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Methyl Group Dynamics in Poly(vinyl acetate): A Neutron Scattering Study

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ABSTRACT: The methyl group dynamics in a glassy polymer, poly(vinyl acetate) (PVAc), has been investigated by quasielastic neutron scattering in a temperature range from 50 to 300 K, below its glass transition temperature ($T_g \cong 315$ K). We have used three different neutron spectrometers covering a wide dynamic range from 10^{-8} to 10^{-12} s. The data have been analyzed in the framework of the rotation rate distribution model, which was previously introduced by us to interpret methyl group dynamics in glassy polymers. This framework has proved to be a better approximation than an alternative approach based on the Kohlrausch−Williams−Watts function, when a wide dynamical range is considered. The results obtained for PVAc have been compared with those corresponding to four other polymers: poly(vinyl methyl ether), poly(methyl methacrylate), polyisoprene, and poly(dimethylsiloxane), which have also been analyzed in the same theoretical framework. While the average activation energy barrier for methyl group rotation is determined by the chemical structure of the monomer, the width of the distribution of activation energy barriers seems to be mainly controlled by intermolecular disorder and packing conditions.

1. Introduction

Dynamics in polymer systems involves motion that are spread over a broad range in time scale[1,2] from the very slow processes involved in the viscous flow to the so-called fast dynamical processes detected in the picosecond range. Among them, the more usually investigated are the terminal relaxation, which is strongly dependent on the molecular mass, the segmental dynamics or the α-relaxation, which is connected to the glass transition phenomena characteristic of any glass-forming system, and the secondary relaxations, which are more local and believed to be responsible for the mechanical properties of glassy polymers. However, in polymers having side groups, other processes related to very local internal motions are also expected. In fact, at low temperatures, where the polymer chain backbones are frozen and the secondary relaxations are very slow, motions associated with small units of the side groups attached to the main chain remain active. Depending on the location of a relaxing unit in a side chain and on the local configuration around it, the characteristic relaxation times can be very different. Low barriers to rotations and large rotational constant $B = \hbar^2/2I$ (I is the moment of inertia and $\hbar$ is Planck's constant) of methyl side groups allow a fairly fast rotational motion compared to other side groups. The dynamics of methyl side groups are studied very conveniently by quasielastic and inelastic neutron scattering,[2,3] due to the matching time scale and inherent large scattering cross section of the proton associated with the methyl group. The librational mode, which can be observed in the inelastic neutron scattering (INS) experiments, provides information on the potential barrier hindering the methyl group and it is in general observed when the methyl group is directly linked to the main polymer chain. However, if the methyl group exists as a part of an ester or ether group attached to the main chain as in poly(methyl methacrylate), poly(vinyl methyl ether), and poly(vinyl acetate), for instance, these librational modes are hardly observable. In addition to libration, the methyl group can perform random rotational jumps over the potential barriers. These classical hopping processes can be observed by neutron scattering as a broadening of the elastic line, which is known as quasielastic scattering.[3] In this case, the width of the quasielastic broadening is a measure of the jumping rate and the amplitude contains information of the geometry of the motion.

The quasielastic neutron scattering (QENS) technique has been successfully applied for the last few decades to investigate thermally activated molecular motions in molecular solids and liquids, and an innumerable number of systems have been studied so far. However, only a few QENS studies have been reported for methyl group motions in polymeric systems,[4−10] namely, in poly(methyl methacrylate) (PMMA), poly(vinyl methyl ether) (PVME), poly(propylene oxide) (PPO), polyisoprene (PIP), and poly(dimethylsiloxane) (PDMS). The usual data analysis procedure developed for molecular crystals has resulted in unphysical parameters when attempted on the above-mentioned polymeric systems. Thus forcing fits to a simple model for methyl group rotation can result in inconsistencies in the temperature dependence of relaxation rates as was shown in ref 6. Recently it has been realized that for the amorphous polymeric materials, the effect of structural disorder has to be taken into account to describe the dynamics of methyl groups. Due to the amorphous nature of the materials, the rotating methyl groups are in different local envi-

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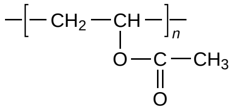
ronments, which in turn produces a distribution of energy barriers instead of a single one. This effect was clearly seen in ethylbenzene, where the methyl group librational mode was found to get broadened drastically for a quenched sample.[11] Distributions of molecular correlation times were used by Connor, among others, to describe the results obtained by NMR measurements and in particular by Schmidt et al. to interpret deuteron NMR data of methyl group reorientation in polycarbonate.[12] In the case of QENS measurements, and in order to take disorder effects into account, two different approaches have recently been attempted. In one case we have used a log-Gaussian function for the jumping rate distribution (rotational rate distribution model (RRDM))[6] to describe the methyl group dynamics in PVME. Very similar and compatible with the RRDM, a Gaussian distribution of activation energies was used by Frick and Fetters[7] to describe the temperature dependence of the energy-resolved elastic scattering data from PIP. In the other case, Arrighi et al.[8] analyzed the data of PMMA and PVME by transforming the experimental spectra into the time domain and assuming a functional form based on the Kohlrausch−Williams−Watts (KWW) (stretched exponential function) for the intermediate scattering law, $I(Q,t)$. A 3-fold rotation of the methyl group is assumed in both methods. In fact, recent computer simulations[13,14] carried out on PMMA and PIP seem to support that a 3-fold rotation for the methyl group is a quite good approximation.

The main problem of QENS measurements is that the dynamical range covered by a single instrument is rather narrow (generally no more than 2 decades) whereas disorder leads to a wide distribution of jumping rates for the methyl group in polymers. Therefore, it is clear that in order to properly check different theoretical models for methyl group dynamics in polymers and disorder systems in general, the experimental dynamical range has to be extended by combining several neutron spectrometers. This is the main goal of the present paper. We have used two time-of-flight (TOF) spectrometers, IN6 and IN5, with dynamical ranges: $10^{-11}-10^{-13}$ s and $10^{-10}-10^{-12}$ s, respectively, and a backscattering spectrometer, IN16, with dynamical range $10^{-8}-10^{-10}$ s at the Institute Laue Langevin (ILL), Grenoble, covering 4 decades in the quasielastic energy range. As polymer system, we have used poly(vinyl acetate) (PVAc), a well-known glass former that belongs to the same group of PVME and PMMA, as far as methyl group dynamics is concerned. Moreover, earlier NMR studies[15] have reported that in PVAc the methyl group should have a very low barrier to rotation. Further, the segmental dynamics of PVAc has been studied in great detail[1,16] using several techniques (dielectric, dynamic mechanical, nuclear magnetic resonance measurements, and light scattering), and it seems to be decoupled from any local motions in the temperature range up to the glass transition. Thereby, methyl group dynamics can be explored in a wide temperature range

Experimental details are given in the next section, whereas the theoretical aspects are given in section 3. The results are presented in section 4 and the discussion is given in section 5 where a comparison of the results obtained in the present work and the earlier reported ones for other polymers is also given. The conclusions are given in section 6.

