Molecular Dynamics in a Nano-composite of Poly(methyl methacrylate) Nano-particles with Poly(ethylene oxide) Linear Chains (75wt%/25wt%).
A Quasielastic Neutron Scattering Study

D. Bhowmik,1 J. A. Pomposo,2,3,4 F. Juranyi,5 V. García-Sakai,6 M. Zamponi,7 A. Arbe,2, a) and J. Colmenero1,2,3

1) Donostia International Physics Center, Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain
2) Centro de Física de Materiales (CSIC-UPV/EHU) – Materials Physics Center (MPC), Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain
3) Departamento de Física de Materiales (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain
4) IKERBASQUE - Basque Foundation for Science, Alameda Urquijo 36, 48011 Bilbao, Spain
5) Laboratory for Neutron Scattering, Paul Scherrer Institut, CH-5232 Villigen, Switzerland
6) ISIS Facility, Rutherford Appleton Laboratory, Harwell Science & Innovation Campus, Chilton, Didcot, OX11 0QX, United Kingdom
7) Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH, outstation at Heinz Maier-Leibnitz Zentrum, Lichtenbergstr.1, 85747 Garching, Germany

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We have selectively studied the component dynamics in a nano-composite where PEO [poly (ethylene oxide)] linear chains are mixed with PMMA [poly(methyl methacrylate)] soft nano-particles by means of quasi-elastic neutron scattering (QENS) experiments on partially deuterated samples. Regarding the nano-particles, the α-methyl group dynamics of PMMA –to which the QENS experiments are most sensitive in the temperature range investigated– is hardly affected by the presence of PEO, though hints for more heterogeneous environments for methyl groups in the nano-composite than in bulk PMMA are found. The investigation of the PEO component has been performed considering the equivalent blend of linear chains as reference. When the systems approach their glass-transition –provoked by the slowing down of the PMMA-based component– PEO dynamics displays the same deviations with respect to the expected equilibrium behavior independently of the topology of the other component. This finding supports the interpretation of the motions of the fast PEO component as confined by a surrounding rigid matrix. Contrarily, well above the glass-transition of the slow component, PEO dynamics differ in both systems. In the blend, PEO segments move with the typical features of supercooled polymers in metastable equilibrium, while in the nano-composite PEO dynamics develops larger and larger deviations from Gaussian behavior with increased mobility of the nano-particles. PEO segments are seemingly trapped for a very long time –more than two orders of magnitude longer than in bulk or surrounded by linear PMMA chains– in effective cages imposed by the nano-particles before the subdiffusive process leading to segmental relaxation sets in. We speculate that in this trapping mechanism the local loops in the nano-particles may play an important role.

Keywords: Polymer Dynamics, Quasielastic Neutron Scattering, Soft Nanoparticles

I. INTRODUCTION

Because of difficulties in commercializing new polymers, industry has turned increasingly to blend existing polymers to optimize their end-use (e.g., mechanical and rheological) properties. In particular, blends based on thermodynamically miscible polymers are one of the most efficient and economical means to create new materials with tailored features. An alternative route to tune polymer properties is the addition of nano-particles. In this direction, the use of single-chain polymer nano-particles (‘soft’ nano-particles) seems to be particularly promising. Soft nano-particles obtained by intra-molecular cross-linking of linear macromolecules (precursors) are emerging soft nano-objects showing unique and remarkable physicochemical, rheological and sensing properties due to their locally collapsed structure and ultrasmall size1–3. Intriguing nanoscale effects giving rise to a large decrease of melt viscosity, nano-particle segregation to interfaces and dewetting inhibition have been reported for binary nano-composites composed of high-molecular-weight polymer-A and polymer-A soft nano-particles (i.e., athermal all-polymer nanocomposites)1,4,5. Nano-composites consisting of linear polymers mixed with soft nano-particles are in fact blends of polymers where one of the components is internally cross-linked.

Design of tailor-made materials would be enormously facilitated by the understanding of the phenomenon of
mixing the components at a molecular level. Thus, in both kinds of systems – blends of linear chains and nano-composites of linear polymers and nano-particles – the key question to address is: how are the dynamics of each component modified by the presence of the other one? In the case of linear blends a large effort has been made during the last decades to elucidate this problem (see, as general references, the reviews6,7). It is noteworthy that to face it the use of experimental techniques that can be selective to each of the components is mandatory. NMR on deuterium-labeled samples or dielectric spectroscopy when only one of the components is dielectrically active can be highly efficient methods. Quasi-Elastic Neutron Scattering (QENS) combined with isotopic labeling is a technique of special interest since it also provides spatial information through the momentum transfer (Q)-dependence of the measured magnitudes. From diverse investigations by different methods on thermodynamically miscible polymer blends, it has been concluded that blending does not essentially perturb the local dynamics relevant in the glassy state like methyl-group rotations or motions involved in secondary relaxations. Regarding the α-process directly related with the glass-transition phenomenon, one well established feature is the dynamic heterogeneity, i. e., the observation of two different characteristic times for segmental relaxation, each of them corresponding to the dynamics of one component modified by blending. This dynamic heterogeneity implicitly leads to the existence of two different glass transition temperatures $T_g$ as well, which are usually called ‘effective glass transition’, $T_{g,eff}$, of each of the two components in the blend. The consequences of the dynamic heterogeneity are expected to be more dramatic in blends of polymers with large difference in the homopolymer $T_g$-values. This is the case of binary mixtures of poly(ethylene oxide) (PEO) ($T_g^{PEO} \approx 220$ K) and poly(methyl methacrylate) (PMMA) ($T_g^{PMMA} \approx 400$ K). In fact, these blends have attracted great attention in the scientific community8–53. Due to crystallization problems already for moderate contents of PEO, most investigations were focused on compositions rich in the PMMA component (about 80% in PMMA). We note that in such cases, the glass transition feature accessed e. g. by calorimetry is largely dominated by the effective glass-transition of the PMMA component $T_{g,eff}^{PMMA}$. Interestingly enough, NMR experiments10,12,20 revealed a strong decoupling between PEO and PMMA dynamics. QENS results on the PEO component pointed to a dramatically stretched relaxation dynamics which was accounted for by invoking very broad distributions of relaxation times with a temperature dependent width24,28. These broad distributions in the dynamics of the fast component were interpreted28 as a consequence of the nonequilibrium situation reached by this component in the vicinity of the effective $T_{g,eff}$ of the slow-component in the blend (PMMA). There, the chain and segmental dynamics of the slow component (matrix) could be considered to be completely frozen on the time scale of the segmental motions of the fast component. In that situation, the motions of the fast component can be expected to be localized and rather heterogeneous. Extending this kind of investigations to blends of PEO with other linear polymers with high $T_g$-values with respect to $T_g^{PEO}$ corroborated this scenario. Hints for similar confinement effects were also found in a selective QENS investigation of the blend PEO/polyvinylacetate (PVAc, 20/80%), where the glass transition temperatures of the homopolymers differ by about 199 K ($T_g^{PVAc} = 314$ K)54. In that work, a crossover in the behavior of PEO was found around 70 K above the calorimetric $T_g$ of the blend: at high temperatures, PEO behaves like a ‘standard’ glass-forming system in supercooled regime, whereas signatures of confined dynamics can be identified when decreasing the temperature toward the average $T_g$ of the blend. Similar findings were obtained from the viscoelastic and dielectric relaxation investigation of the blend PEO/PVAc55, and from QENS on a blend of PEO with polyethersulfone (PES) ($T_g^{PES} = 382$ K)56.

