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Local segmental and sub-Rouse modes in polyisobutylene by photon correlation spectroscopy

Apostolos K. Rizos*
University of Crete, Department of Chemistry and Foundation for Research & Technology-Hellas, PO Box 1527 Heraklion 71110, Greece

and Kia L. Ngai
Naval Research Laboratory, Washington, DC 20375-5320, USA

and Donald J. Plazek
University of Pittsburgh, Materials Science and Engineering Department, Pittsburgh, PA 15261, USA

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Photon correlation spectroscopy has been successfully employed to study the dynamics of the local segmental and sub-Rouse motion of a monodisperse polyisobutylene near and above the glass transition temperature. The separation between the maxima of the two peaks corresponding to these two viscoelastic mechanisms is obtained for several temperatures. The temperature dependence of the local segmental relaxation times as compared to the sub-Rouse modes relaxation times is noticeably stronger. The segmental correlation function can be well described by a Kohlrausch's stretched exponential function with an exponent $\beta_\alpha = 0.56$. At this time, photon correlation spectroscopy is the only experimental means that can determine the correlation of the local segmental motion of polyisobutylene directly. The small value of the coupling parameter of PIB, $n_\alpha = 1 - \beta_\alpha = 0.44$, among amorphous polymers support the interpretation of its unusual viscoelastic properties. This value of n_α directly determined from photon correlation spectroscopy, is consistent with the value deduced indirectly from other experiments. © 1997 Elsevier Science Ltd.

(Keywords: segmental and sub-Rouse modes; photon correlation; coupling parameter)

INTRODUCTION

Polyisobutylene (PIB) is an interesting polymer from several standpoints[1-5]. Even though it is sterically hindered with respect to skeletal bond rotations it has a low glass transition temperature (T_g). It is characterized by a very efficient intermolecular packing as evidenced by the relatively low specific volume. 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. Thus, it is expected to have small capacity for intermolecular coupling which is manifested in the unique viscoelastic properties[6-12] of this polymer. Normally, for many amorphous polymers the coupling parameter can be directly obtained from the stretched exponential form of the correlation function which can be deduced from dielectric[16,17] and mechanical[18] experiments. However, PIB is not dielectrically active and the distinct character of its viscoelastic spectrum that has a much broader dispersion in the glass–rubber transition region makes it difficult, if not impossible, to isolate the local segmental relaxation contribution from mechanical relaxation[19] or compliance measurements.

In our previous paper[20] the viscoelastic response of PIB has been investigated for the first time by dynamic light scattering. Photon correlation spectroscopy (PCS) has proven to be useful to characterize the local segmental dynamics[20-24] of amorphous polymers near and above T_g. PCS has remained not fully explored as an option to determine the correlation function for segmental motion of PIB since it is relatively difficult to obtain dynamic light scattering data near and above T_g for this polymer. The early PCS experiment[20] demonstrated the existence of the local segmental relaxation as well as a new molecular weight independent relaxation mode that is intermediate (in both length scale and time scale) between the fast segmental and the Rouse modes. We have called this new mode *sub-Rouse mode*[19,20,25]. Viscoelastic measurements that combine different instruments to cover a dynamic range of about nine decades have also found the sub-Rouse modes[25]. Since the previous samples used in PCS experiments were not monodisperse, the quality of the data obtained has not been optimized. For this reason we have undertaken new

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*To whom correspondence should be addressed measurements from *monodisperse* PIB samples. The quality of the PCS data to be reported in this paper is better than that obtained before[20]. The better quality of the data has enabled determination of the spectra of the local segmental and the sub-Rouse modes over a range of temperatures. In this paper, the experimental results of PIB including the temperature shift factors of the two modes and the coupling parameter, $n_\alpha \equiv 1 - \beta_\alpha$, of the local segmental (α) mode are reported and discussed in connection with the distinct viscoelastic properties of PIB.

EXPERIMENTAL

Samples

The polyisobutylene sample studied in this work is quite monodisperse with $M_n = 29\,500$, $M_w/M_n = 1.05$. PIB was dissolved in toluene and then precipitated from the solution with the addition of methanol. This cycle of solvent–nonsolvent fractionations (toluene–methanol) was repeated several times to generate samples of better optical quality and reduced polydispersity. Finally the PIB solution was filtered several times through a Millipore filter and then the resulting dust free solution was filtered into a dust free light scattering cell. The solvent was removed with the help of a vacuum over a period of several weeks. The glass transition temperature of −75°C was obtained from a dilatometric cooling curve at a rate of $0.2\,\mathrm{deg\,min^{-1}}$.

