Rotation of Methyl Side Groups in Polymers: A Fourier Transform Approach to Quasielastic Neutron Scattering. 1. Homopolymers

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ABSTRACT: The rotational motion of the ester methyl group in poly(methyl methacrylate) (PMMA) was investigated using quasielastic neutron scattering (QENS). A comparison between our results and the QENS data reported in the literature for PMMA-d_5 indicates that the amount of quasielastic broadening is highly dependent upon the energy resolution of the spectrometer. This anomalous behavior is here attributed to the method of analysis, namely, the use of a single rotational frequency. Such a procedure leads to a non-Arrhenius temperature dependence, to a temperature-dependent elastic incoherent structure factor, and to values of rotational frequency which are resolution dependent. We propose an alternative approach to the analysis of the QENS data which accounts for the existence of a distribution of rotational frequencies. The frequency data are Fourier transformed to the time domain, and the intermediate scattering function is fitted using a stretched exponential or Kohlraush–Williams–Watts function. The excellent overlap between data from different spectrometers leaves no doubt on the adequacy of our procedure. Measurements of the ether methyl group rotation in poly(vinyl methyl ether) (PVME) are also reported. The PVME data confirm that the behavior observed for PMMA-d_5 is likely to be a common feature to all polymeric systems.

1. Introduction

The polymer chain backbone is frozen into rigid conformations in the glassy and crystalline states. Any long-range motion ceases below the glass transition temperature T_g although some dynamics still persists on a more local scale. Vibrations of atoms about their lattice sites and/or rotations of side groups about the chemical bonds which attach them to the main chain may occur. The study of side group reorientations is vital for characterizing the mechanical behavior of glassy polymers.

Side chain motion in polymers has been investigated using a variety of experimental techniques, especially nuclear magnetic resonance, mechanical and dielectric relaxation techniques, and neutron scattering in an attempt to associate the observed relaxations with specific molecular mechanisms.[1] The choice of the experimental technique depends both on selection rules and on the frequency range available.

The rotational barrier for methyl groups is usually of the order of a few kJ mol^{-1}, much lower than that of other side groups. It gives rise to a fast rotational motion which can be easily observed by neutron scattering. Both incoherent inelastic neutron scattering (IINS) and quasielastic neutron scattering (QENS) have been employed to investigate the rotational motion of side groups.[2–5] The first technique allows the barrier height hindering the CH_3 group reorientation to be determined from the vibrational frequencies, whereas the second technique gives the rotational scattering law. This contains detailed information both on the frequency of the rotation and, through the elastic incoherent structure factor (EISF), on the geometry of the motion.

IINS spectroscopy has been successfully used in the past to measure the fundamental torsional frequencies of methyl groups in a number of polymers such as poly(propylene oxide), poly(propylene), poly(methyl methacrylate) (PMMA), and poly(dimethylsiloxane) (PDMS).[2,3] In all these experiments the use of deuterium labeling has proven to be extremely advantageous for an unambiguous identification of the torsional mode. The potential barrier for hindered CH_3 rotations was calculated from the IINS frequencies. However, these calculations rely on a knowledge of the shape of the potential barrier hindering the rotation. A threefold symmetry is generally assumed for CH_3 reorientations.

Alternatively, the rotational hopping of methyl groups between equivalent sites over the potential barrier can be observed by quasielastic neutron scattering. A study of the temperature dependence of the rotational frequency gives a measure of the activation energy, which is related to the height of the potential barrier. Detailed information on the shape of the potential barrier can be inferred.

Only a few QENS studies on CH_3 rotational motions in polymeric systems have been reported in the literature.[6–11] These include a study of the rotational motion of the ester methyl group in PMMA[6,7] and of methyl group rotations in poly(propylene oxide),[8] poly(methylphenylsiloxane),[9] poly(vinyl methyl ether) (PVME),[10] and 1,4-polybutadiene.[11]

Early studies of the rotational motion of the ester methyl group in PMMA reported by Gabrys et al. showed a peculiar temperature dependence of the width

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of the quasielastic component.[6] Plots of full width at half-height (fwhh), 2Γ, versus inverse temperature did not follow a simple Arrhenius law: an apparent activation energy was measured which varied from 7 kJ mol^{-1} at room temperature to 1 kJ mol^{-1} at 150 K.[6]

At room temperature, the rotational motion of the ester CH_3 was successfully explained by a purely threefold potential. However, it was observed that at low temperature 2Γ values were higher than predicted from an Arrhenius law. Both quantum mechanical tunneling and the inclusion of higher terms in the Fourier series expansion of the potential associated with the methyl group rotation were discussed as possible ways to explain the peculiar temperature dependence. The latter explanation was preferred.[12] It was in fact argued that the onset of nonlinearity of the $\ln(2\Gamma)$ versus $1/T$ plots occurred at too high a temperature (125 K) for tunneling to be effectively dominating the relaxation process. Tunneling should not be observable above 70 K.

Further studies[13,14] on the high-resolution backscattering spectrometer *IRIS* (Rutherford Appleton Laboratory) gave values of 2Γ which were much lower than those previously determined by Gabrys et al.[6] The results seemed at first to indicate the occurrence of two distinct processes and to support the idea of a non-purely threefold potential barrier.

In this work we present QENS data of the ester CH_3 group in PMMA and the methyl group rotation in PVME as measured on different spectrometers at energy resolutions ranging from 15 to 170 μeV. It will be shown that values of rotational frequency measured from the QENS spectra analyzed in terms of a single rotational frequency are resolution dependent. Although this procedure has been successfully employed to analyze side group rotations in molecular crystals, for polymers, it produces inconsistent results. First the rotational frequency does not follow a simple Arrhenius law, secondly it depends on the energy resolution of the spectrometer, and thirdly the EISF which is measured in this way is higher than predicted from theoretical models.

In agreement with recent publications,[10,11] we suggest that, due to the absence of crystallinity in polymers, there exists a distribution of rotational frequencies for the methyl groups.

Two different approaches have been recently used. Chahid et al.[10] fitted the QENS spectra of PVME to a Gaussian distribution of rotational frequencies. Similarly, a Gaussian distribution of activation energies was used by Frick et al.[11] to analyze the temperature dependence of the elastic window scan in selectively deuterated 1,4-polybutadiene.

Here we propose an alternative approach. The frequency data are converted to time by fast Fourier transform (FFT) and the time-domain data are fitted using a distribution of relaxation times. By using this method, we show that the spectroscopic data measured on different instruments overlap at a given temperature and scattering vector Q. Furthermore, the EISF is no longer temperature dependent and agrees with calculated values for a threefold rotation. Any difference due to instrumental resolution disappears.