What happens if now the rigid component in the system is present not as linear macromolecules but as single-chain soft nano-particles? What is the impact of internal cross-linking of the slow component on the confinement effects of the fast component? These are the main questions we address in this work, moving from linear chains to soft nano-particles of PMMA in the mixtures. With these ideas in mind, we have performed QENS experiments on nano-composites consisting of 25wt% PEO linear chains and 75wt% PMMA nano-particles (PMMA-NPs). The PMMA-NPs were deuterated in order to minimize their contribution to the scattered intensity. Then, the recorded signal reveals the incoherent scattering function of the protons in the system, accessing thereby direct information on the self-motions of PEO’s hydrogens in the Å to nm length scale. To discuss the results in a comparative way, we also carried out analogous measurements (in a more reduced dynamic window though) on a blend with linear PMMA chains that serves as direct reference. In addition, we considered the problem of the effects of the presence of PEO on the dynamics of the nano-particles observed by QENS. To solve it, the opposite labeling was considered, namely a nano-composite where PEO was deuterated and the PMMA-NPs were protonated.

II. EXPERIMENTAL

A. Samples

Two nano-composites containing 25wt% PEO and 75wt% PMMA-NPs were prepared (dPEO/hNPs and hPEO/dNPs, respectively, where d stands for deuterated and h for protonated) by weighing appropriate amounts of deuterated PEO (dPEO, $M_w = 89$ kDa, $M_w/M_n = 1.08$, Polymer Source, Inc.) and protonated PMMA-NPs (hNPs, $M_w = 72$ kDa, $M_w/M_n = 1.1$) as well as protonated PEO (hPEO, $M_w = 94$ kDa, $M_w/M_n = 1.08$, Polymer Source, Inc.) and deuterated PMMA-NPs (dNPs, $M_w = 92$ kDa, $M_w/M_n = 1.08'$). The blends were prepared by dissolving the polymer components in N,N-dimethylformamide, followed by casting in N,N-dimethylformamide and subsequent slow drying in a vacuum desiccator. The samples were cut into thin slices of about 200 µm thickness and pressed under 10 MPa pressure. The glass transition temperatures of the PMMA-NPs and the PMMA/NPs blend were determined by differential scanning calorimetry (DSC) in a Perkin-Elmer DSC800 calorimeter.
cently reported in Ref. 57. The dPEO/hNPs and hPEO/dNPs mixtures were dissolved in chloroform and further precipitated in methanol. The resulting dPEO/hNPs and hPEO/dNPs blends were dried at 80°C under dynamic vacuum until constant weight. Specimens for QENS experiments were prepared by pressing the dried dPEO/hNPs and hPEO/dNPs systems in a hot-plate hydraulic press (Labopress 200-T, VOGT). Both hNPs and dNPs were synthesized through Michael addition-mediated multidirectional self-assembly of appropriate individual polymeric chains at room temperature in tetrahydrofuran, by following a procedure recently reported in Ref. 57. Echylene glycol diacrylate (EGDA) (90%, Sigma-Aldrich) was used as intrachain cross-linking agent. A schematic diagram of the synthesis process is depicted in Fig. 1. By means of dynamic light scattering in dilute solution, the average hydrodynamic radius of the NPs was determined to be of 7.4 nm (hNPs) and 8.1 nm (dNPs). For comparison of the results on the hPEO/dNPs system we also considered a sample consisting of a blend of linear hPEO and dPMMA chains (also 25%/75% in weight), with \( M_w = 25 \) kDa and \( M_w/M_n = 1.03 \) (hPEO), \( M_w = 27 \) kDa and \( M_w/M_n = 1.04 \) (dPMMA). We will refer to this sample as hPEO/dPMMA. In all cases the average glass-transition temperature –attributable to the PMMA-component \( T_{g, eff} \) was found to be \( \approx 330 \) K.

**B. QENS**

Three different spectrometers were used to carry out the QENS measurements: (a) FOCUS at the Paul Scherrer Institute (PSI), (b) IRIS at the ISIS Facility and (c) SPHERES\(^58\) at the FRM II. Among them FOCUS is a direct-geometry spectrometer while IRIS and SPHERES are backscattering (BS) spectrometers. Combining the treated data from these three different spectrometers, a wide window of correlation time (from the order of \( 10^{-13} \) to \( 10^{-9} \)s) is covered where the time window for individual spectrometer spreads as follows: \( \sim 10^{-13} \) to \( 10^{-11} \)s (FOCUS), \( \sim 10^{-12} \) to \( 10^{-10} \)s (IRIS) and \( \sim 10^{-10} \) to \( 10^{-9} \)s (SPHERES). Flat aluminum cells were used as sample holder with a thickness adjusted for attaining close to 90% transmission. Empty sample holder signal was subtracted from the raw data followed by a correction of the detector efficiency. An incident neutron beam with \( \lambda = 6.01 \AA \) leading to a resolution with full-width at half-maximum (FWHM) of \( \sim 42 \)µeV was used for FOCUS while \( \lambda = 6.27 \AA, \) FWHM=0.65µeV and \( \lambda = 6.65 \AA, \) FWHM=17.5µeV were employed for SPHERES and IRIS, respectively. The energy range \( (h\omega) \) extended from \( \sim 1 \) meV to 500 meV (FOCUS), \( \sim 30.64 \) to 30.8µeV (SPHERES) and \( \sim 0.5 \) to 0.5 meV (IRIS). The scattering angle, \( 2\theta \) was transformed to momentum transfer vector \( (Q) \) covering \( 0.4 \AA^{-1} < Q < 1.8 \AA^{-1} \) for FO-

The QENS spectra were Fourier transformed and de-convoluted from the instrumental resolution. This procedure delivers the intermediate scattering function in the time domain \( I(Q,t) \) and allows merging data from different instruments. The details about the procedure followed, the assumptions made and the modelization of the scattering functions of the different components in the samples are fully described in Appendix A.
III. RESULTS AND DISCUSSION

