New Interpretation of Local Dynamics of Poly(Dimethyl Siloxane) Observed by Quasielastic Neutron Scattering

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Synthetic and natural polymers have complex dynamic behavior with distinct motions taking place on a wide range of time and length scales. For poly(dimethyl siloxane) we show that, at temperatures above the melting point, the reorientation of the CH_3 groups provides a non-negligible contribution to the incoherent dynamic structure factor. Analysis of the quasielastic neutron scattering data is carried out using a model function that includes fast rotational motion of the CH_3 groups and local conformational transitions between isomeric states. By using this model, detailed comparison between experimental data and theoretical predictions at distances where deviations from the traditional Rouse model are expected becomes possible.

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The long chain nature of polymers is responsible for their unique dynamic properties. Because of chain connectivity, polymer motion extends over many orders of magnitude in time and length scale ranging from librations in the picosecond time range, high frequency torsional and vibrational motions of sidegroups up to the slow reorientation of whole molecules which approaches macroscopic times [1]. Similarly complex molecular motions are observed in biological polymers [2,3]. Dynamic studies on both synthetic polymers and biomolecules are essential to establish a relationship between viscoelastic behavior and chemical structure and therefore fully understand their properties and biological function.

Understanding polymer motion over a broad time and distance scale poses a great challenge to both experimentalists and theoreticians. In fact, as a consequence of the wide dynamic range, vastly different motions may be probed by different experimental techniques, obscuring the connection among micro-, meso-, and macroscopic behaviors. However, as an added bonus this feature makes polymers highly suited to follow in real time the melting behavior and/or the glass transition over many length scales, ranging from the most local to the collective ones, unlike low molar mass compounds.

Theoretical models were developed to describe large scale chain motion: the reptation model of de Gennes [4,5] and the bead-spring Rouse model [6] provide universal laws describing the motion of chains above and below their entanglement length, respectively. These coarse-grained models are strictly applicable for distances larger than the statistical segment length. When the latter is approached, the universal behavior breaks down and local relaxation processes need to be considered. Theoretical treatments [7,8] were proposed to extend the Rouse model to distances of the order of the monomer size. These comprise both coarse-grained models that account for chain stiffness, and realistic treatments that consider the local stereochemistry. Alternatively, a generalized Rouse model was proposed to describe the dynamics of polymers and of biological macromolecules (proteins), including also the sidegroup motion, by taking into account the memory function matrix with a mode-coupling procedure [9].

In this Letter, we present a study of local dynamics in poly(dimethyl siloxane) (PDMS) using quasielastic neutron scattering (QENS). PDMS is one of the most thoroughly investigated systems through a wide range of experimental methods including nuclear magnetic resonance [10] and neutron scattering [11–13]. With wavelengths (a few angstroms) similar to the monomer size, QENS is able to probe microscopic motion from sidegroup rotation to segmental dynamics occurring in the time range from 10^{-13} to 10^{-10} s and on a length scale up to ca. 15 Å [12]. QENS measurements were carried out on PDMS in order to extract information on both methyl group reorientation and segmental chain dynamics across the melting temperature T_m. We show, for the first time, that once an account is made for the fast hopping of the CH_3 groups over the threefold rotational barrier as deduced from its sub-T_m motion, the dynamic incoherent structure factor is in good agreement with recent theoretical results that realistically account for the local stereochemistry [14]. Moreover, we show that the results are fully consistent with rheological data, thus providing a link between the microscopic and the macroscopic polymer dynamics.

The PDMS sample used in this work had a weight average molar mass of 92×10^3 g/mol (from Hopkin & Williams), a calorimetric glass transition (T_g) at 148 K, cold crystallization at 182 K, and two melting peaks (T_m) located at 230 and 236 K [15]. Accordingly, one can measure the local motion for $T < T_g$ and for

$T_g < T < T_m$, or the larger scale segmental dynamics for $T > T_m$, which is not possible with nonpolymeric materials. QENS measurements were carried out on the high resolution backscattering spectrometer IRIS at ISIS (Rutherford Appleton Laboratory, U.K.), using the PG(002) analyzer, with resolution equal to 15 μeV (measured as full width at half height). Two experiments were performed with different setups giving energy ranges from -0.4 to 0.4 meV (for $T < T_m$) and -0.2 to 1.2 meV (for $T > T_m$). In both experiments, the Q range varied from 0.25 to 1.9 Å^{-1}. Standard corrections for absorption and empty cell subtraction were carried out using ISIS routines.