Direct analysis of the QENS spectra relative to the ester CH_3 rotation in PMMA has been already presented in refs 6, 7, 13, and 14. Here we only highlight the inconsistencies of the single rotational frequency analysis and we add a few unpublished results from the spectrometers *MIBEMOL* (Laboratoire Leon Brillouin, Saclay) and *QENS* (IPNS, Argonne National Laboratory, U.S.A.). Unpublished data of PVME are reported in section 4.2. The results of the FFT data analysis are discussed in section 5.

2. Rotational Motion by QENS[15-17]

In a neutron scattering experiment the scattered intensity is analyzed as a function of both energy and momentum transfer Q ($=4/\pi \sin(\theta/2)$, θ being the scattering angle). The quantity measured experimentally is the double differential scattering cross section $d^2\sigma/(dE\ d\Omega)$ which represents the probability that a neutron is scattered with energy change dE into the solid angle $d\Omega$. The cross section σ includes both coherent and incoherent contributions. However, since the incoherent cross section of hydrogen is much larger than those of other atoms contained in polymer molecules, when protonated samples are used, one mainly observes the incoherent scattering from hydrogens.

The rotation of side groups with fixed center of mass (i.e., below the glass transition temperature) gives rise to a Doppler broadening of the elastic line. The scattered intensity therefore consists of two components:

$$S_{\mathrm{inc}}^{\mathrm{rot}}(Q,\omega) = A_0(Q)\ \delta(\omega) + S_{\mathrm{inc}}^{\mathrm{qel}}(Q,\omega) \qquad (1)$$

a purely elastic component, $A_0(Q)\ \delta(\omega)$, and a quasielastic line, $S_{\mathrm{inc}}^{\mathrm{qel}}(Q,\omega)$. $A_0(Q)$, the so-called elastic incoherent structure factor (EISF), provides a measure of the time-averaged spatial distribution of the protons which completely characterizes the geometry of the rotational motion.

The theory for side group rotations in molecular crystals is well developed, and expressions for the scattering law, $S_{\mathrm{inc}}^{\mathrm{rot}}(Q,\omega)$, have been derived for a variety of systems.[15-17] Generally, the jump reorientational model is applied where it is assumed that the atoms undergo librational motions during an average time τ after which they jump within a set of preferred orientations. The jumps are assumed to be instantaneous.

The rotational motion of methyl groups can be represented by instantaneous jumps between three equidistant sites on a circle of radius r, as implied by the threefold symmetry. When all orientations are equally probable, the incoherent scattering law becomes

$$S_{\mathrm{inc}}^{\mathrm{rot}}(Q,\omega) = A_0(Q)\ \delta(\omega) + \frac{1}{\pi}[1 - A_0(Q)]L(\omega) \qquad (2)$$

where $A_0(Q)$, the EISF, is now expressed by

$$A_0(Q) = \frac{1}{3}[1 + 2j_0(3^{1/2}Qr)] \qquad (3)$$

$j_0(x)$ being the zero-order spherical Bessel function and $L(\omega)$ a Lorentzian function:

$$L(\omega) = \frac{2\tau/3}{1 + \omega^2(2\tau/3)^2} = \frac{\Gamma}{\Gamma^2 + \omega^2} \qquad (4)$$

The full width at half-height (fwhh) defined by the above equation is equal to 2Γ or $3/\tau$, τ being the average time between two consecutive jumps. Expressions analogous to eq 3 can be obtained for different symmetries or more complex rotations.

As indicated in eq 4, τ is Q independent. Its temperature dependence is given in terms of the Arrhenius

law:

$$\tau = \tau_0 \exp(E_a/RT) \tag{5}$$

where E_a represents the activation energy which is related to the height of the potential barrier hindering the rotational motion.

Experimentally, $S_{inc}^{rot}(Q,\omega)$ is folded with the instrumental resolution and it is a common procedure to convolute the resolution with a model function in order to fit the QENS spectra. The EISF is then extracted from the fitting parameters using the relationship

$$\text{EISF} = \frac{I_{el}}{I_{el} + I_{qel}} \tag{6}$$

where I_{el} and I_{qel} represent the integrated elastic and quasielastic intensity, respectively. The accuracy of the experimental value clearly depends on how well the quasielastic broadening can be separated from the resolution and from the background, apart of course from the validity of the model function itself.

The procedure of data analysis outlined above has been successfully applied to side group rotations in molecular crystals. Similarly, early experiments on polymeric materials exploited the same model functions. As will be discussed in the following sections, it has become clear that when the QENS spectra are analyzed using a single Lorentzian line (and hence assuming a single relaxation process) a series of inconsistencies arises: the rotational frequency shows a non-Arrhenius behavior, it is resolution dependent, and the EISF is temperature dependent.

It is well known that relaxation processes in glass-forming materials cannot be expressed in terms of a single exponential relaxation time.[1,18] In general, the relaxation process is described as the sum of elementary processes, each one characterized by a relaxation time τ. The relationship between the distribution of relaxation times $\varrho(\tau)$ and the relaxation function $\phi(t)$ is given by

$$\phi(t) = \int_0^\infty \varrho(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau \tag{7}$$

Usually, the experimental data are expressed in terms of empirical functions. One which has been widely accepted is the Kohlrausch–Williams–Watts (KWW) function,[19,20] not least because theoretical models explaining nonlinear relaxations make use of the KWW parameters.

The KWW function, also called the stretched exponential function,

$$\exp\left(-\frac{t}{\tau_c}\right)^\beta \tag{8}$$

is characterized by two parameters: the characteristic time τ_c and the exponent β, an empirically determined parameter varying between 0 and 1 which gives a measure of the nonexponentiality.

If the KWW function is assumed to arise from the superposition of exponential processes individually characterized by an exponential behavior, then the following relationship holds:

$$\exp\left(-\frac{t}{\tau_c}\right)^\beta = \int_0^\infty \exp\left(-\frac{t}{\tau}\right) \varrho(\tau)\, d\tau \tag{9}$$

The distribution of relaxation times $\varrho(\tau)$ can be determined from the relaxation function $\phi(t)$ via inverse Laplace transform.[21] For a given β, $\varrho(\tau)$ can be expressed by a series of the form

$$\varrho(\tau) = -\frac{\tau_c}{\tau^2 \pi} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \sin \pi\beta k\, \Gamma(\beta k+1) \left(\frac{\tau}{\tau_c}\right)^{\beta k+1} \tag{10}$$

where Γ represents a gamma function.