A. dPEO/hNPs-sample: α-methyl group rotations in the NPs

Figure 2 presents the QENS results on the dPEO/hNPs sample for selected temperatures and $Q$-values. Data from the three instruments employed have been combined, covering in this way about three decades in time-scale. As shown in Appendix A, these functions are dominated by the incoherent contribution from the hydrogens in the NPs. In analogy to the case of hydrogens in PMMA-NPs in a nano-composite with high content of PEO (25wt% NPs) recently investigated by us, the expected dynamics contributing to our spectra are the rotations of the α-methyl groups in PMMA. The dPEO/hNPs data were thus described in the framework of the rotational rate distribution model usually applied for this kind of process in amorphous systems. This model introduces the ingredient of disorder through an underlying distribution of rotational barriers. As can be seen in Fig. 2, the data were successfully described under these assumptions. The parameters $\sigma$ and $\tau_{MG}$—width and average value of the distribution of characteristic times for classical hopping respectively, see Eq. 56—were determined from these fits as function of temperature. They are represented in Fig. 3. The widths $\sigma$ follow well Eq. 56 in solid line in Fig. 3(a), delivering a width of the underlying distribution of activation energies $\sigma_E = \sigma_{bulk} = 56$ meV. For comparison, in the same figure we have reproduced the corresponding results for bulk PMMA (dashed-dotted line). In this case, the distribution is narrower ($\sigma_{bulk} = 39$ meV)\textsuperscript{28}. Such an additional broadening of the distribution of rotational barriers could be due to the more heterogeneous environments for MGs in the presence of PEO chains. Conversely, within the uncertainties, the results obtained for $\tau_{MG}$ in the NPs can be described with an Arrhenius law with the same average activation energy as that found in the bulk (solid line in Fig. 3(b), $\langle E_{\alpha}^{MG} \rangle_{(bulk \ PMMA)} = 290$ meV). We recall that this question was also addressed in the linear blend with the same PEO relative content (QENS experiments on a dPEO/hPMMA sample\textsuperscript{28}). For such system, the α-MG dynamics was also found to be rather insensitive to the presence of PEO (see squares in Fig. 3(b)). However, this was not the case of the nano-composite with the opposite concentration recently investigated by us. In that PEO-rich sample, the characteristic times for α-MG rotation were found to be smaller than in bulk. This observation was interpreted as a consequence of the plasticization induced by the surrounding PEO chains. Apparently, such an effect only becomes important for high contents of the fast component.

FIG. 2. Fourier transformed and deconvoluted neutron scattering data of the dPEO/hNPs sample at different temperatures and the indicated values of $Q$(Å$^{-1}$). Solid lines are fitting curves considering α-MG rotation as the main process above $\approx 2$ ps.

B. PEO Dynamics

QENS results on the samples with protonated PEO allow us accessing the dynamics of the PEO component in both, the nano-composite and the linear blend. The function revealed by the experiments is actually the incoherent scattering function of the hydrogens of PEO, $S_{inc}^{PEO}(Q,t)$. Unfortunately, the number of assumptions involved in the modelization of the data (see Appendix A) and the limited dynamic window accessible by QENS (even combining the three instruments here employed) prevent an unbiased and univocal determination of the functional form of this function. Therefore, we have made use of the information provided by fully atomistic MD-simulations on the blend of linear chains PEO/PMMA of similar composition as that here investigated, which was reported in Ref.\textsuperscript{41}. In that work, $S_{inc}^{PEO}(Q,t)$ was parametrized in terms of Kohlrausch-Williams-Watts (KWW) functions

$$S_{inc}^{PEO}(Q,t) \approx e^{-(t/\tau)^\beta}.$$  \hspace{1cm} (1)  

Here $\beta$ is the shape parameter accounting for the deviations from a single exponential function and $\tau$ is a $Q$-
and $T$-dependent characteristic time. The values of the shape parameter $\beta$ obtained for the different temperatures simulated are displayed in Fig. 4(a). They continuously decrease with decreasing temperature and can be well parametrized by the law $\beta = 0.547 - 73.7 / T [K]$ (solid line in the figure).

We used these $\beta$-values (or their extrapolation) to describe $S^\text{PEO}_\text{inc}(Q, t)$ for PEO in both, the nano-composite with NPs and in the blend with linear chains. Figures 5 and 6 show the obtained fitting curves (see Appendix A for the complete expressions used in each case). They reproduce very well all the experimental results above 2 ps, giving support to the choice of the shape parameter on the basis of the MD-simulation results.

Due to the variation of the shape parameter with temperature, in the following we will discuss the results obtained for the characteristic time in terms of the average time $\langle \tau \rangle$, which in the case of KWW functions is related with the parameter $\tau$ in Eq. 1 through the expression $\langle \tau \rangle = \tau \Gamma(1/\beta)/\beta$. Let us first consider the temperature dependence of the characteristic times at a representative $Q$-value. This is shown in the Arrhenius representation of Fig. 7, which compiles the average characteristic times obtained by QENS at $Q = 1 \ \text{Å}^{-1}$ for bulk PEO$^{28}$ and PEO in the two systems investigated in this work. We have chosen $Q = 1 \ \text{Å}^{-1}$ because it is approximatelly at this $Q$-value where the QENS characteristic times usually match those determined by other spectroscopic techniques like dielectric spectroscopy$^{64,65}$. As can be seen in Fig. 7, this is also the case of bulk PEO when NMR data$^{12}$ (inverted empty triangles) are considered. The solid line through the bulk PEO data is a fit of a Williams-Landel-Ferry (WLF) expression:

$$ \log \tau(T) = \log \tau(T_g) - \frac{C_1(T - T_g)}{C_2 + (T - T_g)} . $$

with the parameters $T_g = 221 \ \text{K}$, $C_1 = 8.0$ and $C_2 = 58 \ \text{K}$ as determined in the NMR investigation$^{12}$. Nowadays it is well known that in a polymer blend in equilibrium the segmental relaxation time of one of the components is usually well described by the same WLF expression...
FIG. 5. Fourier transformed and deconvoluted neutron scattering data of the hPEO/dNPs (nano-composite) sample at different temperatures and the indicated values of $Q (\text{Å}^{-1})$. Solid lines are fitting curves considering a KWW functional form for the intermediate scattering function of the PEO component (see the text).