2. Experimental Details

The poly(vinyl acetate) sample investigated had an average molecular weight of $\bar{M}_w = 93\,080$. The chemical formula of the repeating unit of PVAc is



$$-[-CH_2-CH(-O-C(=O)-CH_3)-]_n-$$

Differential scanning calorimetric (DSC) measurement showed a glass transition temperature (T_g) of 315 K at a heating rate of 10 K/min. Sample films were made by casting from adequate solutions of the polymer and dried under vacuum at about $T_g + 80$ K. A sample of thickness 0.07 mm was used to get a transmission higher than 90% allowing multiple scattering effects to be neglected. The samples were kept in a flat aluminum sample holder.

The neutron quasielastic scattering experiments were carried at the ILL, Grenoble. Time-of-flight (TOF) spectrometers, IN6 and IN5, with incident neutrons of wavelength, λ, equal to 5.12 and 6.5 Å respectively provide elastic energy resolutions (full width at half-maximum, fwhm) of about 100 and 45 μeV. In the IN16 backscattering spectrometer the wavelength of the incident neutrons was set to 6.3 Å resulting in an elastic energy resolution of nearly Gaussian shape with fwhm of 1 μeV and a Q (momentum transfer) range between 0.2 and 1.9 Å^{-1}.

Quasielastic spectra were recorded at different temperatures in the range from 50 to 300 K. The raw data were corrected for detector efficiency, sample container, and absorption using the standard programs available at the ILL. For IN6 and IN5 data, the scattering function $S(Q,\omega)$ at constant Q was obtained from $S(\theta,\omega)$, where θ is a given scattering angle and $\hbar\omega$ is the energy transfer, by interpolation using the code *Ingrid*. After this procedure the practical Q-range for IN5 and IN6 was reduced to 0.6−1.8 Å^{-1}.

The resolution functions of the spectrometers were determined from the measurement of a standard vanadium sample having solely elastic scattering.

3. Theoretical Aspects

(a) Simple Rotational Model for Methyl Group Rotation. In a neutron scattering experiment the measured intensity is proportional to the double-differential cross section[3]

$$\frac{\partial^2\sigma}{\partial\omega\partial\Omega} \propto \frac{\kappa}{\kappa_0}[\sigma_{\mathrm{coh}}S_{\mathrm{coh}}(Q,\omega) + \sigma_{\mathrm{inc}}S_{\mathrm{inc}}(Q,\omega)] \qquad (1)$$

where $S(Q,\omega)$ is known as the scattering law and the subscripts coh and inc denote the coherent and incoherent components. $\mathbf{k}$ and $\mathbf{k}_0$ are the final and initial wavevectors being $Q = |\mathbf{k} - \mathbf{k}_0|$. Polymeric systems mainly contain protons that have a large incoherent neutron scattering cross section (80 barns, with respect to its coherent part, 1.7 barns, and with respect to the other elements in the monomer: 5.5 barns total cross section for C atoms, 4.2 barns for O atoms). Therefore, in a neutron scattering experiment from a protonated polymer the observed dynamics mainly corresponds to the self-correlation function of the protons $S(Q,\omega) \cong S_{\mathrm{inc}}(Q,\omega)$. The incoherent scattering law for methyl side groups, $S_M(Q,\omega)$, undergoing simple jump rotations with the same jumping rate can be written as[3]

$$S_M(Q,\omega) = A(Q)\delta(\omega) + \{1 - A(Q)\}L(\omega) \qquad (2)$$

The first term in the above equation is the pure elastic component with $A(Q)$ representing the so-called elastic incoherent structure factor (EISF), which provides information related to the geometry of the motion. It can be shown[3] that in the case of methyl groups performing rotational jumps within a 3-fold potential $A(Q)$ can be written as

$$A(Q) = \frac{1}{3}[1 + 2j_0(Qr_{\mathrm{H-H}})] \tag{3}$$

where $j_0(x)$ is the zeroth-order Bessel function and $r_{\mathrm{H-H}}$ is the hydrogen−hydrogen distance in the CH_3 group. The second term in eq 2 is the quasielastic part with $L(\omega)$ a Lorentzian function which is given by

$$L(\omega) = \frac{1}{\pi}\,\frac{\Gamma}{\Gamma^2 + \omega^2} \tag{4}$$

where Γ, the half width at half-maximum (hwhm) of the Lorentzian function, is the jumping rate that is inversely proportional to the reorientation time, τ. The temperature dependence of Γ is usually expressed by an Arrhenius law:

$$\Gamma(T) = \Gamma_\infty \exp\left(-\frac{E}{k_{\mathrm{B}}T}\right) \tag{5}$$

where E is the activation energy barrier for rotation and k_{B} the Boltzmann constant. The prefactor, Γ_∞, is related to the attempt frequency. In this model it is assumed that the molecule oscillates about the equilibrium orientations for an average time τ and then instantaneously jumps to a new equilibrium orientation.

(b) Rotational Rate Distribution Model (RRDM) for Methyl Group Rotation. The simple model described above is generally used for molecular crystals, but as mentioned in the Introduction, it does not work for glassy systems. Due to the existence of the structural disorder, which is inherent to the glassy state, the methyl groups in a glassy polymer have different local environments arising from both the lack of regularity of the main-chain conformation and the different local packing conditions. This manifests itself in different rates of rotation. Starting from this basic idea, we introduced in ref 6 a rotation rate distribution model (RRDM) to describe the methyl group dynamics in glassy polymer systems. In the RRDM, the jumping rate is assumed to be distributed but the origin of such a distribution can be either a distribution of the activation energies or a distribution of the attempt frequencies, or both simultaneously. Thus, the incoherent scattering model function, $S_{\mathrm{M}}(Q,\omega)$, is constructed by generalizing expression 2 with a continuous distribution of jumping rates $g(\log \Gamma)$

$$S_{\mathrm{M}}(Q,\omega) = A(Q)\delta(\omega) + \{1 - A(Q)\}\int_{-\infty}^{\infty} g(\log \Gamma)\frac{1}{\pi}\frac{\Gamma}{\Gamma^2 + \omega^2}\,\mathrm{d}(\log \Gamma) \tag{6}$$

