Isotope effect on the rotational tunneling transitions of methyl groups in glassy polymers

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(Received 4 August 1998)

By using selectively deuterated samples of poly(methyl methacrylate) (PMMA) and exploiting the strong isotope effect on the rotational tunneling of symmetric molecular groups, we show that the quasielastic neutron scattering observed at low temperature ($T \approx 2$ K) in the glassy polymers poly(vinyl acetate) and PMMA can unambiguously be assigned to rotational tunneling transitions of the ester methyl group. The experimental results are quantitatively described, without adjustable parameters, in the framework of the rotation-rate-distributed-model for methyl group dynamics in glassy polymers. [S0163-1829(99)03711-X]

Quantum rotational tunneling describes the phenomenon of the librational states of a molecule whose rotating atoms are indistinguishable, being the energy states multiplets. The splitting between substates is called tunnel splitting. Quantum rotational tunneling of symmetric molecular groups such as methyl groups is nowadays well established in crystalline low molecular weight materials, but still not in glassy systems like amorphous polymers.[1-3] Rotational tunneling transitions are accessible at low temperatures ($T < 50$ K) by various spectroscopic methods such as nuclear magnetic resonance (NMR), optical spectroscopy using the hole burning technique, and infrared spectroscopy. However, no method yields such direct model independent insight into the system as inelastic neutron scattering (INS), although, due to the limited instrumental resolutions currently available, the range of stronger potentials cannot be investigated by this technique. By means of INS the tunneling transitions of crystalline samples are directly observed as inelastic peaks in the μeV range of the measured scattering spectra at low temperature. Searching for tunneling effects in glassy systems, we have reported in a recent paper[4] on low-temperature INS measurements carried out by high-resolution backscattering techniques on a well known glassy polymer: poly(vinyl acetate) (PVAc). This polymer has an ester methyl group in its monomeric chemical structure, showing a rather low average barrier (≈ 450 K) for classical rotation. The experimental spectra $S(Q, \omega)$, where $\hbar Q$ and $\hbar \omega$ are the momentum transfer and the energy transfer, respectively, measured at $T = 2.4$ K showed a clear quasielasticlike broadening instead of the expected inelastic tunneling peaks. This quasielastic feature, which at this very low temperature cannot be understood in terms of classical hopping processes, was considered the first direct experimental evidence of quantum rotational tunneling of methyl groups in glassy solids. These results were interpreted in the framework of a model, the rotation-rate-distribution-model (RRDM),[5,6] which takes into account a distribution of potentials associated with the disorder inherent to the amorphous state. This distribution of potentials implies both a distribution of activation barriers for random hopping of methyl groups in the classical regime (high temperature) and a distribution of the tunneling frequencies in the quantum regime (low temperature). The distribution of tunneling frequencies, calculated from the measured distribution of activation barriers, turns out to be rather asymmetric with the maximum located in the very low energy range and with a long tail extending into the high energy range. Due to the limited instrumental resolution of neutron spectrometers, only this high-energy tail would be visible in the measured scattering spectra, even using the instrument IN16 (ILL, Grenoble, France) which is the backscattering spectrometer showing the best instrumental resolution currently available. This should explain why an apparent quasielastic feature is observed instead of a broad inelastic peak.

In spite of this successful interpretation, it is clear that a direct experimental proof of rotational tunneling of methyl groups would be desirable. In this paper, by using selectively deuterated polymer samples and taking advantage of the strong isotope effect for rotational tunneling transitions,[1-3] we show that the apparent quasielastic broadening measured at low temperature can unambiguously be assigned to methyl group rotational tunneling. Moreover, the obtained results are also quantitatively interpreted in the framework of the RRDM.

The tunnel splitting of the different torsional levels of a given methyl group can be calculated by solving a stationary Schrödinger equation which for a pure threefold potential $[V(\phi) = V_3(1 - \cos 3\phi)/2]$ takes the form of the well-known Mathieu equation.[1-3] The solutions allow one to correlate the values of the potential parameter V_3 with the corresponding values of the ground-state tunnel splitting (tunnel frequency), $\hbar \omega_t$. This splitting decreases almost exponentially with the increase of the potential strength. In the range of potentials which are relevant for neutron spectroscopy, an approximate relationship can be established as

$$\hbar \omega_t = c \left(\frac{V_3/B}{d} \right)^{0.75} \exp\left[-\left(\frac{V_3/B}{d} \right)^{0.5} \right] \quad (1)$$

TABLE I. Scattering cross sections of the samples investigated and of the different nucleus present. The MG subscript refers to the methyl group protons (or deuteriums).