FIG. 6. Fourier transformed and deconvoluted neutron scattering data of the hPEO/dPMMA (linear blend) sample at different temperatures and the indicated values of $Q (\text{Å}^{-1})$. Solid lines are fitting curves considering a KWW functional form for the intermediate scattering function of the PEO component (see the text). At 400 and 375 K the decay above $\approx 2$ ps is just a small tail which cannot be properly modeled by KWW functions with realistic prefactors.

of the corresponding homopolymer but with a different value of $T_g$. This new (effective) $T_{g,\text{eff}}$ value can be calculated, for instance, in the framework of the model proposed by Lodge and McLeish$^{66}$ (LMcL), based on the concept of the "self-concentration" $\phi_{\text{self}}$. The LMcL model assumes that the mobility of a polymer segment in a blend is determined by the chemical composition of the region centered in this segment and within one Kuhn length ($\ell_K$) of this polymer. Within this volume the concentration of the polymer is enhanced over the bulk concentration due to chain connectivity. In the case of PEO, $\phi_{\text{self}}(\ell_K)$ is 0.15, leading to an effective concentration of PEO of 0.36 instead of the average concentration of 0.25. The consequence is a shift of the effective glass transition of this component with respect to the average blend glass transition. From the relative variation of $T_{g,\text{eff}}$ predicted by the Fox$^{12,67}$ equation, this shift can be estimated to be of about 23 K. The insertion of the effective $T_g$ value ($T_{g,\text{eff}}^{PEO} = 310$ K) in Eq. 2 gives the prediction of this model for the timescales of PEO in the blend. It is represented by the dotted line in Fig. 7. As can be seen, the data obtained for PEO in the blend are compatible with this curve only at high temperatures. Approaching the glass-transition of the system (which, as previously commented, is dominated by the freezing of the PMMA-component $T_{g,\text{eff}}^{PMMA}$), the characteristic times become faster than the expected behavior in equilibrium. As it has been mentioned in the Introduction, this behavior has been interpreted$^{28}$ as a consequence of the confinement effects induced by the freezing of the PMMA component on the faster PEO segmental dynamics. The results of PEO in the nano-composite are semiquantitatively the same. Close to the main glass-transition, the characteristic times of both systems are nearly identical. In the glassy state, they follow very similar behavior, and the extension toward lower temperatures performed in the nano-composite confirms the trend of the data in the blend. The confinement effects thus seem to be very similar in both cases. We can also see from Fig. 7 that the dynamics of PEO at low temperatures is difficult to identify with that of secondary relaxations as taking place in the bulk. Looking now in detail in the high-temperature data, a slight difference can be found between the results in both systems: in the nano-composite, the temperature dependence of PEO dynamics seems to be weaker than in the blend (see magnification in the figure).

Now let us analyze the $Q$-dependence of the characteristic times—a unique information provided by QENS
FIG. 7. (a) Inverse-temperature dependence of the average characteristic times obtained by QENS at $Q = 1\ \text{Å}^{-1}$ for PEO in the nano-composite (filled circles), PEO in the blend with linear PMMA (empty squares) and bulk PEO (filled diamonds). For bulk PEO, NMR results\textsuperscript{12} (inverted empty triangles) and dielectric data on the $\gamma$-process\textsuperscript{68} (empty triangles) are also shown. Solid line is a WLF fit of the bulk data. Dotted line is the Lodge & McLeish prediction for segmental relaxation time of PEO in the blend on the basis of this law. The arrow marks the main glass-transition temperature of the mixtures. The inset magnifies the high-temperature results in the mixtures.

spatial resolution. This is shown for the different temperatures investigated in Fig. 8(a) for PEO in the nano-composite and in Fig. 8(b) for PEO in the linear blend. In both kinds of environments the behavior of $\langle \tau \rangle$ is qualitatively the same: in the low-$Q$ range ($Q \lesssim 0.8\ \text{Å}^{-1}$) it follows a power-law in $Q$

\begin{equation}
\langle \tau \rangle = a(T)Q^{-x}
\end{equation}

(see solid lines in the figures) and at higher $Q$-values it tends to deviate from such a law, becoming larger. The values of the $x$-exponent in Eq. 3 are displayed in Fig. 4(b). For temperatures $T \lesssim 350\ \text{K}$ they are, within the uncertainties, identical for both kinds of environments. At the two highest temperatures investigated though, the $x$-parameter corresponding to the nano-composite tends to dramatically decrease with increasing temperature and becomes smaller values than those found for the linear blend.

Considering explicitly the $Q$-dependence of the characteristic times (Eq. 3) in the intermediate scattering function of PEO (Eq. 1) we obtain

\begin{equation}
S_{\text{inc}}^{\text{PEO}}(Q, t) \approx e^{-a(T)^{-1/2} Q^{x/2} t^{\beta}}.
\end{equation}

If $x\beta=2$, this expression corresponds to a Gaussian function in the $Q$-variable $[e^{-\langle r^2(t)\rangle Q^2/6}]$. Then, the mean-squared displacement of the hydrogens would be directly obtained as $\langle r^2(t)\rangle \propto t^\beta$, i.e., the atoms undergo sub-linear diffusion. The condition for Gaussian behavior $x = 2/\beta$ is represented by the dotted line in Fig. 4(b). The results obtained for PEO in the linear blend fulfill, within the uncertainties, the Gaussian approximation in the whole temperature range investigated. This finding fully agrees with the MD-simulations results of Ref.\textsuperscript{41}. From the simulated atomic trajectories it is namely possible to quantify the deviations from Gaussian behavior through the calculation of the non-Gaussian parameter $\alpha_2$ ($\alpha_2 = 0$ in the Gaussian case). This parameter turned out to present very small values for PEO in the blend. Accordingly, after the decaeging regime ($t \gtrsim 30\ \text{ps}$), the mean-squared displacement of PEO’s hydrogens in the
simulated blend was found to increase sublinearly with time as \( \langle r^2(t) \rangle \propto t^y \) with \( y \approx \beta \). Our experimental results thus provide an additional source of validation for those MD-simulations.

For PEO in the NPs, the exponents found in the low-\( Q \) range also indicate close to Gaussian behavior in the temperature range \( T \leq 350 \) K. However, for the two highest temperatures they clearly deviate from the Gaussian prediction. We will discuss this result later.

As pointed out above, in the high-\( Q \) range investigated the \( Q \)-dependence of the characteristic times tends to deviate from the asymptotic low-\( Q \) power law (Eq. 3) for PEO in both systems and all the temperatures investigated. These deviations consist of a kind of flattening of \( \langle \tau \rangle \). They occur in a rather similar way for both samples for 325 and 300 K, but at higher temperatures they become more pronounced for PEO in the nano-composite.

Deviations from the Gaussian behavior \( (\tau \propto Q^{-2/3}) \) can be rationalized invoking the temporary localization of the microscopic motions underlying the sublinear diffusion. For simple diffusion, this ingredient is captured by the jump diffusion model. In this model, an atom remains in a given site for a time \( \tau_o \), where it vibrates around a center of equilibrium. After \( \tau_o \), it moves rapidly to a new position. These jumps are assumed to be randomly orientated and their moduli \( \ell \) are distributed according to a function

\[
f_o(\ell) = \frac{\ell}{\ell_o} e^{-\left( \frac{\ell}{\ell_o} \right)}.
\]

The parameter \( \ell_o \) is the preferred jump distance. This model was generalized for the case of subdiffusive motions—which are those usually observed in glass-forming systems, in particular in polymers—by the anomalous jump diffusion (AJD) model. The intermediate scattering function in the AJD model is a stretched exponential [Eq. 1] where the characteristic time follows the law

\[
\tau_{AJD} = \tau_o \left( 1 + \frac{1}{\ell_o^2 Q^2} \right)^{-\frac{1}{\beta}}.
\]

with \( \tau_o (\ell_o Q)^{-2/3} \) and \( \tau_o \) as asymptotic low-\( Q \) and high-\( Q \) limits respectively. In the AJD model, at large length scales / long times the resulting mean squared displacement asymptotically follows a sublinear increase with time

\[
\langle r^2(t) \rangle = 6\ell_o^2 (t/\tau_o)^{3/2}.
\]

The AJD model has been successfully applied to a number of polymers, including bulk PEO in the nano-composite (filled circles) and in the linear blend (empty squares) in terms of the anomalous jump diffusion model: average residence time (a); preferred jump distance (b). The arrow marks the main glass-transition temperature of the mixtures.