As a first approximation g(logΓ) is assumed to be Gaussian-like (log-normal distribution), i.e.:

$$g(\log \Gamma) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2\sigma^2}\log^2\left(\frac{\Gamma}{\Gamma_0}\right)\right] \tag{7}$$

where σ^2 is the variance of the distribution function and Γ_0 the hwhm of the most probable Lorentzian component. To compute numerically the scattering law a discrete form of eq 6 is more convenient

$$S_{\mathrm{M}}(Q,\omega) = A(Q)\delta(\omega) + \{1 - A(Q)\}\sum_{i=1}^{N} g_i L_i(\omega) \tag{8}$$

where now $L_i(\omega)$ are Lorentzian functions of hwhm Γ_i and the weight factors g_i are obtained by sampling the distribution of jumping rates, that is, $g_i \propto g(\log \Gamma_i)$. The proportionality constant is taken to ensure the condition $\sum_{i=1}^{N} g_i = 1$, and the values of $\log[\Gamma_i/\Gamma_0]$ are taken equally spaced in the range $\pm 3\sigma$. We have found that a number N of Lorentzian components equal to 20 is sufficient to evaluate $S_{\mathrm{M}}(Q,\omega)$, in the sense that a higher number does not modify significantly the calculated $S_{\mathrm{M}}(Q,\omega)$ functions.

In polymeric systems, normally, one has contributions to the total scattering from scattering centers other than the methyl group protons. In particular, one can have main-chain protons and other atoms that do not participate in the methyl group rotation. At low temperatures, all of these contributions can be assumed to be elastic, that is, having characteristic times much higher than the reciprocal of the hwhm of the resolution function corresponding to the used spectrometers. It is also assumed that vibrational motions of the atoms and reorientational motions of the methyl group are uncoupled. Thus, the model function for the total scattering from the sample should be written as

$$S(Q,\omega) = e^{-2W}\,[c_{\mathrm{fix}}\delta(\omega) + (1 - c_{\mathrm{fix}})S_{\mathrm{M}}(Q,\omega)] \tag{9}$$

where c_{fix} refers to the fraction of the total scattering due to all the atoms other than the methyl group protons, and the factor $\exp(-2W)$, which accounts for the intensity loss due to vibrational motions, corresponds to what is known as the Debye−Waller factor (DWF), with $W = Q^2\langle u^2\rangle/6$, $\langle u^2\rangle$ being an effective mean square displacement.

4. Results

Typical quasielastic spectra from PVAc obtained with the above mentioned three different instruments (IN5, IN6, IN16) are shown in Figure 1 in comparison with the corresponding instrumental resolution functions. To facilitate the comparison, the spectra have been plotted in the same unified scale (5% of the intensity of the elastic peak). The contribution of the methyl group dynamics in the different energy windows covered by the different instruments is clearly evident. The temperatures at which a clear quasielastic broadening is observable change with the chosen spectrometer. It is apparent that at low temperature the instrument having higher resolution (IN16) is suitable to study the methyl group dynamics whereas IN5 and IN6 instruments are more adequate for the intermediate and high temperatures. Thus, the whole temperature range (50 K < T < 300 K) can be studied conveniently by combining these three instruments.

The $S(Q,\omega)$ data have been analyzed in the framework of the RRDM which was already applied to PVME[6] as mentioned in the Introduction. The fitting procedure was also very similar to that adopted for PVME. We used the scattering law corresponding to the RRDM (eqs 8 and 9) convoluted with the instrumental resolution. We have assumed an additional flat background for the analysis of IN5 and IN6 data since low-frequency vibrations could contribute in the energy window (~meV)

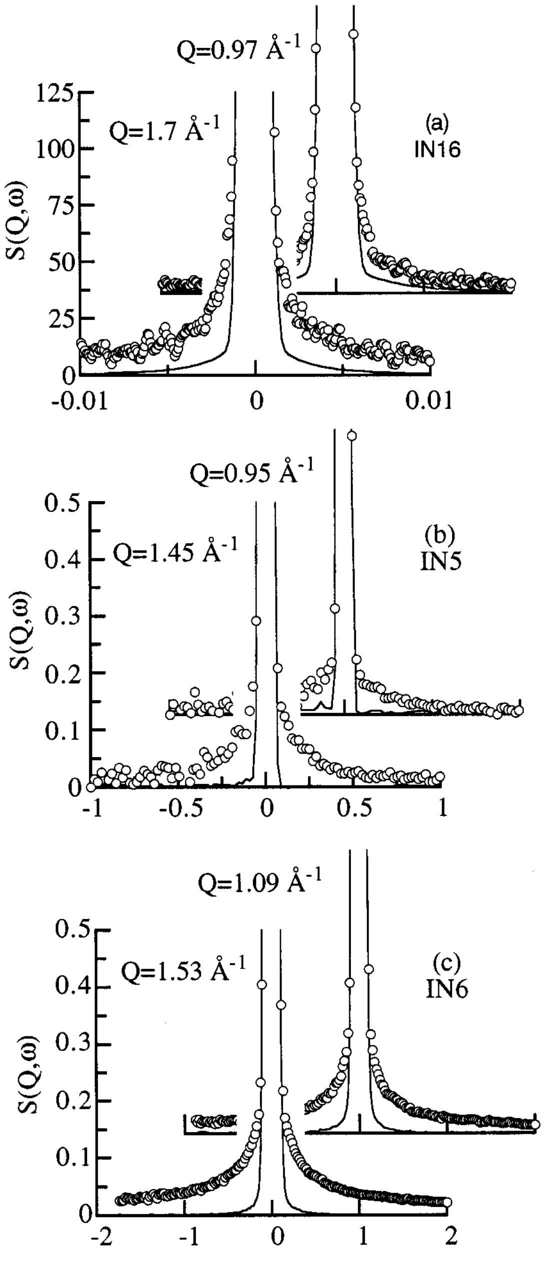


Figure 1. Typical quasielastic spectra as measured on different instruments: (a) IN16 at $T = 70$ K for $Q = 0.97$ and 1.7 Å^{-1}; (b) IN5 at $T = 140$ K for $Q = 0.95$ and 1.45 Å^{-1}; (c) IN6 at $T = 200$ K for $Q = 1.09$ and 1.53 Å^{-1}. The respective instrumental resolution functions (solid lines) are also shown for comparison. The vertical axes are scaled to 5% of the peak elastic intensities.

of these instruments. These effects are not expected for the IN16 data due to the low-energy range covered by the experimental window of this instrument (<10 μeV).