	σ^{incoh}	σ^{coh}	σ_{MG}^{incoh}	σ_{MG}^{coh}
H	80.3	1.8		
D	2.0	5.6		
C	0.0	5.5		
O	0.0	4.2		
PMMA-d5	250.9	69.3	240.9	5.4
PMMA-d8	16.0	80.7	6.0	16.8

FIG. 1. Logarithmic representation of the neutron scattering spectra of PMMA-d5 (circles) and PMMA-d8 (triangles) samples as measured by IN16 at $T=1.4$ K and $Q=1.8$ Å^{-1}. The thin solid line is the resolution of IN16.

with c and d phenomenological parameters whose values depend on the energy range considered. A similar expression, but in terms of the activation energy (i.e., the energy difference between the top of the barrier V_3 and the ground state), was previously proposed in Ref. 4. In the range of interest here, $10 < V_3/B < 200$, we found $c=2.58$ meV and $d=0.580$. $B=\hbar^2/2I$ is the rotational constant of the methyl group, where I is the moment of inertia. It is evident from Eq. (1) that the relevant rotational potential is the absolute potential scaled by the rotational constant B. The value of B for a $-CH_3$ group is 7.6 K, while for $-CD_3$ it is 3.8 K. Therefore, deuteration of a protonated methyl group doubles the relevant scaled rotational potential. The exponential dependence of Eq. (1) clearly shows that there is a uniquely strong isotope effect for tunneling transitions compared to other lattice modes.

With these ideas in mind, we have carried out low-temperature INS measurements on a well-known polymer: poly(methyl methacrylate) (PMMA) $[-CH_2-(CH_3)C(COO-CH_3)-]$, by means of a high-resolution spectrometer. PMMA was chosen instead of the system previously investigated, PVAc, because, in contrast to PVAc, samples of PMMA with similar characteristics (microstructure, molecular weight, glass transition temperature, etc.) but with different isotopic substitutions can easily be synthesized. On the other hand, PMMA has an ester methyl group showing a high-temperature dynamic behavior similar to the ester methyl group of PVAc.[6] Therefore, we should also expect a similar behavior in the low-temperature quantum regime. Two different PMMA samples have been used in this investigation: PMMA-d5 and PMMA-d8. In the case of PMMA-d5, all but the ester methyl group protons have been replaced with deuterium. In the case of PMMA-d8 sample, all the protons of the sample have been replaced by deuteriums. In this way, the scattering of the PMMA-d5 sample is dominated by the incoherent contribution of the protons of the ester $-CH_3$ because the incoherent cross section of a proton is much higher than the coherent one and also higher than the incoherent and coherent cross sections of the rest of the atoms in the sample (see Table I). This would allow an unambiguous assignment of the scattering effects observed to the ester methyl group. On the other hand, a strong suppression of the apparent quasielastic scattering reflecting the methyl group quantum dynamics is expected in the case of the PMMA-d8 sample due to both the isotope effect on the rotational tunneling transitions and the incoherent cross section of deuterium. The measurements were carried out by means of the new backscattering spectrometer,
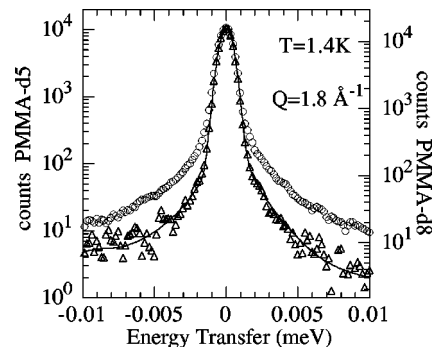
IN16 at the Institute Laue-Langevin (ILL, Grenoble), which, at an incident wavelength λ of 6.27 Å and with deformed Si(111) as monochromator and analyzer, provides a resolution of nearly Gaussian shape with a half-width at half-maximum of ≈ 0.45 μeV. This makes the instrument very sensitive to small quasielastic wings close to the elastic line. Flat samples of appropriate thickness (0.75 mm for PMMA-d5 and 0.85 mm for PMMA-d8) in order to get a transmission higher than 90% were used, thus allowing us to neglect multiple scattering effects. The experimental spectra $S(Q,\omega)$ were recorded in the Q range from 0.2 to 1.9 Å^{-1} and at a temperature of $T=1.4$ K. The experimental resolution function was obtained from measurements at 1.4 K of a sample of vanadium, which in the instrumental window of IN16 only shows pure elastic scattering. The raw data were corrected for detector efficiency and sample container.

Figure 1 shows the scattering function $S(Q,\omega)$ measured on the two different PMMA samples investigated at a Q value of 1.8 Å^{-1}. Similar results are obtained for other Q values in the range investigated. The measured instrumental resolution, $R(Q,\omega)$, is also included in the figure for comparison. The $S(Q,\omega)$ corresponding to the PMMA-d5 sample shows a clear quasielasticlike broadening, which is similar to that reported for fully protonated PVAc.[4] Since in the PMMA-d5 sample the scattering is mainly due to the incoherent contribution from the protons of the ester methyl group, the observed quasielastic feature should be due (at $T=1.4$ K) to tunneling effects of such a group. Figure 1 also shows that the measured $S(Q,\omega)$ corresponding to the fully deuterated PMMA-d8 sample is close to the resolution function, showing up a strong isotope effect. However, the measured $S(Q,\omega)$ contain contributions from scattering centers other than methyl group protons (or deuteriums).