![FIG. 9. Inverse-temperature dependence of the parameters involved in the description of the characteristic times of bulk PEO (empty diamonds) and PEO in the nano-composite (filled circles) and in the linear blend (empty squares) in terms of the anomalous jump diffusion model: average residence time (a); preferred jump distance (b). The arrow marks the main glass-transition temperature of the mixtures.](image)
We now focus on temperatures above \( T_{PMMA}^{g,eff} \approx 330 \) K. In this regime, the local dynamics of PEO dramatically differs in both samples. In the blend, the average residence times become faster with increasing temperature and the distances involved in the elementary jumps for sublinear diffusion do not sensitively vary. On the contrary, in the nano-composite we observe that the value of the elementary time remains approximately the same as at the glass-transition and the preferred jump length drastically increases with increasing temperature. In this temperature range we can compare the results with the corresponding ones for bulk PEO —there are available data above its melting point. With respect to the bulk, in the blend the motions of PEO at local length scales are somewhat less Gaussian: the value of the preferred jump length is slightly larger, and consequently the distribution of jump lengths a little bit broader [see Fig. 10(a)]; moreover, the residence time is 3 to 5-fold longer. The vicinity of PMMA mobile —but slower—chain segments thus induces an additional source for distributed environments and slows down the PEO local dynamics. Nevertheless, the behavior displayed by PEO in the blend is qualitatively the typical one observed for glass-forming polymers in equilibrium, and these results could perfectly be rationalized in the light of the existing knowledge on polymer blend dynamics, invoking the concepts of dynamic heterogeneity and concentration fluctuations. We remind that this was also the situation reported from the QENS studies of the minority PEO component in blends with PVA and PES. This is not the case of PEO in the nano-composite. The values of the average residence times \( \langle \tau_o \rangle \) are extremely long —more than 100-fold longer than in bulk. We note that these times are directly related with the decaeging processes, and in the supercooled liquid (metastable) equilibrium regime are expected to be located typically in the pico-second region. Thus, these results suggest that in the nano-composite PEO segments are momentarily highly efficiently trapped by the PMMA nano-particles —even at temperatures where the latter are above their glass-transition temperature. The ‘effective cage’ imposed to a PEO hydrogen in a PMMA-NPs-rich environment takes an extremely long time to ‘soften’. However, once PEO segments get rid of this cage, the jumps can be relatively large with respect to those taking place in the PEO or linear PMMA chains environments, as can be seen in the distributions of jump lengths depicted in Fig. 10. With increasing temperature, the extent of the local motions becomes larger in average, leading to larger values of the resulting mean squared displacements (Eq. 7). Simultaneously, the broader and broader distributions of relatively long elementary jump lengths lead to larger deviations from Gaussian behavior of PEO motions, as manifested in the value of the \( x \)-exponent in Eq. 3 (Fig. 4).

Once the PMMA component starts to be mobile, its topology seems thus to be a determining ingredient in the dynamics of PEO segments. The presence of linkages between PMMA monomers causes the temporary blockage of the more flexible component and, when the latter can leave such an imposed cage, it jumps over larger distances as those characteristic for the motions either in bulk or in an environment of linear PMMA chains. In this trapping mechanism the local loops in the nano-particles may play an important role. As it has been shown by MD-simulations and is schematically illustrated in Fig. 1, a relatively large number of the crosslinks occur between nearest monomers (or monomers very close in real space). These bonds do not contribute to the collapse of the macromolecule into a globular structure —this is con-
trolled by crosslinks involving monomers separated by large contour distances— but it could be expected that they would strongly restrict the local motions of the PMMA portions involved in the loops with respect to those in a linear macromolecule. The local relaxation of the such affected PMMA segments would be severely obstructed and this might greatly hamper the development of PEO’s motions.

IV. SUMMARY AND CONCLUSIONS

Quasielastic neutron scattering on labeled samples has allowed characterizing the component dynamics in a nano-composite of PEO linear chains and PMMA-nanoparticles, with high concentration of nano-particles. The α-methyl group dynamics of PMMA—the main process accessed in the investigated temperature/time window—is hardly affected by the presence of PEO, with exception of showing a slightly broader distribution of potential barriers. This can be attributed to more heterogeneous environments for methyl groups in the nano-composite than in bulk PMMA. The investigation of the PEO component has been performed considering the equivalent blend of linear chains as reference. We have shown that once the blend approaches the glass-transition—provoked by the slowing down of the slow component—PEO dynamics displays deviations with respect to the expected equilibrium behavior. The freezing of the PMMA-based component leads to a dynamical response of PEO which shows the same features independently of the topology of the former. This finding supports the interpretation of the motions of the fast PEO component as confined by a surrounding rigid matrix. Interestingly enough, the differences in PEO dynamics emerge above the glass-transition of the slow component, when the surrounding environment of PEO starts to be mobile. There both, the blend and the nano-composite are in the supercooled liquid (metastable) equilibrium state. Linear PMMA motions are enough to leave PEO segments move with the typical features of supercooled polymers in metastable equilibrium. The presence of PMMA just leads to more distributed environments and moderately slows down PEO local dynamics. Contrarily, in the nano-composite PEO dynamics develops larger and larger deviations from Gaussian behavior with increased mobility of the nano-particles. These enhanced deviations are caused by an increase of the spatial extent of the elementary jumps of PEO for segmental dynamics with increasing temperature. These jumps appear to be very heterogeneous and would take place after the segment being trapped for a very long time—more than two orders of magnitude longer than in bulk or surrounded by linear PMMA chains—in effective cages imposed by the nano-particles. We speculate that in this trapping mechanism the local loops in the nano-particles may play an important role.