All the atoms except the protons of the methyl group were assumed to have no other motion than vibration in the temperature range investigated and therefore should not contribute to the quasielastic part of the spectrum. Taking into account that in PVAc the 50% of protons are in the methyl group, the value of c_{fix} in eq 9 was calculated and kept fixed to a value of 0.53. The amplitude scaling factor, which includes the DWF, was chosen to reproduce the intensity at the maximum. Thus, the spectra were fitted individually with the model function having three adjustable parameters: σ, Γ_0, and the background (only for TOF data). A standard least-squares minimization procedure in the logarithm scale of $S(Q,\omega)$ has been used. Since at a given temperature Γ_0 and σ did not show systematic Q dependence, they were kept fixed to their average value, and for the TOF data only the background was varied. It is worthy of remark that the obtained values of the background were rather low (less than 0.1% of the peak intensity) and clearly lower than those obtained for PVME (about 0.5%).[6] Although the explanation of these different values is beyond the aim of this paper, it can be related with the question of the so-called low-frequency excitations (Boson peak), which are characteristic of glassy-systems in general. While a clear Boson peak is visible in the low-temperature $S(Q,\omega)$ of PVME at about 1.3 meV, the corresponding scattering spectra of PVAc do not show any clear evidence of these excitations. By following the above mentioned procedure, good fits were obtained in the whole temperature (50 K $< T <$ 300 K) and Q (0.6 Å^{-1} $< Q <$ 1.8 Å^{-1}) ranges investigated. Typical fitted spectra at an intermediate temperature $T = 120$ K, at which the quasielastic broadening can be observed with the three different instruments, are shown in Figure 2. The quasielastic components corresponding to methyl group rotations are also shown in the figure. The broadening observed at 120 K for PVAc even by IN6 (Figure 2c) with the worst resolution used (100 μeV) clearly suggests a very fast dynamics for the methyl group in PVAc. This fact is further evident in the IN16 spectra (Figure 2a), with the best resolution (1 μeV), where most of the methyl group dynamics do not contribute to the measured $S(Q,\omega)$ in the IN16 window. The obtained variations of Γ_0 and σ with the inverse of temperature are shown in Figure 3. It is worthy of remark the good agreement found between the Γ_0 and σ values obtained by means of the different spectrometers used, that is at different energy ranges. This agreement is particularly evident in the case of $T = 120$ K, where, as it has been aforementioned, the quasielastic broadening due to methyl group dynamics is observable through the three different instruments (see Figure 2). On the other hand, a nearly linear behavior of both, $\log(\Gamma_0)$ and σ vs $1/T$ is evident. Figure 3a shows that $\log(\Gamma_0)$ starts to deviate from this behavior at high temperatures ($T > 200$ K). However, in this temperature range, the value of the $\Gamma_0(T)$ obtained is of the order of 1 meV (equivalent time scale of the order of picoseconds), which is in the same range where the so-called "fast dynamics", characteristic of any glass forming system, is usually detected.[2,17] Therefore, it is expected that the quasielastic spectra at high temperatures could be affected by these dynamical processes. On the other hand, the $\sigma(T)$ values obtained from the IN16 data show deviations from the $\sigma \propto 1/T$ behavior below 100 K. This could be due to the presence of quantum rotational tunneling of the methyl groups in PVAc as has recently been reported by us[18] at $T \leq 70$ K. The quantum rotational tunneling in PVAc has been observed by means of IN16 as an apparent quasielastic feature at 2 K, which remains almost unaltered up to 40 K. Although the spectra at 70 K can be explained on the basis of the classical motions (RRDM), it is difficult to be sure that the quantum features are not contributing at all to the spectra observed by this instrument. In fact the crossover from classical to quantum dynamics seemed to lie over a broad T-range.[18] However, almost the whole distribu-

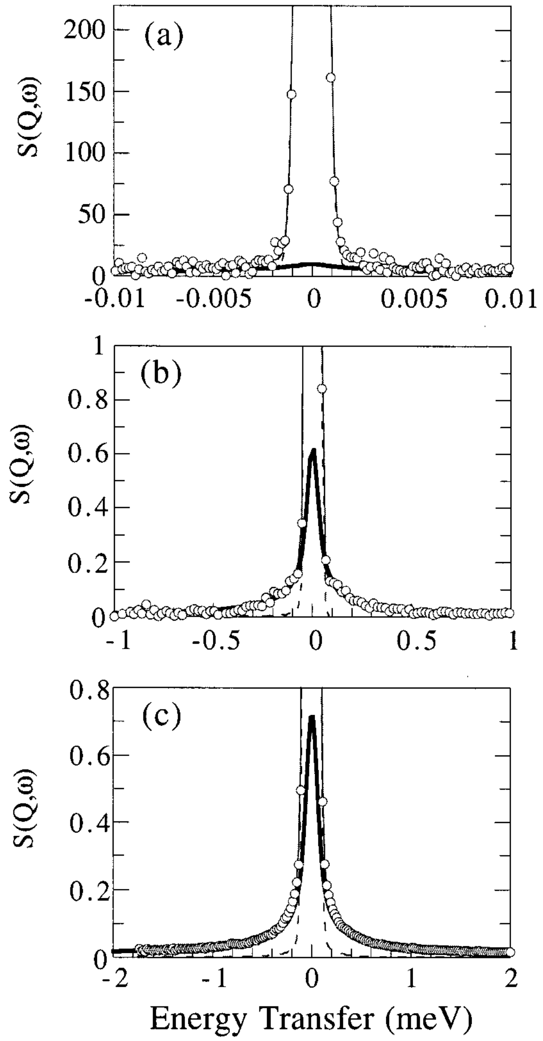


Figure 2. Typical fit of the data from PVAc at $T = 120$ K as obtained by (a) IN16 at $Q = 1.57$ Å^{-1}; (b) IN5 at $Q = 1.45$ Å^{-1}, and (c) IN6 at $Q = 1.53$ Å^{-1}. The vertical axes are scaled to 10% of the peak elastic intensities. Solid lines through the points are the fitted curves. The thick solid lines correspond to the quasielastic components of the RRDM. Short dashed lines represent the resolution functions of the spectrometers.

tion of tunneling frequencies observed by IN16[18] is inside the instrumental resolution of IN5. Therefore the quantum effects should hardly affect the IN5 low-temperature results. This is evident in Figure 3b where the σ values obtained from the IN5 data at 70 and 50 K are plotted. They almost follow the behavior found at higher temperatures.