Dynamic light scattering

Samples of high optical quality are a prerequisite for photon correlation spectroscopic studies in bulk polymers. The experimental autocorrelation function was measured with an apparatus equipped with an argon ion laser (Spectra Physics 2020) operating at a wavelength of 488 nm. The incident and scattered beams were polarized with Glan and Glan–Thompson polarizers with extinction coefficients better than 10^{-6} and 10^{-7}, respectively. An ALV-5000 multibit, multi-τ full digital correlator was used that covered a broad dynamic range of about 10 decades.

Data analysis

The dynamic light scattering experimental correlation functions were treated in the homodyne limit. The measured intensity autocorrelation function $G(q,t)$ is related to the desired normalized field correlation function $g(q,t)$ (where $q = (4\pi n/\lambda)\sin(\theta/2)$ is the scattering vector, n is the refractive index of the bulk polymer, θ is the scattering angle and λ the laser wavelength) by

$$G(q,t) = A[1 + f\,|ag(q,t)|^2] \tag{1}$$

where f is the instrumental factor, calculated by means of a standard, a is the fraction of the total scattered intensity associated with density fluctuations with correlation times longer than 10^{-6} s and A is the baseline. Typical normalized correlation functions are shown in *Figure 1*. Two types of analyses have been performed for the $g(q,t)$ correlation functions. First, we used the sum of two Kohlrausch–Williams–Watts (KWW) functions,

$$ag(q,t) = A_\alpha \exp[-(t/\tau_\alpha)^{\beta_\alpha}] + A_{sR}\exp[-(t/\tau_{sR})^{\beta_{sR}}] \tag{2}$$

with parameters $\{A_\alpha, \tau_\alpha$ and $\beta_\alpha\}$ and $\{A_{sR}, \tau_{sR}$ and $\beta_{sR}\}$ that give the contrast, relaxation time and shape of the fast segmental and slow sub-Rouse processes, respectively. From this analysis we found that the relaxation times of the fast segmental process had a stronger temperature dependence as compared to the relaxation times of the slower sub-Rouse process. To verify this finding, a second type of analysis which does not assume any functional form for the correlation functions was also made with the use of the inverse Laplace transform (ILT) of the time correlation functions using the CONTIN algorithm[26],

$$\begin{aligned} ag(q,t) &= \int_0^\infty A(\tau)\exp(-t/\tau)\,\mathrm{d}\tau \\ &= \int_0^\infty \tau A(\tau)\exp(-t/\tau)\mathrm{d}\ln\tau \end{aligned} \tag{3}$$

The results of the ILT analysis at different temperatures are illustrated in *Figure 2*. The ILT result shows a double peak structure with peaks that shift to longer times with decreasing temperature. The increase of the local segmental relaxation times with decreasing temperature is larger than that of the slower sub-Rouse modes. As a consequence of this thermorheological complexity, the local segmental relaxation spectrum encroaches and overlaps the spectrum of the sub-Rouse modes as temperature continues to fall.

RESULTS AND DISCUSSION

The present dynamic light scattering measurements give clear evidence for the existence of two processes at temperatures near and above the glass transition. The faster process among the two has all the characteristics of the local segmental motion. It has been repeatedly found in many amorphous polymers that the correlation function of the fast segmental process is well represented by the KWW stretched exponential function. Also theoretically the coupling model[11–15] has suggested that the correlation function of local segmental motion should have the stretched exponential form. According to the coupling theory the intermolecular interactions in the polymer give rise to mutual dynamic constraints or cooperativity between molecular moieties and concomitantly slow down the local segmental relaxation. In neat polymers the correlation function of α-relaxation is given by the stretched exponential KWW function, $C_\alpha(t) = \exp[-(t/\tau^*)^{1-n_\alpha}]$ where n_α is the coupling parameter. Intermolecular cooperativity measured by n_α has lengthened the primitive relaxation time, τ_0, to the effective relaxation time, τ_α, related to each other by the following relation, $\tau_\alpha = [t_c^{-n_\alpha}\tau_0]^{1/(1-n_\alpha)}$, where t_c, is the microscopic cross-over time after which the relaxation is slowing down and has the magnitude[27–29] of a few picoseconds. Thus, in the context of the coupling model, β_α in equation (2) is to be identified with $(1 - n_\alpha)$.