It will be shown in the following sections that, due to the absence of crystallinity in amorphous glassy polymers, the existence of a distribution of rotational frequencies cannot be neglected for a correct analysis of the QENS spectra. This concept is now well established in NMR data analysis but has only recently been adopted to treat QENS data.[10,11]

A Gaussian distribution of correlation times was used by Chahid et al.[10] to fit the PVME data. The rotational scattering law was expressed by the following equation:

$$S_{inc}^{rot}(Q,\omega) = A_0(Q)\, \delta(\omega) + [1 - A_0(Q)] \sum \frac{1}{\pi} g_i L_i(\omega) \tag{11}$$

where $L_i(\omega)$ is a Lorentzian function whose weight is given by g_i. The distribution of rotational frequencies was described by Chahid et al.[10] as a log-Gaussian distribution.

In section 5 we propose an alternative procedure which relies on the Fourier transform. The QENS data are converted to the time domain, and the intermediate scattering function $I(Q,t)$ is thus obtained. For a single relaxation process with fixed center of mass $I(Q,t)$ is given by

$$I(Q,t) = A_0(Q) + [1 - A_0(Q)] \exp\left(-\frac{t}{\tau}\right) \tag{12}$$

which is exactly the Fourier transform of the incoherent scattering law given by eq 2: a Lorentzian line in the frequency domain corresponds to a single-exponential decay in the time domain.

In our method developed for the analysis of side group rotations in polymers we have assumed that the FFT data can be described by an intermediate scattering function of the type

$$I(Q,t) = A_0(Q) + [1 - A_0(Q)] \exp\left(-\frac{t}{\tau_c}\right)^\beta \tag{13}$$

Equation 13 is equivalent to eq 12 with the incorporation of a distribution of relaxation times through the empirical KWW function. Apart from the obvious disadvantage of having to perform a Fourier transform, the time-domain data analysis via eq 13 is rather simple. The nonexponential behavior is immediately recognized by attempting a fit with eq 12, and the EISF can now be extracted directly as the long-time limit of $I(Q,t)$. In addition, the instrumental resolution is easily accounted for by dividing the FFT data by the resolution. Any convolution problem which is related to the frequency data fit is now eliminated.

3. Experimental Section

3.1. Materials. Selectively deuterated poly(methyl methacrylate) (PMMA-d_5) in which all but the ester methyl hydrogens were replaced by deuterium was used for QENS experiments. The polymer synthesis is described in ref 6. The sample used was constituted of predominantly syndiotactic

Table 1. Sample Characteristics

sample	formula	M_w	M_w/M_n	T_g (K)
PMMA	$C_5H_3D_5O_2$	250 000		380
PVME	C_3H_6O	95 000	2.5	250

triads. Films of 0.2−0.3 mm thickness were prepared by casting from methyl ethyl ketone solutions. The solvent was first allowed to evaporate at room temperature and then the films were dried under vacuum for several days.

Poly(vinyl methyl ether) (PVME) was purchased from Scientific Polymer Products and consisted of a 50% by weight polymer solution in toluene. PVME samples were prepared by solution casting. After evaporation of most of the solvent at room temperature, samples were placed in a vacuum oven until complete dryness. The characteristics of the polymers used during the experiments are listed in Table 1.

3.2. QENS Measurements. Neutron scattering experiments on PMMA and PVME were carried out on different spectrometers: the *IRIS* backscattering spectrometer[22] at the ISIS pulsed neutron source (Rutherford Appleton Laboratory, U.K.), the time-of-flight spectrometer *MIBEMOL* at the Laboratoire Leon Brillouin (Saclay, France), and the *QENS* spectrometer[23] (IPNS, Argonne National Laboratory, U.S.A.).

QENS measurements on PVME were performed on IRIS using both the pyrolytic graphite (002 reflection) and the mica analyzers (006 reflection) with energy resolution (fwhh) of 15 and 11 μeV, respectively. The spectral range accessible varied from −0.4 to +0.4 meV, and the Q range was from 0.25 to 1.9 Å^{-1}.

Neutron scattering experiments on PMMA-d_5 were carried out on MIBEMOL using an incident neutron wavelength of 6.7 Å^{-1}, thus giving an energy resolution of 70 μeV and a Q range from 0.981 to 1.745 Å^{-1}.

The energy resolution of the QENS spectrometer was of the order of 70 μeV. The particular instrumental setup used during the experiment allowed data to be collected at three different Q values: 0.9, 1.88, and 2.4 Å^{-1}.

In all experiments, samples were contained in aluminum cells. The sample thickness was about 0.2 mm, thus giving a transmission of 0.9. This ensures that multiple scattering is kept to a minimum.

Experiments were performed in a wide temperature range: from 4 K to below the glass transition temperature for all polymers.

Data analysis was carried out according to the RAL, LLB, and IPNS routines in order to obtain the dynamic structure factor $S(Q,\omega)$ as a function of energy transfer. Data were then Fourier transformed using a RAL routine, FURY.[24]

4. Results and Discussion

4.1. Poly(methyl methacrylate). It has been already shown that molecular motion in PMMA sets in at very low temperatures and it is observable on the high-resolution backscattering spectrometer IRIS just above 60 K.[13] Because the scattering in the selectively deuterated PMMA-d_5 mainly arises from the hydrogens in the ester CH_3, it is this group which has been associated with the relaxation mechanism.[6,13,14]

A plot of the full widths at half-height (fwhh), 2Γ, of all QENS data available for the ester methyl group rotation in predominantly syndiotactic PMMA-d_5 is shown in Figure 1. All fwhh values reported in this graph were obtained from conventional methods of analysis, i.e., by fitting the frequency data using a δ function and a single Lorentzian line convoluted with the instrumental resolution plus a flat background. As shown in Figure 1, there is a considerable difference between fwhh values measured on different spectrometers. In particular, the results seem to be affected by the instrumental resolution of the spectrometer. IRIS is a backscattering spectrometer with a resolution of 15 μeV (measured as fwhh of the elastic line), QENS and

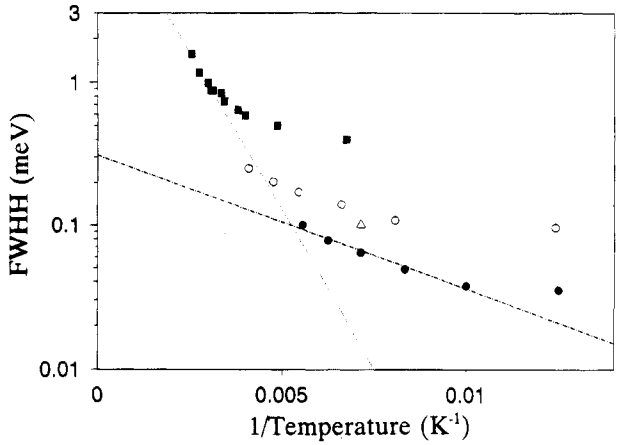

Figure 1. Full width at half-height (fwhh) versus inverse temperature for PMMA-d_5 measured: (○) on MIBEMOL, this work; (△) on QENS, this work; (■) on IN5 and IN6 by Gabrys et al.;[6] (●) on IRIS.[13] All data were analyzed using a single Lorentzian line convoluted with the instrumental resolution on top of a flat background. The lines indicate a fit to the high- and low-temperature data.