Taking into account the above raised arguments, we have considered the range 70K $< T <$ 250 K as a temperature range of confidence, where the classical methyl group rotation observed by the three instruments used should not be affected by other processes. In this temperature range, the Γ_0 values were fitted by means of an Arrhenius law (eq 5), which is shown in Figure 3a as a solid line. An activation energy $E_0 = 3.7 \pm 0.4$ kJ/mol and a value $\Gamma_\infty = 9.1 \pm 3.0$ meV (i.e., $(1.4 \pm 0.4) \times 10^{13}$ s^{-1}) are obtained. This Arrhenius law also describes the low temperature values rather well, suggesting that the average jumping rate is hardly affected by the quantum rotational tunneling. The obtained value of the activation energy for methyl group rotation (3.7 kJ/mol) is very low and even lower than the rotational barrier in gaseous acetaldehyde (4.8 kJ/mol).[19] It may be noted that the earlier NMR results on PVAc[15] also suggested a very low rotational barrier (<4.2 kJ/mol). To the best of our knowledge this is the lowest activation energy for methyl group rotation in polymeric systems reported so far. On the other hand, the prefactor, $\Gamma_\infty = 9.1$ meV, which is related to the attempt frequency of the methyl group, suggests the possibility of the presence of a methyl group librational mode located in such a frequency range, which should be observable as a peak in the vibrational density of states. The effective density of states, $g(\omega)$, for PVAc calculated from IN6 data at 120 K as

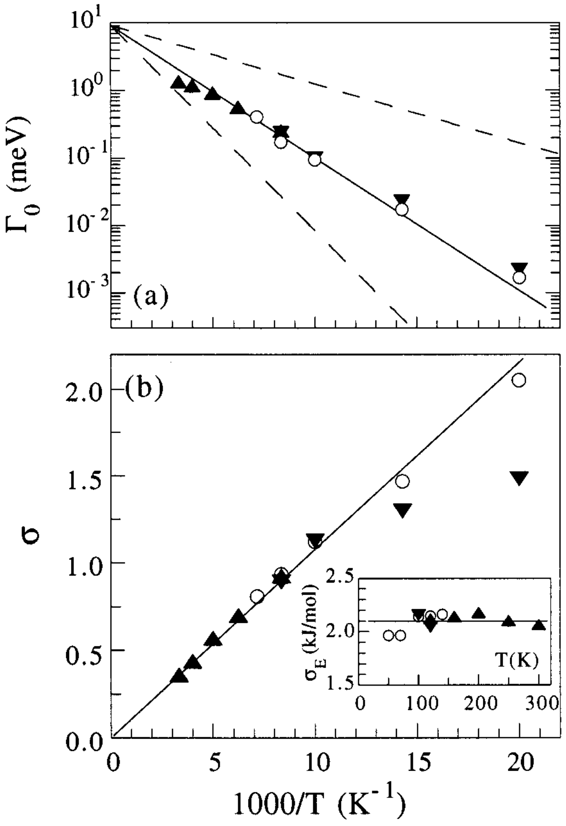


Figure 3. Temperature dependence of the parameters obtained from the fit of QENS data of PVAc with the RRDM: IN6 (▲), IN5 (○), and IN16 (▼). (a) Plot of the width (Γ_0) of the most probable Lorentzian component vs $1/T$. The solid line corresponds to an Arrhenius law. The dashed lines correspond to Γ_+ and Γ_- (see the text). (b) Plot of the width of the distribution function, σ vs $1/T$. The solid line represents a linear description. The inset shows the width of the corresponding activation energy distribution (see the text).

$$g(\omega) \propto \frac{\omega[\exp(\hbar\omega/k_BT) - 1]}{\exp(\hbar\omega/kT)} \frac{S(Q,\omega)}{Q^2} \qquad (10)$$

shows (see Figure 4) a very broad feature below 20 meV, which is characteristic of any glassy polymer, even without a methyl group.[20] Thereby, it is very difficult to distinguish the possible contribution of a methyl group libration to this broad peak.

$\sigma(T)$ was also fitted in the same temperature range (70 K $< T <$ 250 K) by using a linear law against $1/T$ (solid line in Figure 3b). The obtained $\sigma(T)$ behavior can be well approximated by: $\sigma(T) \cong C/T$ ($C = 109$ K). This approximate temperature dependence implies that the width of the jumping rate distribution at the asymptotic temperature limit $T \to \infty$, is zero, that is, all the jumping rates Γ_i approximately display the same

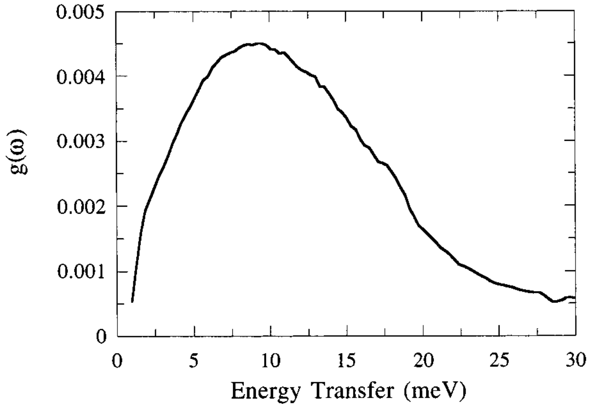


Figure 4. Effective vibrational density of states g(ω) calculated from the IN6 spectrum at T = 120K and an average Q value of 2.0 Å^{-1}.

value of the attempt frequency Γ_∞. Taking into account these results, as well as the resulting Arrhenius law for each jumping rate, $\Gamma_i = \Gamma_\infty \exp[-E_i/k_BT]$, the weight factors g_i can be rewritten as

$$g_i \propto \exp\left[-\frac{1}{2(C/T)^2}\log^2\left[\exp\left(-\frac{E_i - E_0}{k_BT}\right)\right]\right] \qquad (11)$$

which transforms into

$$g_i \propto \exp\left[-\frac{(E_i - E_0)^2}{2(Ck_B/0.4343)^2}\right] \qquad (12)$$

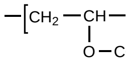
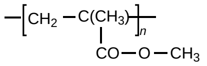
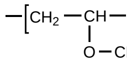
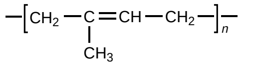
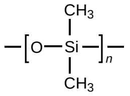
Equation 12 corresponds to a Gaussian distribution of activation energies with an average value E_0 and a temperature independent variance $\sigma_E{}^2$ given by $\sigma_E = Ck_B/0.4343$. Therefore, the temperature-dependent log-Gaussian distribution of jumping rates found for PVAc can be understood as a consequence of a temperature independent Gaussian distribution of activation energy barriers. This is similar to the earlier reported results for PVME[6] and PIP.[7] The resulting σ_E values for PVAc are shown against temperature in the inset of Figure 3b. An almost constant value of $\sigma_E = 2.1 \pm 0.1$ kJ/mol is obtained. The effect of this σ_E value on the jumping rate distribution is also shown in Figure 3a where the temperature dependence of the jumping rates Γ_+ and Γ_-, defined as $\Gamma_\pm = \Gamma_\infty \exp[-(E_0 \pm \sigma_E)/k_BT]$, is displayed by dashed lines.