In this work we have repeated PCS measurements on a monodisperse PIB sample of molecular weight 29 500. The result of the fit of the measured correlation function at 224 K to the sum of two KWW stretched exponential functions is shown in *Figure 3*. Good fits were obtained with $\beta_\alpha = 0.56$ and $\beta_{sR} = 0.39$. The coupling parameter, n_α, of the local segmental relaxation can be immediately obtained from the relation, $n_\alpha = 1 - \beta_\alpha = 0.44$. The sub-Rouse modes have length scales interpolating between that of the local segmental motion and the shortest

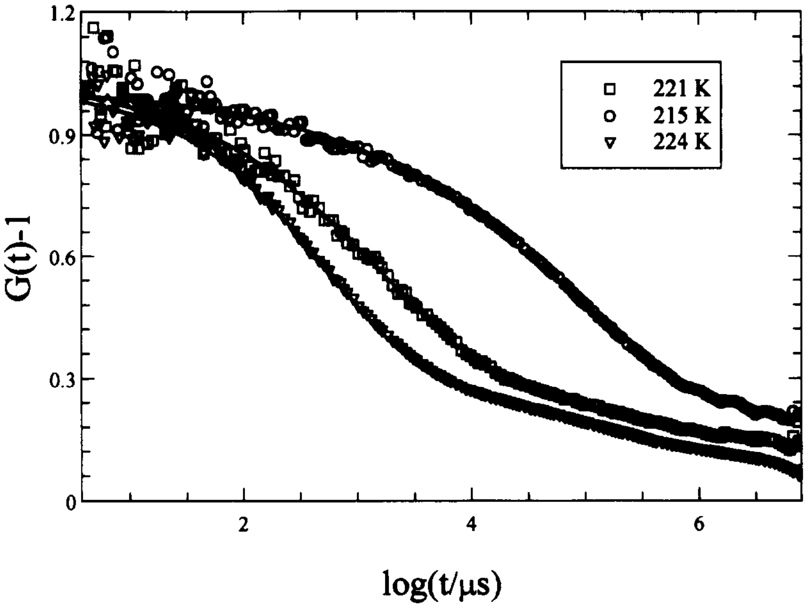

Figure 1 Measured correlation functions for PIB at a scattering angle of 90° at 215, 221 and 224 K

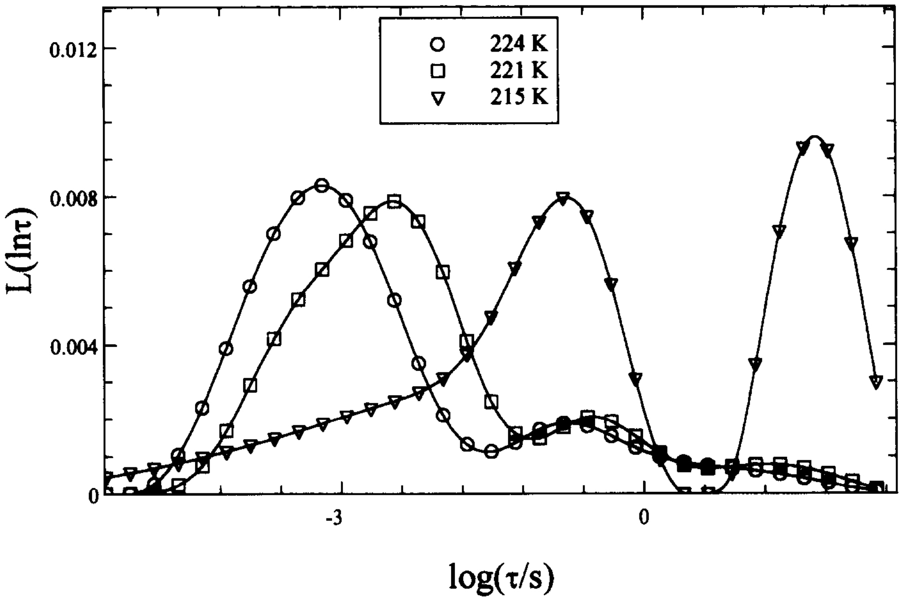

Figure 2 Retardation time spectra, $L(\ln\tau)$ at three temperatures as obtained from the inversion of the time correlation functions using the ILT technique