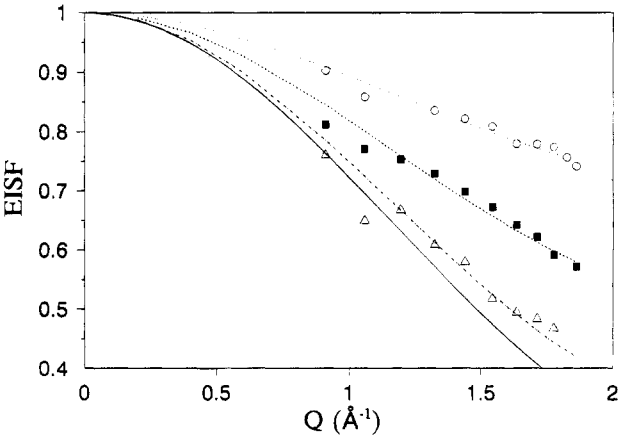

Figure 2. Experimental EISF for PMMA-d_5 after subtraction of coherent scattering at (○) 80, (■) 100, and (△) 180 K and comparison with $A_0(Q)$ calculated for a (■) threefold jump model (—). The lines indicate a fit to the experimental data according to eq 14.

MIBEMOL have a resolution of 70 μeV in these measurements, and the time-of-flight spectrometers IN5 and IN6 have energy resolutions of 170 μeV and in the range between 80 and 150 μeV, respectively, as reported by Gabrys et al.[6]

By considering the energy resolutions, it is evident that the lowest 2Γ values in Figure 1 are measured on the highest resolution spectrometer (IRIS) whereas the largest values are determined at the lowest resolution (IN5/IN6).

The non-Arrhenius temperature dependence of the IN5/IN6 data (Figure 1) was already discussed by Gabrys et al.[6] in terms of a non-purely threefold potential or quantum tunneling at low temperature. The mechanism associated with the ester methyl group rotation in PMMA-d_5 appeared to be more complicated when the rotational frequencies from IRIS were compared to the IN5/IN6 data.[14] It was at first thought that the occurrence of two distinct processes could explain the discrepancy between the IN5/IN6 and IRIS fwhh values.[14] This hypothesis was supported by the observed temperature dependence of the EISF. As illustrated in Figure 2, the EISF measured on IRIS was found to decrease with increasing temperature from 80

to 180 K. At low temperatures, values are higher than expected for a simple threefold rotation, and only above 180 K were the experimental data approaching the theoretical values. To explain the increase of the EISF, a temperature-dependent elastic contribution should be added to eq 2. This would imply that a temperature-dependent number of methyl groups participates to the rotational motion over the threefold symmetric barrier. This number would increase with increasing temperature.

The experimental EISF is then expressed by the following relationship:[14]

$$A(Q,T) = \frac{p_f}{p_{tot}}(T) + \frac{p_m}{p_{tot}}(T)\,A_0(Q) \qquad (14)$$

where $A_0(Q)$, already defined in eq 3, was calculated taking $r = 1.032$ Å. The ratios p_f/p_{tot} and p_m/p_{tot} represent the fraction of fixed and mobile protons, respectively ($p_{tot} = p_f + p_m$). As illustrated in Figure 2, eq 14 gives a good fit to the experimental data. The temperature dependence of p_f/p_{tot} indicates that the fraction of "fixed" protons decreases with increasing temperature.

At low temperature only a small fraction of protons perform angular jumps over the threefold symmetric barrier while the "frozen-in" protons give rise to an additional elastic contribution. With increasing temperature, an increasing number of methyl groups begin to perform angular jumps, and this results in a decrease of the elastic intensity through the ratio p_f/p_{tot}.

Although this model seemed plausible, it remained to be explained why a number of fixed CH_3 groups needed to be included in the EISF. A possible explanation could be given by a non-purely threefold potential barrier. However, recent *ab initio* calculations did not support the idea of a non-purely threefold potential.[25]

In addition, the inconsistency of this model is clearly indicated by the QENS data obtained from the MIBEMOL and QENS spectrometers which are also shown in Figure 1. The new MIBEMOL and QENS results clearly rule out the possibility of occurrence of two distinct processes for the ester CH_3 in PMMA. The most probable explanation for the observed resolution dependence of the rotational frequency is that of a distribution of rotational frequencies. A data analysis according to this procedure will be discussed in section 5.

4.2. Poly(vinyl methyl ether). QENS experiments were also carried out on poly(vinyl methyl ether) (PVME). The rotational motion of the ether CH_3 group has been recently investigated by Chahid and coworkers[10] in the temperature range from 160 to 300 K on the IN6 spectrometer (ILL, resolution 70μeV). Here we explore the low-temperature behavior on the higher resolution spectrometer IRIS.

The fwhh of the Lorentzian line is plotted in Figure 3 as a function of inverse temperature. The temperature dependence is apparently Arrhenius in the range from 100 to 200 K with an activation energy of 2.9 kJ/mol. This is close to the potential barrier calculated from incoherent inelastic neutron scattering data assuming a threefold symmetry (2.5 kJ/mol)[26] and to the activation energy measured by Chahid et al.[10] from the lowest temperature data. These authors reported that PVME follows a non-Arrhenius behavior with values of E_a between 2.95 kJ mol^{-1} in the range from 160 to 240 K and 7.85 kJ mol^{-1} in the higher temperature range up to 300 K.