The double differential scattering cross section, $\partial^2\sigma/(\partial E \partial \Omega)$, i.e., the probability that a neutron is scattered with energy change ΔE into the solid angle $\Delta\Omega$, is measured experimentally. Since the incoherent cross section of hydrogen is much larger than that of other atoms, the scattering cross section σ is dominated by the incoherent scattering. Data fitting is achieved by a suitable choice of model function that provides an expression for the incoherent scattering law, $S_{\text{inc}}(Q, \omega)$. The latter is related to the double differential scattering cross section:

$$\left(\frac{\partial^2\sigma}{\partial\Omega\partial E}\right)_{\text{inc}} = \frac{N\boldsymbol{k}}{\boldsymbol{k}_0}\Delta b^2 S_{\text{inc}}(\boldsymbol{Q}, \omega), \tag{1}$$

where N is the number of atoms, $\boldsymbol{k}$ and $\boldsymbol{k}_0$ are the scattered and incident wave vectors ($k = 2\pi/\lambda$), and $Q = 4\pi\sin(\theta/2)/\lambda$ is the momentum transfer, θ being the scattering angle. Δb^2 is related to the incoherent cross section (i.e., $\sigma_{\text{inc}} = 4\pi\Delta b^2$).

In the glassy state, when the backbone motion is frozen in, only the reorientation of sidegroups, e.g., methyl groups, contributes to $S_{\text{inc}}(Q, \omega)$. In a random environment, $S_{\text{inc}}(Q, \omega)$ can be described as a sum of two contributions:

$$S(Q, \omega) = \left[[1 - A_0(Q)]\Sigma g_i \frac{1}{\pi}\frac{\Gamma_i}{\Gamma_i^2 + \omega^2} + A_0(Q)\delta(\omega)\right], \tag{2}$$

an elastic term (the delta function) and a quasielastic component. For amorphous polymers below T_g, the quasielastic broadening is described by a Gaussian distribution of Lorentzian lines with width Γ_i and weight g_i [16,17]:

$$g_i = \frac{1}{\sigma_\Gamma\sqrt{2\pi}}\exp\left[-\frac{(\ln\Gamma_i - \ln\Gamma_0)^2}{2\sigma_\Gamma^2}\right], \tag{3}$$

where Γ_0 is the width of the most probable Lorentzian, σ_Γ is the standard deviation of the distribution of $\ln\Gamma$, and the weights g_i satisfy the condition $\Sigma g_i = 1$.

For a threefold rotation, the elastic incoherent structure factor, $A_0(Q)$, is

$$A_0(Q) = \tfrac{1}{3}[1 + 2j_0(\sqrt{3}Qr)], \tag{4}$$

where $j_0(x)$ is a zero-order spherical Bessel function and r is the distance between the moving protons and the rotation axis (1.032 Å).

PDMS is a semicrystalline polymer and therefore segmental motion is expected to be very slow at least up to T_m. Thus, for $T < T_m$ the only contribution to the quasielastic broadening arises from hopping of the CH$_3$ groups over the potential barrier. Our QENS data up to $T = 215$ K are well represented by Eqs. (2) and (4).

Similarly to other sub-T_g relaxations, the temperature dependence of Γ_0 follows an Arrhenius law which is clearly in contrast to the non-Arrhenius dynamics of many viscous liquids close to T_g [18]:

$$\Gamma_0 = \Gamma_\infty \exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

yielding the activation energy E_a. The width of the distribution of rotational frequencies σ_Γ depends on temperature unlike the corresponding width of the distribution of activation energies σ_E up to 215 K. We find $E_a = (4.5 \pm 0.5)$ kJ/mol and $\sigma_E = (1.1 \pm 0.1)$ kJ/mol. The attempt to escape frequency is $\Gamma_\infty = 0.63$ meV. These results are in excellent agreement with our analysis of elastic window scan data [15].