ACKNOWLEDGMENTS

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Appendix A: Neutron Scattering Data Evaluation

In neutron scattering (NS) experiments the scattered intensity \(I_{\text{exp}}(Q, \omega)\) is recorded as a function of energy transfer (\(\hbar \omega\)) and wave vector transfer \(Q\); in isotropic systems, for simplicity the modulus \(Q\) of this vector is considered. Being \(R(Q, \omega)\) the normalized instrumental resolution function, for a monoatomic sample \(I_{\text{exp}}(Q, \omega)\) can be expressed as:

\[
I_{\text{exp}}(Q, \omega) = \left[ I_{\text{inc}}S_{\text{inc}}(Q, \omega) + I_{\text{coh}}(Q)S_{\text{coh}}(Q, \omega) \right] \otimes R(Q, \omega).
\]

\(I_{\text{inc}}\) and \(I_{\text{coh}}(Q)\) represent respectively the 'static' incoherent and coherent intensities or differential cross-sections –its sum \(I_{\text{tot}} = I_{\text{inc}} + I_{\text{coh}}(Q)\) is the magnitude recorded in a diffraction experiment. They can be expressed as \(I_{\text{inc}} = I_{n}\sigma_{\text{inc}}\) and \(I_{\text{coh}}(Q) = I_{n}\sigma_{\text{coh}}S(Q)\), being \(I_{n}\) an instrument-dependent factor, \(S(Q)\) the static structure factor and \(\sigma_{\text{inc}}\) and \(\sigma_{\text{coh}}\) the incoherent and coherent scattering cross sections of the atom. \(S_{\text{inc}}(Q, \omega)\) and \(S_{\text{coh}}(Q, \omega)\) are respectively the incoherent and the normalized coherent scattering functions. They are the Fourier transform of the intermediate incoherent scattering function \(S_{\text{inc}}(Q, t)\) and the normalized dynamic structure factor \(\tilde{S}_{\text{coh}}(Q, t) = S_{\text{coh}}(Q, t)/S_{\text{coh}}(Q, t = 0) = S_{\text{coh}}(Q, t)/S(Q)\), defined as:

\[
S_{\text{inc}}(Q, t) = \frac{1}{N} \sum_{i=1}^{N} e^{iQR_{i}(t)}e^{-iQR_{i}(0)}
\]

\[
S_{\text{coh}}(Q, t) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} e^{iQR_{i}(t)}e^{-iQR_{j}(0)}
\]

where \(R_{i}(t)\) is the position vector of atom \(i\) at time \(t\) and \(N\) is the total number of atoms in the system. Thus, incoherent scattering reveals correlations of the position of a single atom at different times while coherent scattering relates to collective features through atomic pair correlations.

Most systems consist of different kinds of isotopes \(\alpha\) (e.g. \(\alpha = \text{H, D, C, O, ...}\)). Then, the situation is more complicated because the contributions of each isotope are differently weighted –the cross sections vary from one isotope \(\alpha\) to another. Then, Eq. A1 can still be used properly redefining the magnitudes involved. The cross sections of the total sample are obtained as \(\sigma_{\text{inc(coh)}}(\alpha \text{coh}) = \sum_{\alpha} N_{\alpha} \sigma_{\alpha, \text{inc(coh)}}/N\). Here \(N_{\alpha}\) is the number of nuclei of kind \(\alpha\), \(\sigma_{\alpha, \text{inc(coh)}}\) is the incoherent (coherent) cross section of isotope \(\alpha\) and \(N = \sum_{\alpha} N_{\alpha}\). The values of \(\sigma_{\alpha, \text{inc(coh)}}\) for the different isotopes composing the samples investigated in this work are listed in Table I.

<table>
<thead>
<tr>
<th>isotope</th>
<th>(\sigma_{\text{inc(barns)}})</th>
<th>(\sigma_{\text{coh(barns)}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>79.91</td>
<td>1.76</td>
</tr>
<tr>
<td>D</td>
<td>2.04</td>
<td>5.60</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td>4.24</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>5.56</td>
</tr>
</tbody>
</table>

TABLE I. Neutron scattering cross-sections for different isotopes present in the samples investigated.

1. Determination of Coherent and Incoherent Contributions

From the values of \(\sigma_{\alpha, \text{inc(coh)}}\) in Table I, the theoretical values of the cross sections of the samples investigated can be calculated. We note that in the NPs a fraction of the hydrogen atoms \(n_{\text{PMMA}} = 0.45\) is located in the PMMA monomers and the rest in the AEMA+EGDA part of the macromolecule \(n_{\text{X-link}} = n_{\text{AEMA}} + n_{\text{EGDA}}\), \(n_{\text{AEMA}} = 0.42\), \(n_{\text{EGDA}} = 0.13\). Such \(n_{\text{X-link}}\) fraction remains hydrogenated in the deuterated NPs. Taking this into account, the obtained ratios \(\sigma_{\text{coh}}/\sigma_{\text{tot}}\) are listed in Table II. For both samples this ratio is small, indicating that most of the scattered intensity is expected to be incoherent in nature. However, since the coherent intensity \(I_{\text{coh}}(Q)\) depends on \(Q\) through the (partial) structure factor, the value of \(\sigma_{\text{coh}}/\sigma_{\text{tot}}\) only corresponds to the \(Q \to \infty\) asymptotic limit of the ratio \(I_{\text{coh}}(Q)/I_{\text{tot}}(Q)\). The full information about this function is provided by polarization analysis. If the incoherent scattering is originated only due to the spin disorder, the spin of the neutrons is flipped with a probability of \(\frac{1}{2}\), while in case of coherent scattering no such spin flip occurs. Using a polarized incident neutron beam, from the spin-flipped \((I_{\text{NSF}})\) and non-spin-flipped \((I_{\text{NSF}})\) intensities, the ratio between coherent and incoherent scattering cross sections \(I_{\text{coh}}(Q)\) and \(I_{\text{inc}}\) is obtained as

\[
\frac{I_{\text{coh}}(Q)}{I_{\text{inc}}} = \frac{I_{\text{NSF}}(Q) - \frac{1}{2}I_{\text{NSF}}(Q)}{\frac{1}{2}I_{\text{NSF}}(Q)}
\]

In this work, the separation of coherent and incoherent contributions to the neutron intensity scattered by the nano-composites was carried out by diffraction experiments with polarization analysis by means of the diffuse scattering spectrometer DNS92 at Jülich Centre of Neutron Research (JCNS) at Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II). Using an incident neutron wavelength of \(\lambda=4.2\) a reciprocal length scale from \(Q=0.2\) \(\text{Å}^{-1}\) to 2.67 \(\text{Å}^{-1}\) was covered. Figure 11 shows the DNS results obtained on the two nano-composite samples with complementary deuteration labeling. At high Qs the DNS results agree well with the theoretical asymptotic values. The increase in the low-Q region arises from the contrast due to the labelled components, revealing the form factors. In the Q-range above \(\approx 0.5\) \(\text{Å}^{-1}\), the coherent neutron intensity reflects...
FIG. 11. Relative fraction of coherently scattered intensity determined by DNS for the two differently labeled nano-composites: hPEO/dNPs (empty circles) and dPEO/hNPs (filled circles).

the partial structure factors. There the relative coherent contribution remains in the range $\sim 12\%$-$24\%$. For the linear blend, DNS results reported in Ref.\textsuperscript{28} show similar features. This means, in all the samples the dominant contribution is the incoherent one.