5. Discussion

(a) Comparison of the Methyl Group Dynamics in Different Polymers. As mentioned above, the methyl group dynamics have been investigated in a few polymer systems with different chemical formulas and microstructures. An important question is how the results obtained for the different systems compare. Here we compare the results obtained in the framework of the RRDM for different polymers.

The RRDM was previously used to describe the methyl group dynamics of PVME.[6] Moreover, the methyl group dynamics of PIP and PDMS has been analyzed in a framework that is equivalent to the RRDM.[7,10] It may be mentioned that for both PIP and PDMS different kinds of neutron experiments (fixed elastic window scan technique, FEW) were performed and the values of Γ_∞ were taken as the frequencies of the respective methyl group librational modes. For these two polymers the methyl group librational mode is located at quite high energies (~23.5 meV for PIP and 18.5 meV for PDMS) and are well resolved in the inelastic neutron scattering spectra. Finally, from the available results on PMMA[8] and recent IN16 measurements,[9] we have also determined the RRDM parameters for PMMA. In this way we have been able to compare the parameters of the RRDM corresponding to the methyl group rotation in five different polymers. The obtained values of the parameters are summarized in Table 1 and the behavior of σ(T) for all these systems is shown in Figure 5. As can be seen in Table 1, the values of the average activation energy barrier, E_0, depend on the molecular chemical structure of the polymer considered. It is clear that when the methyl group is directly linked to the main chain, E_0 is considerably higher than the obtained values when the methyl group is attached to an ester group. Moreover,

Table 1. Comparison of the RRDM Parameters for the Methyl Group Dynamics in Different Polymers

polymer	E_0 (kJ/mol)	Γ_∞ (meV)	σ_E (kJ/mol)
poly(vinyl acetate), PVAc  $-\left[\mathrm{CH_2}-\underset{\mathrm{O-CO-CH_3}}{\mathrm{CH}}-\right]_n-$	3.7	9.1	2.1
poly(methyl methacrylate), PMMA[9]  $-\left[\mathrm{CH_2}-\underset{\mathrm{CO-O-CH_3}}{\mathrm{C(CH_3)}}-\right]_n-$	5.9	4.8	2.0
poly(vinyl methyl ether), PVME[6]  $-\left[\mathrm{CH_2}-\underset{\mathrm{O-CH_3}}{\mathrm{CH}}-\right]_n-$	8.4	7.6	1.8[b]
polyisoprene, PIP[a,7]  $-\left[\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\mathrm{C}}=\mathrm{CH}-\mathrm{CH_2}-\right]_n-$	12.5	23.5	3.1
poly(dimethylsiloxane), PDMS[a,10]  $-\left[\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\right]_n-$	7.0	18.5	1.2

[a] Values estimated from FEW data. [b] Values of σ given in ref 6 correspond actually to decimal logarithm not natural.

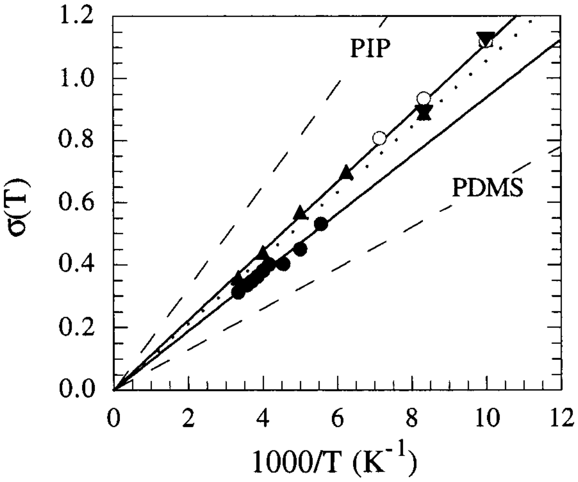


Figure 5. $\sigma(T)$ behavior corresponding to the methyl group dynamics in different polymers. The symbols for PVAc are those used in Figure 3, whereas filled circles correspond to PVME (ref 6). Solid lines correspond to linear descriptions of the data. The dotted line corresponds to the behavior found in PMMA, and the dashed lines indicate the behavior used to describe FEW data of PIP and PDMS.

depending on the location of the methyl group within an ester, the average barrier to rotation is also different (compare for instance the PVAc and PMMA values). On the other hand, it is interesting to point out that the width of the energy barrier distribution, σ_E, seems to be of the same order for all the polymers considered and does not show any clear systematic with the chemical structure of the polymer. This result suggests that the distribution of rotational barriers is mainly controlled by intermolecular disorder and packing conditions. In this respect, it is worth mentioning that the recent molecular dynamics simulations of methyl group rotation in PMMA,[13] mentioned above, have shown that the distribution of rotation energy barriers is quite sensitive to the density changes.

(b) RRDM Versus Empirical KWW Description. As mentioned in the Introduction, the methyl group dynamics as observed by QENS has also been analyzed[8] by Fourier transforming the $S(Q,\omega)$ data to the time domain and assuming a functional form based on the Kohlrausch–Williams–Watts (KWW) function for the intermediate scattering function $I(Q,t)$, which is the Fourier transform of $S(Q,\omega)$. In this framework the normalized intermediate scattering function for methyl group rotations, $I_M(Q,t)$, is written as

$$I_M(Q,t) = A(Q) + \{1 - A(Q)\} \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \qquad (13)$$

where β is a shape-parameter taking values between 0 and 1. It was also suggested[8] that this description and the one obtained by using the RRDM are equivalent to each other, if we consider the limited energy range usually available in QENS investigations. In the framework of the RRDM, the normalized intermediate scattering function for methyl group rotation is given by

$$I_M(Q,t) = A(Q) + \{1 - A(Q)\} \int_{-\infty}^{\infty} g(\log \tau) \exp\left[-\frac{t}{\tau}\right] d(\log \tau) \qquad (14)$$

or in its discrete form by

$$I_M(Q,t) = A(Q) + \{1 - A(Q)\}\sum_{i=1}^{N} g_i e^{-t}/\tau_i \qquad (15)$$

where the weight factors, g_i, correspond to the log-Gaussian distribution function given in eq 7 and the exponential functions, e^{-t/τ_i}, correspond, by Fourier transformation, to the Lorentzian functions $L_i(\omega)$. The characteristic times are defined as $\tau_i = 1/\Gamma_i$. Equations 13 and 14 differ uniquely in the quasielastic term which in the RRDM is taken as a summation of single exponential functions, whereas the former is assumed to correspond to a stretched exponential function. It may be noted that eq 13 can also be written in a similar way as eq 14, because the stretched exponential function can formally be expressed in terms of a distribution of exponential functions

$$\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] = \int_{-\infty}^{\infty} \rho(\log \tau') \exp\left(-\frac{t}{\tau'}\right) d(\log \tau') \qquad (16)$$