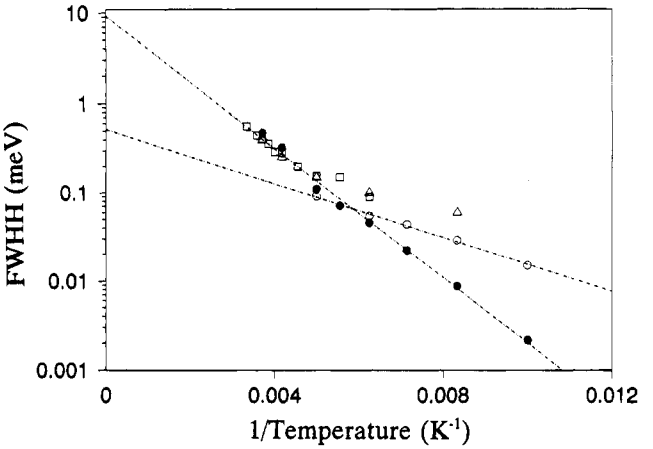

Figure 3. Temperature dependence of fwhh of PVME: (○) IRIS data, (△) QENS data, and (□) data from Chahid et al.[10] using a single Lorentzian line and (●) IRIS and QENS data from $I(Q,t)$ fit (eq 13). The lines indicate interpolation through the experimental points.

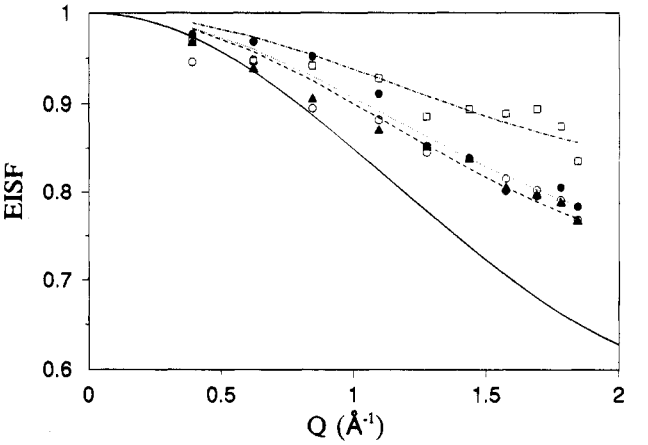

Figure 4. Q dependence of the experimental EISF of PVME at (□) 120, (●) 160, (▲) 180, and (○) 200 K and comparison with values calculated for a threefold rotation (—). The lines indicate a fit through the experimental points at (· — ·) 120, (· · ·) 160, and (— — —) 200 K.

Although our results seem at first to indicate that methyl group rotations in PVME are less complicated than in PMMA-d_5, several facts must be noticed. First a comparison between our QENS data collected on the IRIS and QENS spectrometers (Figure 3) shows the same resolution effect already observed for PMMA. Values of fwhh from Chahid et al.[10] are also reported in Figure 3. Because of the similarity of the energy resolutions of IN6 and QENS, there is an excellent agreement between the amount of quasielastic broadening.

The EISF shows a less pronounced temperature dependence compared to PMMA-d_5. However, the discrepancy between experimental and calculated values for a threefold rotation is very large even when the elastic contribution of the main chain protons is taken into account, as shown in Figure 4. These deviations are much more pronounced than those already reported by Chahid et al.,[10] as expected due to the lower temperature of our measurements.

5. Time-Domain Data Analysis

The discussion above clearly demonstrates that analysis of methyl side group reorientations using a single rotational frequency (hence a single Lorentzian line)

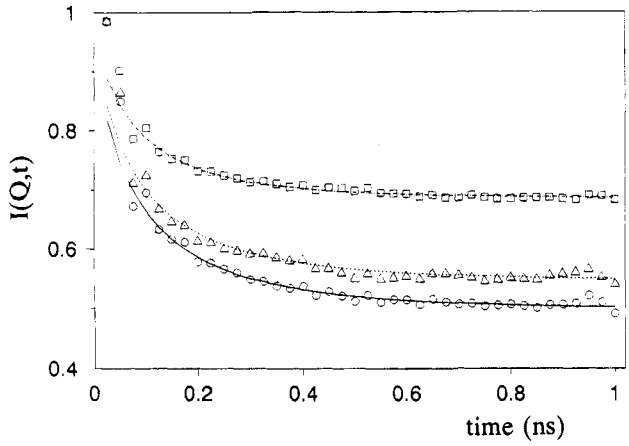

Figure 5. Intermediate scattering function, $I(Q,t)$, of PMMA-d_5 at 160 K and different Q values: (□) 1.20, (△) 1.54, and (○) 1.83 Å^{-1}. The lines indicate interpolation through the experimental points according to eq 13.

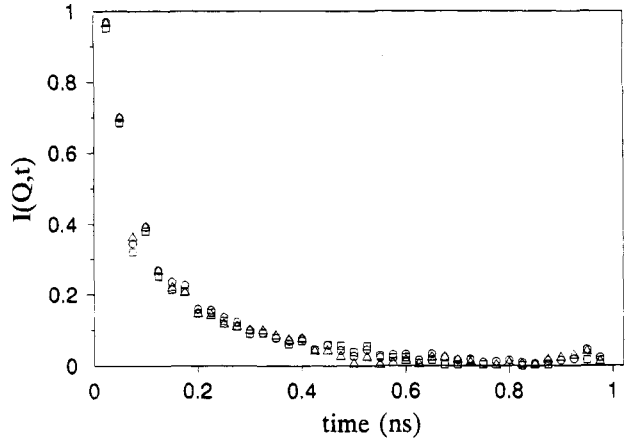

Figure 6. Intermediate scattering function, $I'(Q,t)$, of PMMA-d_5 at 160 K and different Q values: (□) 1.20, (△) 1.54, and (○) 1.83 Å^{-1} after correction for the EISF using eq 15.

leads to inconsistent results when applied to polymeric materials. The EISF is higher than calculated from a threefold jump reorientational model, the rotational frequencies exhibit a peculiar temperature dependence, and their values are highly dependent upon the instrumental energy resolution.

Chahid and co-workers[10] have recently proposed an alternative approach to the single Lorentzian line data analysis. The quasielastic neutron scattering spectra of the ether methyl group in PVME were analyzed by them assuming a random distribution of jumping rates. Their model allows a more realistic and physical representation of side group rotations in polymeric materials. Due to the amorphous nature of these systems, the local environments experienced by individual CH_3 groups differ.

The idea of a distribution of jumping rates to describe side group rotations in polymers is rather old[27] although its practical application to the analysis of QENS data is very recent. In fact it has been long recognized that, due to the absence of crystallinity in glasses, there exists nonequivalence between side groups. Both intra- and intermolecular effects might come into play.

