represents the experimental $I_s(Q,t)$ data as well as the curve based on the DRT analysis. In the insets of Figure 3, the Q dependence of the corresponding fitting parameters β, τ', and $\tau_{\text{slow}}^{\text{KWW}}$ is reported and compared to τ_{slow} and τ_{average} values.

As expected, $\tau_{\text{slow}}^{\text{KWW}}$ is similar in magnitude to τ_{average}, giving a measure of the relaxation time associated with the slower decay of the $I(Q,t)$. The β parameter determined through eq 4 displays a *clear Q dependence*, indicative of a distribution of relaxation times which is Q dependent. This result is better understood in terms of two processes with different Q dependencies, i.e., by a systematic evolution of the DRT's with Q.

The KWW function has been extensively used as model function to describe a wide range of dynamic processes, including QENS data of PIB at $T > T_g$. For example, the neutron spin-echo data[6] of deuterated PIB were fitted using a KWW, leading to highly Q-dependent β values varying from 0.40 and 0.56 in the range $0.8 < Q$ (Å^{-1}) < 2.93. Later reports dealing with hydrogenated PIB have made use of a KWW model with a fixed β value equal to 0.55.[7b,19] While fixing the β parameter of the KWW function is common practice, this choice of $\beta = 0.55$ was simply justified on the basis of the results in ref 6, which, however, led to a range of β values.

Other experimental methods have made use of the KWW model to probe the segmental dynamics of PIB melts. Viscoelastic measurements led to a β parameter equal to 0.45,[11c] while from photon correlation spectroscopy a β value of 0.56 was reported.[11d] Dynamic mechanical spectra indicate a broader relaxation process characterized by $\beta = 0.33$.[18a] While we stress that each technique probes different aspects of the same relaxation process and as such the parameters describing the underlying relaxations may not be directly comparable, the above results reported in the literature show the limitation of models based on the KWW approach.

The results presented here based on fits using a DRT analysis or the empirical KWW function indicate the limitations of the latter in providing a realistic, physical description of local chain dynamics. The DRT analysis of the intermediate scattering function indicates the existence of three relaxation processes occurring in PIB in the time scale from 10^{-1} to 10^{3} ps, thus giving experimental support to findings from a recent MD simulation study. Although we cannot discern between skeletal and side group motions, the negligible Q dependence of the relaxation time exhibited by the intermediate process indicates that the latter corresponds to a fast highly localized process.

Conclusion

We have presented a new approach to the analysis of the QENS intermediate scattering function of PIB, which offers considerable advantages over other methods of analysis, e.g., the use of the empirical KWW function. The availability of QENS data over a wide time range has been of importance in the characterization of the local dynamics in PIB melts, for which the analysis led to the characterization of three different contributions to the loss of correlation at 407 K. At high temperature and relatively high Q values, the details of the chemical structure play a decisive role. This is particularly evident for PIB. The use of empirical functions such as the KWW leads to an overall representation of the polymer dynamics, with a loss of information on the specific motional processes. The importance of the approach used here is evident: when dealing with the complex dynamic behavior of polymer melts (whose chemical architecture might eventually be complex itself), the use of empirical functions such as the KWW may be misleading.

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