2. Analysis of QENS Spectra

The analysis of the quasielastic spectra was based on Fourier transforming the data to the time domain and deconvoluting them from instrumental resolution effects applying the following procedure. A convolution product in $\omega$-space becomes a simple product in Fourier $t$-space. Therefore, the Fourier transform of Eq. A1 into the time domain is:

$$FT \left[ I_{exp}(Q,\omega) \right] = \left[ I_{inc} S_{inc}(Q,t) + I_{coh}(Q) \tilde{S}_{coh}(Q,t) \right] R(Q,t) \quad (A4)$$

where $R(Q,t)$ is the Fourier transform of the resolution function. For $T \to 0$, both $S_{inc}(Q,\omega)$ and $\tilde{S}_{coh}(Q,\omega)$ are expected to be $\delta(\omega)$ functions (completely elastic signal)\textsuperscript{84}. Then, the low-temperature spectra can be written as:

$$I_{exp}(Q,\omega,T \to 0) = [I_{inc} + I_{coh}(Q)] \delta(\omega) \otimes R(Q,\omega) = I_{tot}(Q) \delta(\omega) \otimes R(Q,\omega). \quad (A5)$$

The Fourier transform of Eq. A5 is just $I_{tot}(Q)R(Q,t)$. Then, Fourier transforming the measured spectra at a given temperature and dividing the result by the Fourier transformed low temperature data, we obtain the deconvoluted intermediate scattering function $I(Q,t)$:

$$I(Q,t) = \frac{FT \left[ I_{exp}(Q,\omega) \right]}{FT \left[ I_{exp}(Q,\omega,T \to 0) \right]} = \frac{I_{inc}}{I_{tot}(Q)} S_{inc}(Q,t) + \frac{I_{coh}(Q)}{I_{tot}(Q)} \tilde{S}_{coh}(Q,t). \quad (A6)$$

The ratios $I_{inc}/I_{tot}(Q)$ and $I_{coh}(Q)/I_{tot}(Q)$ are known from the DNS experiments.

The intermediate incoherent scattering function $S_{inc}(Q,t)$ can be decomposed in terms of the contributions from the two components, $S_{inc}(Q,t) = f_{PEO}^{inc} S_{PEO}^{inc}(Q,t) + f_{NPs}^{inc} S_{NPs}^{inc}(Q,t)$ for the nano-composite and $S_{inc}(Q,t) = f_{PEO}^{inc} S_{PEO}(Q,t) + f_{PMMA}^{inc} S_{PMMA}(Q,t)$ for the blend. The fraction $f_{inc}$ (x: PEO, NPs, PMMA) is defined as

$$f_{inc}^x = \frac{\sigma_{inc}^x}{\sigma_{inc}} \quad (A7)$$

where

$$\sigma_{inc}^x = \frac{1}{N} \sum_{i \in x} \sigma_{i,inc} \quad (A8)$$

The index $i$ runs over all atoms belonging to component $x$. In an analogous way, the fractions $f_{coh}$ can be calculated, substituting the incoherent cross sections by the coherent ones in Eqs. A7 and A8. Table II shows the fractions obtained for the PEO component $f_{PEO}^{inc(coh)}$ in the samples investigated in this work (obviously, $1 - f_{PEO}^{inc(coh)}$ is the corresponding fraction of the other component).

In the following we introduce the model functions used to describe the deconvoluted intermediate scattering function $I(Q,t)$ obtained for each of the samples investigated. We note that these functions are intended to account for the behavior at times above $\approx 2$ ps, i.e., after the 'microscopic dynamic' processes. These include e.g. harmonic and anharmonic vibrations, the Boson peak, librations, and the so-called 'fast process' taking place in glass-forming systems which origin has not yet been clarified (see, e.g.\textsuperscript{85}). These microscopic dynamics give rise to the decay of the correlations below the picosecond and their contribution is parametrized as a prefactor in the intermediate scattering function.

<table>
<thead>
<tr>
<th>sample</th>
<th>$f_{coh}$</th>
<th>$f_{PEO}$</th>
<th>$f_{PMMA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>dPEO/hNPs</td>
<td>0.11</td>
<td>0.01</td>
<td>0.29</td>
</tr>
<tr>
<td>hPEO/dNPs</td>
<td>0.13</td>
<td>0.35</td>
<td>0.16</td>
</tr>
<tr>
<td>hPEO/dPMMA</td>
<td>0.27</td>
<td>0.94</td>
<td>0.17</td>
</tr>
</tbody>
</table>

TABLE II. Relative fraction of coherent cross section $\sigma_{coh}$ and relative coherent and incoherent contributions of the PEO component for the samples investigated.
a. \textbf{dPEO/hNPs sample}

Since for the sample with deuterated PEO (dPEO/hNPs) $I_{\text{inc}}^{\text{NPs}} \gg I_{\text{inc}}^{\text{PEO}}$ (Table II), we can approximate the total intermediate scattering function obtained for this sample $I_{\text{tot}}^{\text{dPEO/hNPs}}(Q,t)$ as:

\begin{equation}
I_{\text{tot}}^{\text{dPEO/hNPs}}(Q,t) \approx \frac{I_{\text{inc}}}{I_{\text{tot}}(Q)} S_{\text{inc}}^{\text{NPs}}(Q,t) + \frac{I_{\text{coh}}(Q)}{I_{\text{tot}}(Q)} S_{\text{coh}}(Q,t). \quad (A9)
\end{equation}

We have assumed that the segmental dynamics of the NPs is too slow to give rise to quasielastic scattering in the temperature range investigated. The only process expected to be detected in QENS dynamic window is methyl-group (MG) rotation (see Appendix B). PMMA contains two kinds of MGs: the $\alpha$-MG, directly linked to the main chain and the ester MG. In bulk, this group is restricted by a very low potential barrier which generates a very fast dynamics and its contribution can be fully characterized by the EISF($Q$) (Eq. B3). This is expected to be also the case of ester-MGs in the NPs – both in PMMA and AEMA units. Thus, the intermediate scattering function of hydrogens in the NPs at $t \geq 2\text{ps}$ was written as:

\begin{equation}
S_{\text{inc}}^{\text{NPs}}(Q,t) = A^{\text{NPs}} \left[ n_e EISF(Q) + n_\alpha S_{\text{coh}}^{\text{rot}}(Q,t) + n_C \right] \quad (A10)
\end{equation}

where $n_e$, $n_\alpha$ and $n_C$ are the relative number of the ester, $\alpha$ and chain hydrogen atoms in the NP ($n_e=0.35$, $n_\alpha = 0.17$, $n_C = 0.48$, taking into account the hydrogens located in the cross-linking moieties). $S_{\text{inc}}(Q,t)$ is the intermediate scattering function for MG-rotation in the RRDM model (Eq. B8) and $A^{\text{NPs}}$ is a prefactor accounting for vibrations and fast dynamical processes – the same vibrational microscopic dynamics was assumed for all hydrogens for the sake of simplicity. For the coherent scattering function $S_{\text{coh}}(Q,t)$ we assumed a KWW functional form (Eq. 1) affected by the same vibrational contribution $A^{\text{NPs}}$. The resulting $\beta$ and characteristic times were found to be compatible with those found for the incoherent scattering function of PEO as deduced from the analysis of the hPEO/dNPs sample.