However, the distribution function $\rho(\log \tau)$, which can be obtained by inverse Laplace transformation methods,[21] is asymmetric in contrast to the symmetric log-Gaussian distribution function used in the RRDM. Therefore, it is clear that the RRDM and the KWW approaches cannot be compatible when a wide dynamical range is considered. This is clearly shown in Figure 6 where as a representative example we compare the $I(Q,t)$ of the RRDM, calculated using eq 14 for a typical value of $\sigma = 1$ and an average τ value of 0.1 ns, and the best fit of it by eq 13. It is evident that the agreement is rather poor when the whole decay range is considered. However, when one restricts the time range of comparison to the typical one of a single spectrometer (≤2 decades of time) the agreement can be quite good as shown in Figure 7. In this figure, the same comparison of Figure 6 is now made at three different time ranges. However, the problem is that when different time ranges are used, the resulting values of β are different (see also Figure 7). Thus, it is apparent that if the RRDM is able to fit the experimental behavior over a wide dynamical range, the KWW description could not provide, in principle, a good description in the whole range. This statement can now be directly checked with the experimental data of PVAc at 120 K, where the methyl group dynamics is observed by all the three instruments used in this work, that is, at three different dynamical ranges. To do this, we have fitted the $S(Q,\omega)$ data shown in Figure 2 by considering the Fourier transform of eq 13 as a model function for methyl group rotation. As usual, the fitting procedure involved convolution of the model function with the instrumental resolution function of the corresponding spectrometer. The obtained results are shown in Table 2 in comparison with those obtained by means of the RRDM at the same temperature. It is evident that in the case of the KWW approach, the values of the parameters of the model, τ and β, depend on the energy range considered (i.e., on the instrument used) beyond the experimental uncertainty. On the other hand, in the case of the RRDM, they are quite stable, as discussed in the previous section of the results. In addition, it is found that the correlation between the two model fitting parameters ($\log \Gamma_0$ and σ for the RRDM and $\log \tau$ and β for the KWW description), measured by the corresponding covariance coefficient, is lower in the case of the RRDM. Therefore, the RRDM seems to provide a better description of the methyl group dynamics than the empirical KWW approach, when the dynamics is investigated in a wide dynamical range. Recent molecular dynamics simulation of methyl group dynamics in PMMA[13] also suggest that the KWW function may not be a good choice for describing the methyl group relaxation process. More-

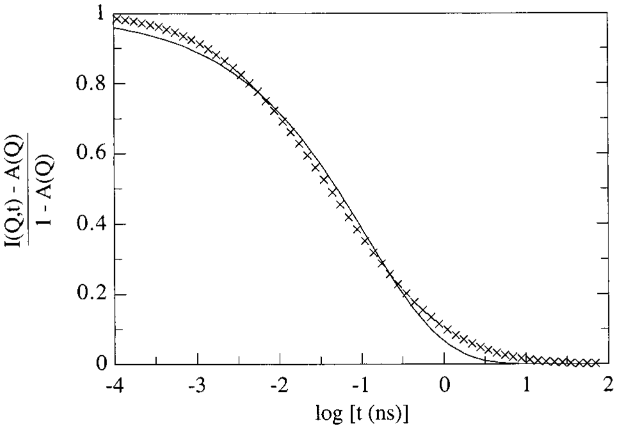


Figure 6. Comparison of the $I(Q,t)$ calculated by the RRDM (crosses) and the KWW description (line) in a very wide time range.

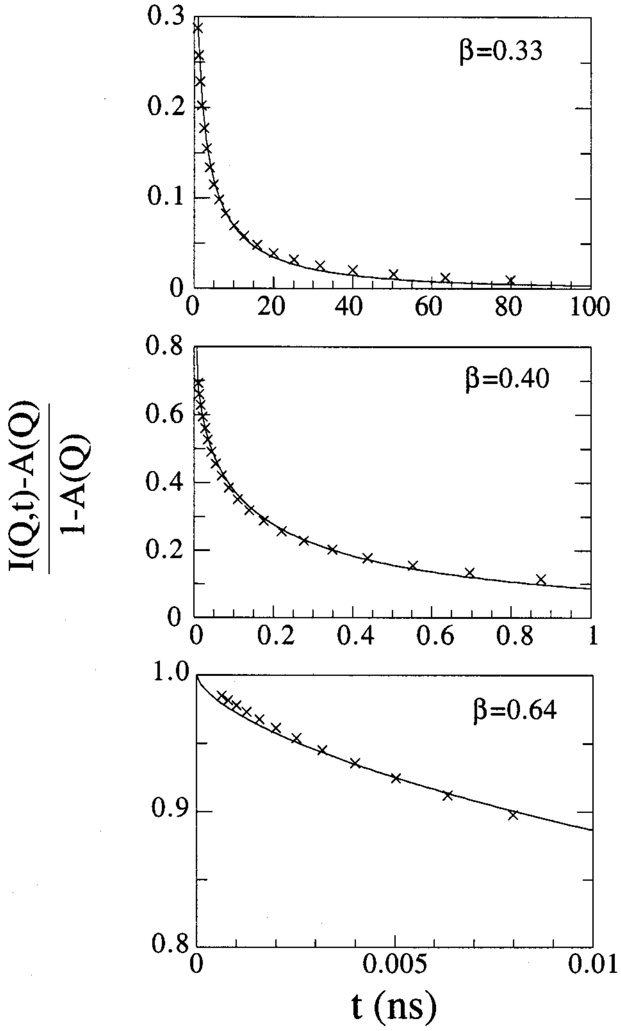


Figure 7. Comparison of the $I(Q,t)$ calculated by the RRDM (crosses) and the KWW description (lines) in different restricted time ranges of about 2 decades.