In this work we propose a different approach to the analysis of the quasielastic neutron scattering data using the fast Fourier transform (FFT) to obtain the intermediate scattering function $I(Q,t)$. The first and new result obtained applying this procedure is that the time-domain data cannot be fitted by an exponential decaying function at any temperature on any spectrometer. This proves directly what was inferred indirectly from the inadequacy of the model parameters. In the frequency domain, a single Lorentzian line gives a more than satisfactory fit to the experimental data, and it is only through peculiarity of the fit parameters that a revision of the model becomes necessary. The analysis of the intermediate scattering function now substantiates the existence of a distribution of rotational frequencies.

The PMMA-d_5 IRIS data are well fitted by eq 13, i.e., using a stretched exponential decay. This is shown in Figure 5, where the experimental $I(Q,t)$ data of PMMA-d_5 at 160 K are plotted for different Q values together with a fit to eq 13. The scattering appears to reach a plateau at long times, and this provides a measure of the EISF. Both the exponent β and the characteristic time τ_c are Q independent. This is clearly demonstrated in Figure 6, where the experimental intermediate

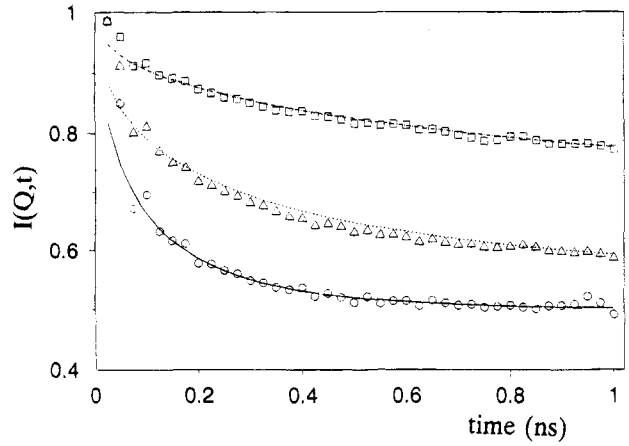

Figure 7. Intermediate scattering function, $I(Q,t)$, of PMMA-d_5 at $Q = 1.83$ Å^{-1} and at (□) 80, (△) 120, and (○) 160 K. The lines indicate interpolation through the experimental points according to eq 13.

scattering function corrected for the EISF contribution according to

$$I'(Q,t) = \exp\left(-\frac{t}{\tau}\right)^{\beta} = \frac{I(Q,t) - A_0(Q)}{1 - A_0(Q)} \qquad (15)$$

has been plotted. There is a good overlap between $I(Q,t)$ at different Q values, any Q dependence related to the EISF having now been removed.

The temperature dependence of $I(Q,t)$ at $Q = 1.83$ Å^{-1} is illustrated in Figure 7. The fitting parameters β and τ_c are strongly temperature dependent. The infinite time limit should be independent of temperature at a specific Q value. However, as shown in Figure 7, only at the highest temperature has $I(Q,t)$ reached a constant value. At lower T, the intermediate scattering function decreases less rapidly and reaches a plateau only at much longer times beyond the time range of our measurements.

Given the limited time range available on a spectrometer, it is generally not possible to determine β, τ_c, and $A_0(Q)$ correctly at low temperatures. Therefore we can only confirm that the EISF is constant with temperature in a limited T range. Figure 8 shows a comparison between the EISF measured at 140 and 160 K from the analysis of both the frequency- and the time-domain data. Not only does the EISF decrease to predicted values but also any artificial temperature dependence

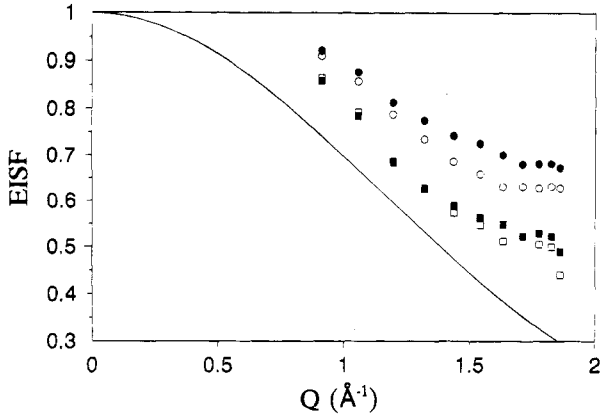

Figure 8. Q dependence of the EISF for PMMA-d_5 at (○) 140 and (●) 160 K from the frequency data and at (■) 140 and (□) 160 K from $I(Q,t)$ and comparison with $A_0(Q)$ calculated for a threefold jump model (—). The difference between (■), (□), and (—) is due to coherent scattering contributions.

is eliminted by our new method of analysis. The residual difference between the data and the calculated curve can be accounted for by coherent scattering contributions.[6,7,13]

At low temperatures the $I(Q,t)$ data were fitted fixing the EISF to those values measured at higher temperatures. The temperature dependence of the EISF which was previously reported[14] can now be easily explained. Due to the limited frequency or equivalent time range which is available on any spectrometer, only a fraction of the quasielastic broadening is actually detected at low temperatures. Some of the CH_3 groups relax at longer times, and hence at smaller frequencies. Their contribution cannot be distinguished from the purely elastic scattering and it therefore increases the apparent elastic incoherent structure factor. The intermediate scattering function, however, provides an excellent way to analyze the data by fixing the EISF.

It remains now to explain the non-Arrhenius temperature dependence of fwhh and its resolution dependence. The latter can be easily demonstrated in the time domain. $I(Q,t)$ is computed by dividing for the instrumental resolution, and although there are restrictions on the useful time range available, it is essentially independent of the type of spectrometer.

Figures 9 and 10 show the intermediate scattering function of PMMA-d_5 as measured on different spectrometers. There is an excellent overlap between IRIS and MIBEMOL as well as between IRIS and QENS data. In particular, the overlap between IRIS and MIBEMOL data at 80 K shown in Figure 10 indicates that the large difference between the quasielastic broadening previously determined (Figure 1) at this temperature was merely an artifact of the method of analysis employed.

The model parameters determined from the frequency and time data fit differ substantially, as illustrated in Figure 9, where the experimental $I(Q,t)$ is compared to the exponential decay corresponding to the frequency fit (eq 13) for both QENS and IRIS. The exponential and nonexponential fits to the overlapped data are also shown in Figure 9. The stretched exponential decay gives a better fit than the exponential one, although the difference is small at this temperature.