Motion of a polymer molecule above T_m (or, for an amorphous polymer, above T_g) is characterized by segmental dynamics and diffusion: broadening of the elastic line is observed at a temperature where the frequency of the motion becomes comparable to the instrumental resolution. Early QENS studies tested the validity of the Rouse model through the scattering law calculated by de Gennes [19] who showed that the intermediate scattering function $I(Q, t)$ is proportional to $\exp[-(\frac{t}{\tau_R})^{0.5}]$, where τ_R is a Q-dependent relaxation time. This $t^{0.5}$ dependence leads to a non-Lorentzian shape of $S_{\text{inc}}(Q, \omega)$ with a quasielastic broadening whose width should vary with Q^4, in the distance scale between the entanglement length and the segment length.

At shorter distances, deviations from the Rouse model are expected and, depending on the monomer structure, various relaxation processes and the intrinsic chain stiffness may need to be considered, as discussed by us [14]. In a simplistic view, at $Q > b^{-1}$, with a segment length b of the order of a few Å, the scattering patterns should be Lorentzian [corresponding to an exponential decay of $I(Q, t)$] due to the short time Brownian diffusion of the single beads. These deviations should be observable within the time and distance range probed by neutron scattering, and particularly through QENS, as indeed found for polyisobutylene and poly(propylene oxide) [20]. In PDMS melts, a similar crossover was identified in one report at $Q = 0.15$ Å^{-1} [21], while other data [13,20] followed the Rouse predictions up to large Qs, actually beyond the range of validity of the model.

In the following we show that the discrepancy between experiment and theoretical predictions is fortuitous.

It is now customary for polymer melts to use as model function the stretched exponential or Kohlrausch-Williams-Watts (KWW) function:

$$I_{\mathrm{inc}}(Q, t) \propto \exp\left[-\left(\frac{t}{\tau_s}\right)^{\beta}\right] \tag{6}$$

characterized by two parameters: (a) the characteristic time τ_s and (b) the exponent β which provides a measure of the nonexponentiality, related to the shape and width of the distribution ($0 < \beta < 1$). Such a function could be simply viewed as a generalization of the Rouse model, which is recovered for $\beta = 0.5$. Incidentally, we point out that the KWW function is often used to empirically describe the response function of liquids close to T_g [18], while in polymers it is simply a result of chain connectivity. Recently, we established a link between chain stiffness and β [14] by fitting theoretical $I(Q, t)$ curves with the KWW function for coarse-grained models and for realistic PDMS chains within the rotational isomeric state scheme. In all cases, at large Qs, we obtained β values that were significantly larger than the theoretical lower limit 0.5. That work provides a starting point to the present analysis.

Following earlier studies carried out on PDMS [20,21], we initially neglected the CH_3 contribution and fitted the QENS data using as model function the Fourier transform of the KWW. Although the QENS spectra are well represented by a KWW with $\beta = 0.45$ (Q and temperature independent) (Fig. 1) [22,23], this result is inexplicable in terms of the $t^{0.5}$ dependence of the Rouse model due to the very small distance scale probed. The shortcomings of this model have been pointed out [24] and the experimental QENS data were explained in terms of the mode-coupling theory for local motion. Here, we take a different view, motivated by our recent work [14].

Our study indicated that β should increase to about 0.65 at large Q and we argued that either the very large flexibility of the Si-O-Si bond angle or the internal structure of the monomers could explain the discrepancy between predicted and experimental β values. In particular, the contribution from the CH_3 motion may not be negligible. Therefore, we fitted the QENS data explicitly considering two dynamic processes: (a) fast methyl group reorientations giving rise to a broad quasielastic component and (b) a slower process due to segmental motion, defined by the Fourier transform of the KWW function. The CH_3 motion is still described through Eq. (2) using the most probable width Γ_0 obtained from extrapolation of Eq. (5) to the desired temperature. The width of the distribution of Γ_i, σ_Γ was calculated from the low temperature data using the relationship $\sigma_\Gamma = \sigma_E/RT$. It is implicit in this procedure that there is no substantial change in the CH_3 motion below and above T_m. Figure 2 gives an example of data fitting for $Q = 1.45$ Å^{-1}, at 275 K. Although most parameters were fixed, the model gives an excellent representation of the experimental data. The β parameter for the segmental motion was found to be Q and T independent and equal to 0.61, in good agreement with our theoretical predictions [14]. We conclude that, if we also consider any underlying fast process (CH_3 rotation in this case), the local dynamics can be predicted by realistically accounting for chain stiffness.