wavelength of the Rouse modes. The existence of a shortest wavelength of the Rouse modes is equivalent to the requirement of a minimum number of monomers before the submolecule is Gaussian and form the basic unit on which Rouse modes, which are purely entropic, can be defined. The spectrum of sub-Rouse modes, indexed by $\{sRi\}$ and each mode I having its own relaxation time, already contribute to the observed dispersion. Additionally, the dynamic constraints on the motion of the sub-Rouse modes give rise to a coupling parameter, n_{sRi}, for each of these modes and contribute to dispersion through the stretched exponential, $\exp[-(t/\tau_{sRi})^{1-n_{sRi}}]$. The observed spectrum, fit to the second term on the right-hand-side of equation (2), $\exp[-(t/\tau_{sR})^{\beta_{sR}}]$, is the sum, $\Sigma_i \exp[-(t/\tau_{sri})^{1-n_{sRi}}]$. Thus, unlike the case of the local segmental motion, the value $\beta_{sR} = 0.39$ should not be identified with $1 - n_{sRi}$ for any i. In fact, we can conclude that n_{sRi} is definitely less than $1 - \beta_{sR}$.

The retardation spectrum $L(\ln\tau)$ is obtained as described in the Experimental section and is shown in *Figure 2*. It is clear that from the two peak structure of $L(\ln\tau)$ two viscoelastic mechanisms have been observed. The prominent short peak comes from the local segmental motion and the long time shoulder is the *sub-Rouse* mode as seen before in polydisperse samples of PIB. The separation between the maxima of the two peaks corresponding to these two viscoelastic mechanisms is obtained for several temperatures and is shown in *Figure 2*. The temperature dependence of the local segmental times as compared to the sub-Rouse times is noticeably stronger. As a consequence the length of the

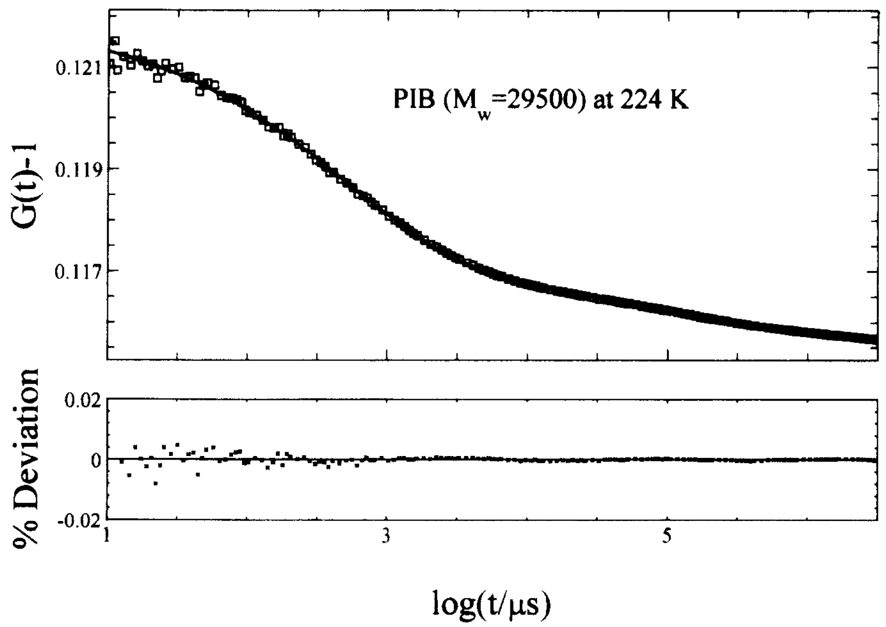

Figure 3 Fit of the experimental correlation function in PIB at 224 K using a double KWW function. The % deviation is shown at the bottom of the figure