The effect of differences between the instrumental resolutions on the FFT data is also illustrated in Figures 9 and 10. Because the energy resolution of QENS is of the order of 70 μeV, the data become unreliable at times

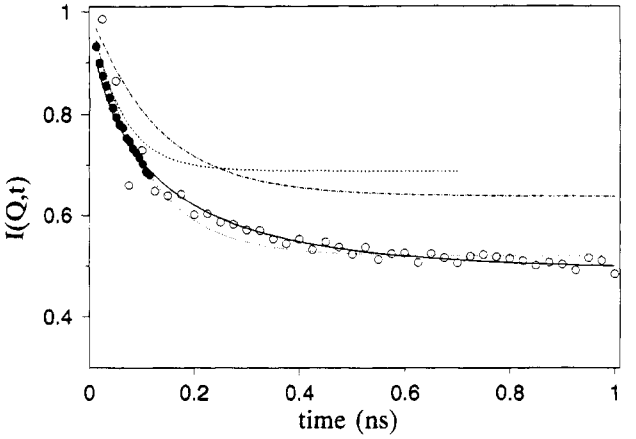

Figure 9. Intermediate scattering function of PMMA-d_5 at 140 K and Q = 1.88 Å^{-1} as measured on (○) IRIS and (●) QENS. The lines indicate fits (· — ·) to the IRIS frequency data using a single Lorentzian, (— — —) to the QENS frequency data using a single Lorentzian line, (···) to $I(Q,t)$ using an exponential fit, and (—) to $I(Q,t)$ using eq 13.

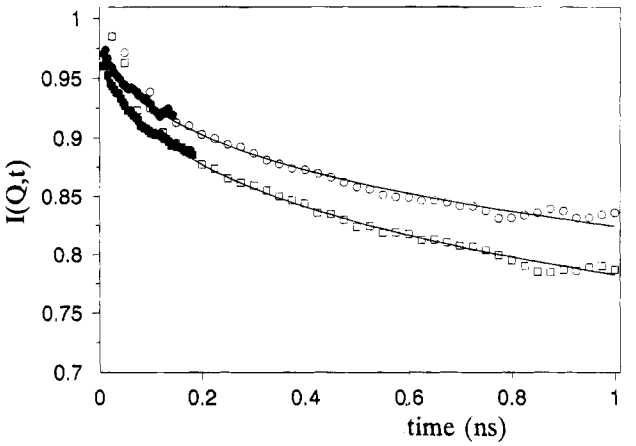

Figure 10. Intermediate scattering function of PMMA-d_5 at 80 K and Q = 1.32 Å^{-1} as measured on (○) IRIS and (●) MIBEMOL and at Q = 1.64 Å^{-1} as measured on (■) MIBEMOL and (□) IRIS. The lines indicate fits through the combined data using eq 13.

longer than 0.15 ns whereas for IRIS this occurs at $t >$ 1 ns. However, the larger frequency range available on QENS and MIBEMOL extends the FFT data range toward shorter times.

Finally, we compare the parameters extracted from the $I(Q,t)$ fit for PMMA-d_5. For convenience, $2/\tau_c$ (in meV) is plotted in Figure 11 versus inverse temperature, τ_c being the characteristic time defined in eq 13. The $2/\tau_c$ values correspond to the fwhh of the Lorentzian components and therefore enable us to make a direct comparison with the frequency data.

Any discrepancy between the rotational frequencies shown in Figure 1 has now disappeared (Figure 11): IRIS, MIBEMOL, and QENS give totally consistent results. Furthermore, the temperature behavior of $2/\tau_c$ is Arrhenius as expected for an activated process such as methyl side group rotations. The activation energy is equal to 5.3 kJ/mol and approaches values determined on IN5/IN6 by Gabrys et al.[6] at high temperatures. The IN5/IN6 data plotted in Figure 11 are the fwhh measured by them using the conventional single Lorentzian line approach. It is interesting to note that only at lower temperatures are deviations from the Arrhenius behavior observed whereas at high T there is an excellent agreement between $2/\tau_c$ and fwhh.

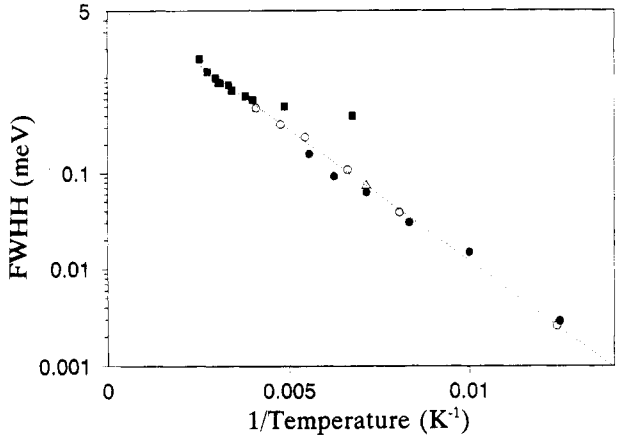

Figure 11. Temperature dependence of fwhh or $2/\tau_c$ (in meV) of PMMA-d_5 measured from $I(Q,t)$: (○) on MIBEMOL, this work; (△) on QENS, this work; (●) on IRIS, this work; (■) comparison with fwhh from IN5, and IN6 measured by Gabrys et al. (the frequency data were analyzed using a single Lorentzian line). The dotted line shows a fit through the experimental points.

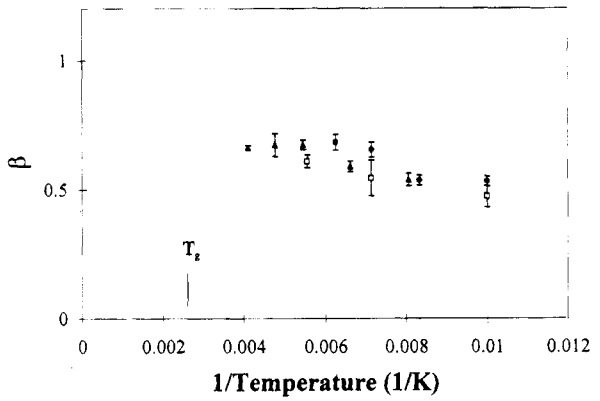

Figure 12. Temperature dependence of β of PMMA-d_5 measured on (●, □) IRIS in different experiments and on (▲) MIBEMOL.

The MIBEMOL $2/\tau_c$ values plotted in Figure 11 were measured by fixing the EISF to values determined at high temperatures. It is in fact clear from Figure 10 that the MIBEMOL data do not cover a wide enough time range at low temperatures for a correct fit with eq 13. However, at high temperatures it is possible to extract complete information from $I(Q,t)$ without the need for fixing any parameters.