Therefore, in order to properly check the isotope effect, it would be desirable to compare the experimental scattering function from the methyl group protons (or deuteriums) instead of the total experimental scattering shown in Fig. 1. At low temperature, the contributions from scattering centers other than methyl group protons (or deuteriums) may be assumed to be elastic. On the other hand, the coherent contributions from methyl group protons (or deuteriums) can also be assumed to be elastic due to the symmetry-equivalent methyl group orientations. Therefore the measured $S(Q,\omega)$ can be written in a general form as
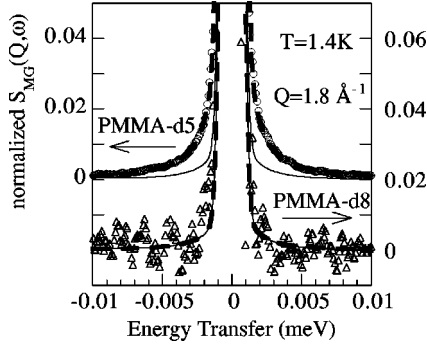
FIG. 2. Normalized methyl group incoherent contribution $S_{MG}(Q,\omega)$ to the measured scattering intensities shown in Fig. 1. The thick dashed lines correspond to the $S_{MG}(Q,\omega)$ calculated by the RRDM for PMMA-d5 and PMMA-d8 samples. The thin solid lines are the resolution of IN16.

$$S(Q,\omega) \propto \{[\sigma^{coh}S(Q)+(\sigma^{incoh}-\sigma_{MG}^{incoh})]R(Q,\omega)$$
$$+\sigma_{MG}^{incoh}S_{MG}(Q,\omega)\}, \qquad (2)$$

where $S_{MG}(Q,\omega)$ is the experimental incoherent scattering function of methyl group protons (or deuteriums). The structure factor, $S(Q)$, is introduced as a correction factor of the total elastic coherent contribution.

$S(Q)$ of the samples PMMA-d5 and PMMA-d8 was measured by spin polarization analysis on D7 spectrometer at the ILL (the results will be published elsewhere). The values of $S(Q)$ at $Q=1.8$ Å^{-1} are about 0.6 and 1 for PMMA-d5 and PMMA-d8, respectively. Taking into account these values and those of the scattering cross sections given in Table I, we can obtain $S_{MG}(Q,\omega)$ from the measured $S(Q,\omega)$. The results obtained are shown in Fig. 2. Similar results are obtained for other Q values in the Q range investigated. In spite of the low incoherent scattering intensity of the PMMA-d8 sample, which produces a rather high uncertainty in the spectrum, a strong suppression of the quasielasticlike scattering from the methyl groups in the PMMA-d8 is also evident in $S_{MG}(Q,\omega)$. This strong isotope effect clearly supports the assignment of the apparent quasielastic broadening to the tunneling transitions of the ester $-CH_3$.

Now we can check whether the results obtained can quantitatively be interpreted in terms of rotational tunneling transitions. To do this, we will use the framework of the RRDM which was first proposed[5] for explaining the classical regime of methyl group dynamics in glassy polymers and later on extended[4] to the quantum regime. This model is based on the fact that due to the structural disorder inherent in amorphous systems in general, the methyl groups in glassy polymers have different local environments which give rise to a distribution of potentials for methyl group rotation. This distribution manifests itself in a distribution of activation energies for classical methyl group rotation at high temperature, as well as in a distribution of tunnel splitting (frequencies) which dominates the methyl group dynamics in the low-temperature range ($T<50$ K). When a pure threefold potential is assumed, the tabulated solutions of the Mathieu equation easily allow one to correlate the strength of the threefold potential V_3, the activation energy E, and the ground-state tunneling frequency $\hbar\omega_t$ [see, for example, Eq. (1)]. By means of these correlations it is quite straightforward to

transform a given distribution of potentials or activation energies into the corresponding distribution of ground-state tunnel frequencies.