In addition, we stress that (i) the characteristic time τ_s of the KWW function follows an Arrhenius temperature dependence, unlike glass-forming liquids close to T_g with a fragile behavior [18]; (ii) from the temperature dependence of τ_s, we obtain an activation energy for the segmental motion equal to 14.6 kJ/mol that is in excellent agreement with our viscosity measurements [15] (inset of Fig. 3); (iii) the $I(Q, t)$ data obey time-temperature superposition with shift factors in agreement again with rheological measurements [15] (Fig. 3). The time shifted $I(Q, t)$ curves can also be fitted by the same model function used in the frequency domain (i.e., using

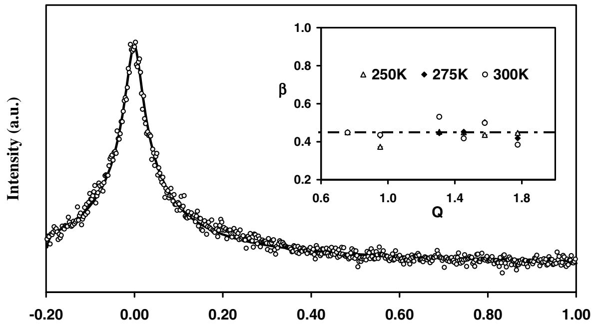

FIG. 1. QENS data of PDMS for $Q = 1.45$ Å^{-1} at 275 K (○) and fit. Inset: Q and temperature dependence of the β parameter.

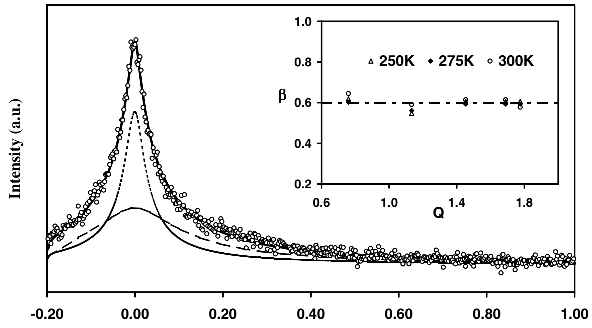

FIG. 2. QENS data of PDMS for $Q = 1.45$ Å^{-1} at 275 K (○). Lines are fits using a model function that consists of broad (dashed line) and narrow components (dotted line).

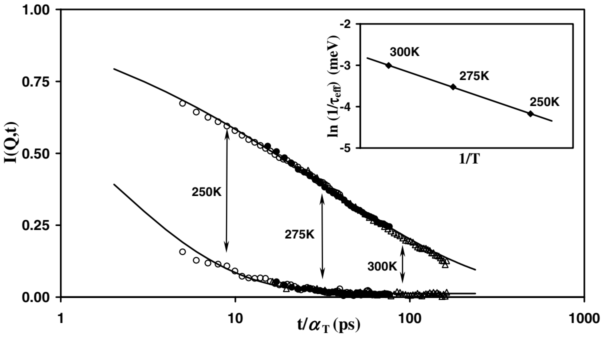

FIG. 3. Time-temperature superposition of $I(Q, t)$ data at 250 K (○), 275 K (●), and 300 K (△) (reference temperature: 303 K). The Q values are 0.55 $Å^{-1}$ (top) and 1.58 $Å^{-1}$ (bottom). The lines correspond to fits to the experimental data (see text). Inset: Arrhenius behavior of $1/\tau_{eff}$ in meV, characterizing the segmental motion.

two components) leading to similar results for the KWW parameters.

Therefore, QENS measurements provide valuable information on local dynamics of PDMS chains. Below T_m, the local dynamics is due to reorientational motion of CH_3 groups. Above T_m, the contribution from the fast CH_3 rotations is far from negligible when compared to the segmental motion. Once these rotations are properly accounted for, one finds good agreement between experimental β values for the segmental dynamics and those predicted theoretically [14].

In conclusion, synthetic and natural polymers show complex dynamic behavior with different molecular processes often contributing simultaneously to the observed dynamics. In this Letter, due to the semicrystalline nature of the polymer under study, we have been able to separate two different dynamic contributions. This procedure allowed us to make a direct comparison between experimental data and theoretical predictions and to achieve a unified picture of macroscopic properties and small scale, microscopic dynamics.

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