The second parameter which is extracted from the $I(Q,t)$ fit is the exponent β. The behavior of various PMMA-d_5 samples is illustrated in Figure 12 for data measured on MIBEMOL and on IRIS. β values are temperature dependent and the increase which is observed with increasing temperature implies that the distribution of relaxation times broadens as the temperature decreases. It is difficult at this stage to establish the specific relationship between β and temperature. Our data so far seem to indicate that the stretched exponent increases from low T and approaches a constant value at temperatures below T_g.

There appear to be some differences between PMMA-d_5 samples which were run in different experiments (Figure 12). Although it might be argued that the sample thermal history and aging affect the distribution of local potential minima, this is only a speculation at this stage. Deviations shown in Figure 12 are also very close to the experimental error.

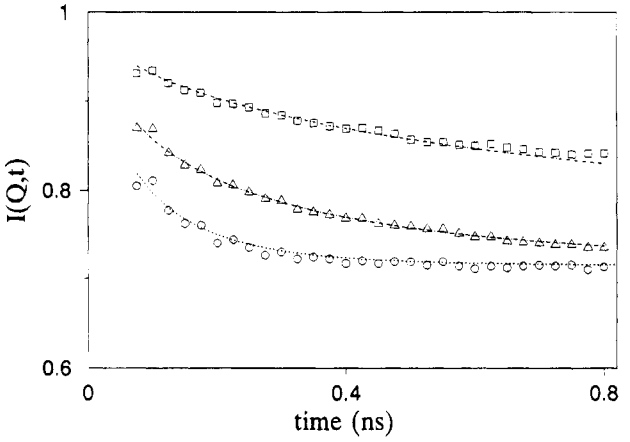

Figure 13. $I(Q,t)$ of PVME at 1.78 Å^{-1}: (□) 120, (△) 160, and (○) 200 K. The lines indicate interpolation through the experimental points according to eq 13.

The scattering behavior of PVME closely resembles that of PMMA-d_5. The IRIS $I(Q,t)$ data at different temperatures and Q = 1.78 Å^{-1} are plotted in Figure 13. Only at the highest temperatures does $I(Q,t)$ reach a plateau within our energy window. At lower temperatures the decay of the intermediate scattering function is much slower and the long-time limit is well beyond the instrumental resolution.

Values of $2/\tau_c$ determined from a fit using eq 13 are plotted in Figure 3 for PVME. The temperature dependence is Arrhenius with an activation energy of 7.01 kJ/mol and it is in good agreement with the work of Chahid et al.,[10] who reported a value of E_a of 8.4 kJ/mol from a fit of the frequency data using a Gaussian distribution of rotational frequencies. The temperature dependence of the β exponent is similar to that observed for PMMA-d_5, with β values increasing with increasing temperature until they reach a constant value. This is equal to 0.75 for PVME, and therefore it is very close to the PMMA value.

6. Conclusions

We have presented a quasielastic neutron scattering study of methyl group rotations in polymers. The QENS technique was already used in the past to investigate the ester methyl group rotation in PMMA-d_5. Apart from presenting some new data from the MIBEMOL and QENS spectrometers, the main purpose of this work was to explain the anomalous behavior of the elastic incoherent structure factor and of the rotational frequency which was observed experimentally for PMMA-d_5.[12-14]

In agreement with the work of Chahid et al.[10] and Frick et al.,[11] we have assumed that the existence of a distribution of rotational frequencies is the molecular feature giving rise to the observed anomalies. The novelty of our work consists in the approach to the analysis of the QENS data. We have demonstrated that the analysis of the intermediate scattering function obtained by Fourier transform of the QENS data provides a particularly advantageous procedure for investigating the dynamics of polymeric systems.

The time-domain data could not be fitted by a simple exponential decay corresponding to a Lorentzian line in the frequency domain. This confirms that a single correlation time does not adequately describe the dynamics of the CH_3 groups.

Many relaxations in polymers are treated using empirical functions in order to describe the existence

of a distribution of correlation times. In particular, the so-called stretched exponential or Kohlrausch–Williams–Watts (KWW) function has received a widespread acceptance. We have applied the KWW function in our study of the time dependence of $I(Q,t)$ to determine the characteristic time τ_c and a parameter β related to the width and shape of the distribution of correlation times as well as the EISF.

The characteristic time exhibits an Arrhenius temperature dependence, and the spatial movement of the CH_3 groups is well described by a threefold rotation. These findings are similar to those reported for methyl group rotation in molecular crystals; the only difference in polymeric systems is that one needs to account for a distribution of relaxation times. This result is not at all surprising since the concept of a nonexponential relaxation process is well established for polymers and it has been long applied in other techniques such as NMR and dielectric and mechanical relaxations.[1,28,29]

We have been able to superimpose the $I(Q,t)$ data collected at different energy resolutions. This confirmed that the discrepancy between the results from different spectrometers arises only because the distribution of rotational frequencies had been ignored. The overlap between the FFT data from different spectrometers can be used advantageously to extend the time range available, particularly when analyzing more than one relaxation process.

The origin of the distribution of relaxation times has been already discussed in the literature in terms of packing in the amorphous phase[28] as well as conformational disorder.[27] Although the nonexponential behavior might be attributed either to a homogeneous nonexponential relaxation or to a distribution of heterogeneous exponential processes, the latter explanation was favored, following the NMR results on the methyl group dynamics in polycarbonate.[28]

In this picture, as a consequence of structural heterogeneities, there exists a distribution of potential barriers hindering the rotation of the CH_3 groups which, in turn, leads to a distribution of rotational frequencies or, alternatively, of correlation times. It is expected that the distribution of activation energies will be temperature independent below the glass transition temperature where the amorphous packing can be considered frozen for a given sample. This has been indeed confirmed experimentally by Chahid et al.[10] using a log-Gaussian distribution of rotational frequencies to analyze the QENS spectra. There is in this case a simple relationship between the width of the rotational frequency distribution, σ, and the distribution of activation energies, σ_E, so that $\sigma_E = \sigma RT$.

The parameter β characterizes the width and shape of the distribution but, as it has been already observed, the stretched exponential is only an empirical function that provides an easy and convenient way to fit data characterized by a distribution of relaxation times. There is not a simple relationship between β and the time distribution,[21] the process involving an inverse Laplace transform.

The temperature dependence of the β parameter indicates that the distribution narrows with increasing temperature until it reaches a constant value for both polymers investigated. This does not necessarily imply a temperature-dependent distribution of activation energies. A detailed study of the relationship between the distributions of correlation times and activation energies is under way, and it will be the subject of a further publication.

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