Table 2. Comparison of the Parameters Corresponding to RRDM and KWW Descriptions Obtained for PVAc at 120 K

	RRDM			KWW		
spectrometer	log (Γ_0/meV)	σ	covariance[a]	log (τ/ps)	β	covariance[a]
IN6	−0.55	0.92	8×10^{-4}	0.07	0.44	5×10^{-3}
IN5	−0.54	0.93	7×10^{-4}	−0.08	0.39	4×10^{-3}
IN16	−0.56	0.90	7×10^{-4}	0.34	0.28	3×10^{-3}

[a] The covariance of two statistical quantities x and y is defined as $\langle x\, y\rangle - \langle x\rangle\langle y\rangle$, where the brackets represent average values.[22]

over, in the framework of the RRDM the distribution of jumping rates (or relaxation times) emerges in a natural way as a consequence of the distribution of activation energy barriers, that is, as a consequence of the distribution of rotational potentials, which is inherent to the glassy state. Although one can expect an almost Gaussian shape for a random distribution of activation energy barriers (or potentials) in a glassy or disordered system, this shape produces, when the average value of the energy barrier is very low and the distribution is extremely broad, some unphysical tail extending to the negative side of the energy scale. In these cases, it may formally be more appropriate to consider the so-called χ^2 distributions[22] in which the random variable can only take positive values. From a practical point of view, and within the usual experimental uncertainties, the χ^2 distribution turns to be similar to a Gaussian one with a sharp cutoff in the zero value of the energy, that is, close to that we have used. It is worthy of remark that a recent modeling of methyl group rotation in PMMA by the quasi-static method[13] results in a similar kind of weak asymmetry for the distribution function of activation energy barriers, which, on the other hand, is opposite to that corresponding to the KWW function.

Last but not least, it is worth mentioning that the distribution of activation energies obtained by the RRDM in PVAc also allows one to describe, without any adjustable parameter, the quantum rotational tunneling effects recently found for the first time in PVAc at very low temperatures.[18] These results give additional and independent support to the RRDM, which, in this way, can be extended to the quantum regime of methyl group dynamics in polymers.[18]

6. Conclusions

By combination of three different neutron scattering spectrometers, the methyl group dynamics in a glassy polymer, PVAc, have been investigated in a wide dynamic range extending from about 10^{-8} to 10^{-12} s and in a temperature range from 50 to 300 K. Such a wide dynamical range means a strong test for the functional form of the scattering law assumed for the methyl group dynamics. From this investigation we can conclude that the RRDM previously proposed by us has been confirmed to be a suitable model for interpreting methyl group dynamics in glassy polymers. However, the approach based on the KWW function seems to be a rougher approximation when a wide dynamical range is considered.

From the comparison of the results obtained for PVAc with RRDM results corresponding to the other polymers shown in Table 1, we can conclude that (i) the average activation energy barrier for methyl group rotation clearly depends on the monomer structure of the polymer considered and (ii) the width of the distribution of activation energy barriers seems to be mainly controlled by intermolecular disorder and packing conditions, being of the same order for all the polymers investigated.

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References and Notes

(1) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymer Solids*; Wiley: New York, 1967.
(2) Frick, B.; Richter, D. *Science* **1995**, *267*, 1939.
(3) Bee, M. *Quasielastic Neutron Scattering*; Adam Hilger: Bristol, 1988.
(4) Grapengeter, H. H.; Alefeld, B.; Kosfeld, R. *Colloid Polym. Sci.* **1987**, *265*, 226.
(5) Chahid, A.; Colmenero, J.; Alegria, A. *Physica A* **1993**, *201*, 101.
(6) Chahid, A.; Alegria, A.; Colmenero, J. *Macromolecules* **1994**, *27*, 3282.

(7) Frick, B.; Fetters, L. J. *Macromolecules* **1994**, *27*, 975.

(8) Arrighi, V.; Higgins, J. S. *Physica B* **1996**, *226*, 1, and references therein.

(9) Moreno, A.; Alegria, A.; Colmenero J.; Frick, B. To be submitted for publication.

(10) Frick, B. *Non-Equilibrium phenomena in supercooled fluids, glasses and amorphous materials*; Giordando, M., Leporini, D., Tosi, M. P., Eds.; World Scientific: Singapore, 1996.

(11) Frick, B.; Williams, J.; Treviño, S.; Erwin, R. *Physica B* **1995**, *213 & 214*, 506.

(12) Connor, T. M. *Trans. Farraday Soc.* **1964**, *60*, 1574. Schmidt, C.; Kuhn, K. J.; Spiess, H. W. *Prog. Colloid Polym. Sci.* **1985**, *71*, 71.

(13) Nicholson, T. M.; Davies, G. R. *Macromolecules* **1997**, *30*, 5501.

(14) Alvarez, F.; et al. To be submitted for publication.

(15) Hoch, M. J. R.; Bovey, F. A.; Davis, D. D.; Douglass, D. C.; Falcone, D. R.; McCall, D. W.; Slichter, W. P. *Macromolecules* **1971**, *4*, 712.

(16) Alvarez, F.; Alegria, A.; Alberdi, J. M.; Colmenero, J. *Proc. Third International Workshop on Noncrystalline Solids*; Conde, A., Conde, C. F., Millán, M., Eds.; World Scientific: Singapore, 1992. Wagner, H.; Richert, R. *Polymer*, **1997**, *38*, 255 Krüger, J. K.; Bohn, K.-P.; Schreber, J. *Phys. Rev.* B **1996**, *54*, 15767.

(17) Colmenero, J.; Arbe, A.; Alegria, A. *Phys. Rev. Lett.* **1993**, *71*, 2603.

(18) Colmenero, J.; Mukhopadhyay, R.; Alegria, A.; Frick, B. *Phys. Rev. Lett.* **1998**, *80*, 2350.

(19) Kilb, R. W.; Lin, C. C.; Wilson, E. B., Jr. *J. Chem. Phys.* **1957**, *26*, 1695.

(20) Frick, B. *Polymer Motions in Dense Systems*; Richter, D., T. Springer, T., Eds.; Springer-Verlag: Berlin, 1988; p 143.

(21) Alvarez, F.; Alegría, A.; Colmenero, J. *J. Chem. Phys.* **1995,** *103*, 798.

(22) Carnahan, B.; Luther, H. A.; Wilkes, J. O. *Applied Numerical Methods*; Wiley: New York, 1969.

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