b. \textbf{hPEO/dNPs sample}

For the opposite labeling (hPEO/dNPs sample) the scattered intensity is still dominated by that of the hydrogens in the sample. However, since part of the majority component (the cross-linking moieties in the dNPs) is not deuterated, a large fraction of such incoherent scattering does not come from the PEO component but from the remaining hydrogenated part of the NPs. This contribution was assumed to be elastic in the QENS window for the temperatures investigated. Also the coherent scattering function, which is dominated by the majority NPs-component, was assumed to be elastic. For both, coherent and incoherent elastic contributions of the NPs, the same constant $A^{\text{NPs}}$ was chosen as representative for the vibrational dynamics. Then,

\begin{equation}
I_{\text{tot}}^{\text{hPEO/dNPs}}(Q,t) \approx \frac{I_{\text{inc}}}{I_{\text{tot}}(Q)} S_{\text{inc}}^{\text{PEO}}(Q,t) + f_{\text{coh}} A^{\text{NPs}} + \frac{I_{\text{coh}}(Q)}{I_{\text{tot}}(Q)} A^{\text{NPs}}. \quad (A11)
\end{equation}

The functional form for the incoherent scattering function for PEO-hydrogens was assumed to be a KWW (Eq. 1).

c. \textbf{hPEO/dPMMA sample}

In the reference blend hPEO/dPMMA sample the majority PMMA component was fully deuterated. Consequently $I_{\text{inc}}^{\text{hPEO}} >> I_{\text{inc}}^{\text{PEO}}$ and $f_{\text{coh}}^{\text{PMMA}} >> f_{\text{coh}}^{\text{PEO}}$. The corresponding deconvoluted function $I_{\text{tot}}^{\text{hPEO/dPMMA}}(Q,t)$ can be approximated by:

\begin{equation}
I_{\text{tot}}^{\text{hPEO/dPMMA}}(Q,t) \approx \frac{I_{\text{inc}}}{I_{\text{tot}}(Q)} S_{\text{PEO}}^{\text{PEO}}(Q,t) + \frac{I_{\text{coh}}(Q)}{I_{\text{tot}}(Q)} S_{\text{coh}}^{\text{PMMA}}(Q,t). \quad (A12)
\end{equation}

As for the PEO component in the nano-composite, $S_{\text{inc}}^{\text{PMMA}}(Q,t)$ was assumed to be a KWW (Eq. 1). The coherent contribution due to PMMA pair correlations was assumed to be elastic and described by a simple prefactor giving account for the vibrations. For simplicity, this was assumed to be the same as that affecting the PEO contribution.

\begin{equation}
V(\phi) = \sum_{n=1}^{\infty} \frac{V_{3n}}{2} [1 - \cos(3n\phi + \delta_{3n})]. \quad (B1)
\end{equation}

Here $\phi$ is one characteristic coordinate, which is measured in the plane perpendicular to the $C_3$-symmetry axis of the methyl group. At high temperatures, the methyl
group dynamics can be described by hopping processes over the potential barriers. Assuming that the hopping time between two equilibrium positions is negligible in comparison with the residence time $\tau_R$ between consecutive jumps in a 3-fold potential, the characteristic time is:

$$\tau = 2\tau_R/3$$

and the intermediate incoherent scattering function for a methyl group can be written as:

$$S^r_{inc}(Q,t) = EISF + (1 - EISF)\exp\left(-\frac{t}{\tau}\right). \quad (B2)$$

The elastic incoherent structure factor EISF carrying the energy:

$$EISF = \frac{1}{3} \left(1 + 2\sin\left(\frac{Qr_{HH}}{Qr_{HH}}\right)\right). \quad (B3)$$

Here $r_{HH} = 1.78$ Å is the distance between the hydrogens in the methyl group. The temperature dependence of $\tau$ is determined by the activation energy $E_{a}^{MG}$, which is defined as the difference between the top of the barrier and the ground state, by the Arrhenius law

$$\tau = \tau_\infty \exp\left[\frac{E_{a}^{MG}}{(KB)T}\right].$$

It is well known that this simple model does not work in glassy systems where the inherent disorder leads to distributions of mobilities. This aspect was introduced by the so-called rotation rate distribution model (RRDM)\textsuperscript{60-63}. The RRDM model introduces a distribution of potential barriers and, consequently, of activation energies $f(E_{a}^{MG})$, arising from the variety of environments in the amorphous material. This distribution is assumed to be Gaussian:

$$f(E_{a}^{MG}) = \frac{1}{\sqrt{2\pi}\sigma_E} \exp\left[-\frac{(E_{a}^{MG} - \langle E_{a}^{MG} \rangle)^2}{2\sigma_E^2}\right] \quad (B4)$$

with average energy $\langle E_{a}^{MG} \rangle$ and standard deviation $\sigma_E$. The preexponential factor $\tau_\infty$ is assumed to be independent of the barrier, leading to a log-Gaussian distribution of characteristic times for classical hopping:

$$H(\log \tau) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(\log \tau - \log \tau_{\infty}^{MG})^2}{2\sigma^2}\right] \quad (B5)$$

where

$$\sigma = \frac{\sigma_E \log(e)}{K_B T} \quad (B6)$$

is the width. $H(\log \tau)$ is centered at the characteristic time $\tau_{\infty}^{MG}$ corresponding to the average activation energy:

$$\tau_{\infty}^{MG} = \tau_\infty \exp\left(\frac{\langle E_{a}^{MG} \rangle}{K_B T}\right). \quad (B7)$$

Thus, the final scattering function is built by adding the scattering functions of the hydrogens located in the different environments weighted by the distribution function,

$$S^{rot}_{inc}(Q,t) = \int_{-\infty}^{+\infty} H(\log \tau) S^r_{inc}(Q,t)d(\log \tau). \quad (B8)$$

PEO confined by PMMA nanoparticles


M. Béé, Quasielastic Neutron Scattering (Adam Hilger, Bristol, 1988).


M. Béé, Quasielastic Neutron Scattering (Adam Hilger, Bristol, 1988).


In the spectra of the sample containing protonated PMMA a quasielastic contribution due to tunneling of the ester MGs is expected. However, such contribution should be very weak with respect to the total elastically scattered intensity at low temperatures.