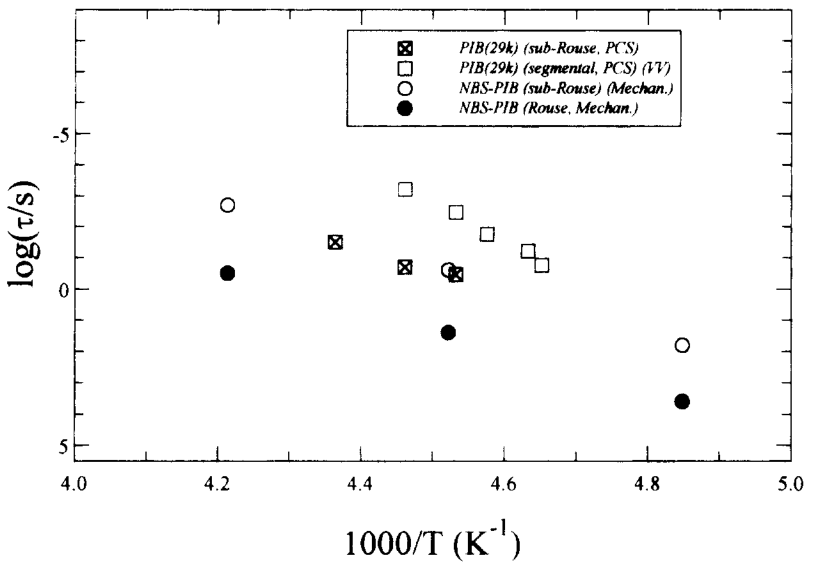

Figure 4 Temperature dependence of the relaxation times of PIB in an Arrhenius representation

Table 1

T (K)	τ_α (s)	β_α	τ_{sR} (s)	β_{sR}[a]	A_{sR}/A_α
224	6.26×10^{-4}	0.56	1.74×10^{-1}	0.22	0.4
221	3.37×10^{-3}	0.50	3.24×10^{-1}	0.55	0.2
217	1.75×10^{-2}	0.47	—		
215	1.74×10^{-1}	0.36	—		

[a] The KWW function of the sub-Rouse modes is used for convenience to represent their contribution to the correlation function. The β value may not be interpreted as the coupling parameter of any of those sub-Rouse modes

plateau (shown in *Figure 1*) shortens leading to a tendency of merging of the decay steps to become apparently a combined process (see also the gradual decrease in β_α shown in *Table 1*). The latter has a broader dispersion than either the local segmental motion or the sub-Rouse modes. This may explain the extremely broad dispersion of mechanical data taken at lower frequencies than that corresponding to our PCS data and modulus level near the local segmental motion[19]. This broad mechanical response is the consequence of the overlap of two processes (segmental and sub-Rouse relaxation processes) which have different temperature dependencies.

In *Figure 4* we plot the temperature dependence of the relaxation times for the segmental α-relaxation process and the sub-Rouse process as probed by PCS. The existence of the sub-Rouse modes is clearly established here since the data collected here from photon correlation spectroscopy display dynamics in between the local segmental and the Rouse modes. There is very good agreement between the mechanical and PCS data points for the sub-Rouse modes. Therefore the PCS data have provided independent evidence for the existence of the sub-Rouse modes. The comparison is limited to a relatively small temperature range since, as was mentioned before, the temperature dependence of the local segmental relaxation times is stronger compared to those of the sub-Rouse relaxation times and the subsequent merging of the two relaxations does not allow clear separation of the processes.

CONCLUSIONS

The study of the dynamics of monodisperse PIB by PCS has revealed some interesting new features. In addition to the segmental α-relaxation mode, a new sub-Rouse process has been identified in agreement with recent mechanical measurements[25]. The temperature shift factors of these two modes are not the same (i.e. not thermorheologically simple), with that of the faster local segmental motion having a stronger temperature dependence. The distribution of relaxation times becomes very broad close to T_g due to the merging of the two relaxation processes because the faster process is encroaching (in the sense of time scale) the slower process as temperature is decreased towards T_g. At higher temperatures the modes separate, so that two distinct viscoelastic mechanisms with different correlation functions are observed simultaneously in the time window of our correlator. The value of the coupling parameter, n_α, of the local segmental motion of PIB has been determined to have the value of 0.44. This value is the smallest among commonly known amorphous polymers, which according to the coupling model is the reason for the special viscoelastic properties of PIB[5-7,11,12,14].

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