For several polymers, including PMMA, the classical hopping processes of methyl groups have been investigated at high temperature by means of INS and interpreted in terms of the RRDM.[5,6] From the analysis of the experimental data, a Gaussian distribution of activation energies is found $g(E)=(\sigma_E\sqrt{2\pi})^{-1}\exp[-(E-E_0)^2/2\sigma_E^2]$. The values of the average activation energy E_0 and the width of the distribution σ_E for different polymers are reported in Ref. 6. For the particular case of PMMA, these values are $E_0=710$ K and $\sigma_E=241$ K. From these values, the corresponding distribution of potentials $G(V_3)$ can easily be calculated due to the linear relationship between E and V_3. In the range of E which is of interest here, 50 K$<E<1500$ K, this linear relationship reads as $V_3=44+1.1E$ (calculated from the tabulated data of Ref. 3). The distribution of potentials calculated as $G(V_3)=g(E)dE/dV_3$ also shows a Gaussian shape but with an average value of $V_{3,0}=823$ K and a width of $\sigma_{V_3}=267$ K. Now, starting from this Gaussian distribution of potentials, the corresponding distribution of ground-state tunneling frequencies $h(\hbar\omega_t)$ for both $-CH_3$ (PMMA-d5 sample) and $-CD_3$ (PMMA-d8 sample) groups can be obtained as $h(\hbar\omega_t)=-G(V_3)dV_3/d(\hbar\omega_t)$. The term $dV_3/d(\hbar\omega_t)$ can be easily calculated using Eq. (1) with $B=7.6$ K for $-CH_3$ and $B=3.8$ K for $-CD_3$. The resulting $h(\hbar\omega_t)$ are shown in Fig. 3. The first relevant feature is that, as in the case of PVAc,[4] these distributions are rather asymmetric with the maximum located at very low values of $\hbar\omega_t$ ($\approx 8\times10^{-3}$ μeV for $-CH_3$ and $\approx 2\times10^{-4}$ μeV for $-CD_3$). It is clear that these values are much lower than the resolution of the IN16 spectrometer (indicated by an arrow in the figure) and thereby cannot be resolved from the instrumental resolution. Only the tail of such distributions can contribute to the experimental scattering spectra, giving rise to the apparent quasielastic feature observed in $S_{MG}(Q,\omega)$.

Figure 3 clearly shows that the tail of $h(\hbar\omega_t)$ contributing to the experimental $S_{MG}(Q,\omega)$ [i.e., the area under $h(\hbar\omega_t)$ for $\hbar\omega_t$ higher than the IN16 resolution] is rather different in both cases, being almost zero in the case of $-CD_3$. Now, starting from these distributions, we can calculate, in the framework of the RRDM, the experimental incoherent scattering curves corresponding to methyl group protons (or deu-
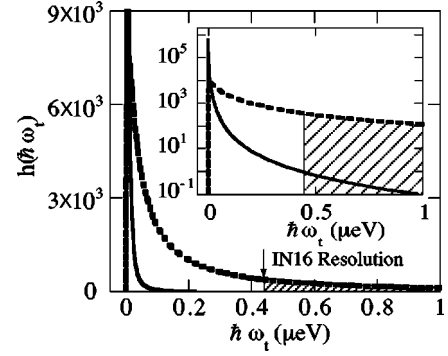

FIG. 3. Calculated distribution of tunneling frequencies for PMMA-d5 (solid line) and PMMA-d8 (dashed line) samples. The inset shows these distributions on a logarithmic scale.

teriums), $S_{MG}(Q,\omega)$. These can be written as $S_{MG}(Q,\omega) = R(Q,\omega) \otimes S_{RRDM}(Q,\omega)$, where the symbol $\otimes$ means convolution product and $S_{RRDM}(Q,\omega)$ is the RRDM scattering function for quantum tunneling of methyl groups, which is constructed[4] by generalizing the one proposed in Refs. 1–3 with a continuous distribution of tunneling frequencies. This function reads as

$$S_{RRDM}(Q,\omega) = [\tfrac{5}{3} + \tfrac{4}{3} j_0(Qr)] \delta(\omega) + \tfrac{2}{3} [1 - j_0(Qr)]$$
$$\times \int_0^\infty h(\hbar\omega_t)[\delta(\omega+\omega_t) + \delta(\omega-\omega_t)]$$
$$\times d(\hbar\omega_t), \tag{3}$$

where j_0 is the zeroth-order Bessel function and r is the hydrogen-hydrogen distance in the methyl group. The calculated $S_{MG}(Q,\omega)$ for the two samples, PMMA-d5 and PMMA-d8, are shown in Fig. 2 in comparison with the experimental functions. It is evident that the agreement is extremely good taking into account that there are not adjustable model parameters [only a scaling factor is considered, to match the intensities at the maxima of $S(Q,\omega)$]. This good agreement found between the experimental data and the model function is also present in the whole Q range available.

In summary, we have shown that by exploiting the strong isotope effect on the rotational tunneling transitions, the apparent quasielastic feature observed by neutron scattering at very low temperature in PVAc and PMMA can be unambiguously assigned to rotational tunneling of methyl groups. The RRDM, with the distribution functions of potentials deduced from the high-temperature classical regime, quantitatively gives account of the experimental observations in the low-temperature quantum regime, including the isotope effect.

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