INFLUENCE OF CONFINEMENT ON POLYMER-ELECTROLYTE RELAXATIONAL DYNAMICS

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ABSTRACT

Conception and industrial production of viable high specific energy/power batteries is a central issue for the development of non-polluting vehicles. In terms of stored energy and safety, solid-state devices using polymer electrolytes are highly desirable. One of the most studied systems is PEO (polyethylene oxide) complexed by Li salts. Polymer segmental motions and ionic conductivity are closely related. Bulk PEO is actually a biphasic system where an amorphous and a crystalline state ($T_m \approx 335$ K) coexist. To improve ionic conduction in those systems requires a significant increase of the amorphous phase fraction where lithium conduction is known to mainly take place. Confinement strongly affects properties of condensed matter and in particular the collective phenomena inducing crystallization. Confinement of the polymer matrix is therefore a possible alternative route to the unpractical use of high temperature.
Results of a quasi-elastic incoherent neutron scattering study of the influence of confinement on polyethylene oxide (PEO) and $(PEO)_8Li^+[(CF_3SO_2)_2N]^-$ (or $(POE)_8$LiTFSI) dynamics are presented. The nano-confining media is Vycor, a silica based hydrophilic porous glass (characteristic size of the 3D pore network ≈ 50 Å). As expected, the presence of Li salt slows down the bulk polymer dynamics. The confinement also affects dramatically the apparent mean-square displacement of the polymer. Local relaxational PEO dynamics is described KWW model. We also present an alternate model and show how the detailed polymer dynamics (correlation times and local geometry of the motions) can be described without the use of such stretched exponentials so as to access a rheology-related meaningful physical quantity: the monomeric friction coefficient.

INTRODUCTION

Up to date many studies have shown the interest and the feasibility of hybrid battery [1] cells where organic and inorganic components are used. One of the most studied systems is PEO (polyethylene oxide) complexed by Li salts. Bulk PEO is actually a biphasic system where an amorphous and a crystalline state ($T_m \approx 335$ K) coexist. Confinement is known to strongly affect properties of condensed mater and in particular the collective phenomena inducing crystallization [2]. A possible alternative solution to this high temperature mode seems therefore the confinement of the polymer matrice.

Structure of polymer chains confined in Vycor porous glass [3,4] have already been reported [5] and found in agreement with theoretical predictions [6]. Restricted geometry effects on dynamics of polymers confined in Vycor have been measured by NMR [7]. We have recently studied by inelastic incoherent neutron scattering the influence of confinement on PEO and $(PEO)_8Li^+[(CF_3SO_2)_2N]^-$ (or $(POE)_8$LiTFSI) dynamics in bulk and confined in Vycor. As measured by small angle neutron scattering, radius of gyration of PEO melt 100,000 g/mol at 371 K is 120 Å [8]. PEO 100,000 g/mol adsorbed into the Vycor 35 Å radius pore [4] is therefore expected to show large confining effects. Those results and the connection to ionic conductivity have been presented elsewhere [9]. In the present paper, we want to focus on the detailed analysis of incoherent inelastic neutron scattering data. We also show, in the specific case of bulk PEO, how to take the detailed local polymer dynamics into account so as to describe the polymer dynamics by an alternative way to stretched exponentials.

EXPERIMENTAL DETAILS

Polymer: PEO used in the present study is hydrogenated PEO (molecular weight = 100,000 g/mol, Aldrich). $(POE)_8$LiTFSI film was prepared by casting onto a Teflon coated plate and stepwise evaporating under dry air, an acetonitrile solution (Aldrich) mixed with right proportions of PEO and LiTFSI. A PEO film was prepared by melting at 95°C the needed amount of PEO under dry air into a similar Teflon coated plate. What we refer as the bulk samples of this work are PEO and $(POE)_8$LiTFSI films of 0.2 ± 0.05 mm thickness. Necessary amount of each of those films was saved and used to prepare the Vycor confined samples.

Confining media: Vycor 7930 glass [3] is made by heating a homogeneous mixture of boron oxide glass and silica above the melting point and then quenching this mixture to a temperature below the spinodal line where the mixture phase separates into two mutually interpenetrating regions. At a certain stage of preparation, the boron rich region is leached out by acid, leaving behind a silica skeleton with a given distribution of pore sizes. Due to numerous surface pending silanol groups (-SiOH), Vycor is extremely hydrophilic.

In order to avoid multiple scattering effects, a main concerned of a neutron scattering experiment is to ensure a sample neutron transmission of 90%. Assuming a full polymer filling of the Vycor network taking into account the Vycor and polymer densities, total neutron scattering cross sections, the optimal sample thickness was found to be 0.4 mm. Several rectangular plates of that thickness were cut out of a 25 mm diameter Vycor (ANL/APS optics laboratory). Plates were then immersed in 30% hydrogen peroxide and heated to 90°C for a few hours to remove any organic impurities absorbed by the glass. The Vycor was then washed several times in distilled water in order to remove the hydrogen peroxide and stored in distilled water. Samples were then pumped under 10^{-5} torr for 3 days, defining what we call a "Vycor sample". The average Vycor pore radius is 35 Å. Porosity is 28% of total volume [4], PEO and Vycor density are 1.1 and 1.4 respectively. Total PEO filling of the porous network is then expected for a ratio $m_{PEO}/m_{DryVycor}$=0.22. Confined samples were prepared by melting, under vacuum at 95°C, onto the Vycor plates pieces of the previously prepared PEO and $(POE)_8$LiTFSI films. After 72 hours, then back to room

temperature, mass of Vycor plates had increased of 23% for PEO and 24% for $(POE)_8LiTFSI$, suggesting a full filling of the Vycor porous network.

Neutron scattering experiment: Bulk and confined polymer dynamics has been measured on the QENS spectrometer (ANL/IPNS) (Fig. 1). Qens is an inverted geometry time-of-flight inelastic neutron spectrometer (Fig. 1). 30 times by second, the sample is illuminated by a white neutron beam originating from the moderator. 22 crystal analyzers devices discriminate the 4.8 Å neutrons that are Bragg reflected on the 145 inelastic detectors.

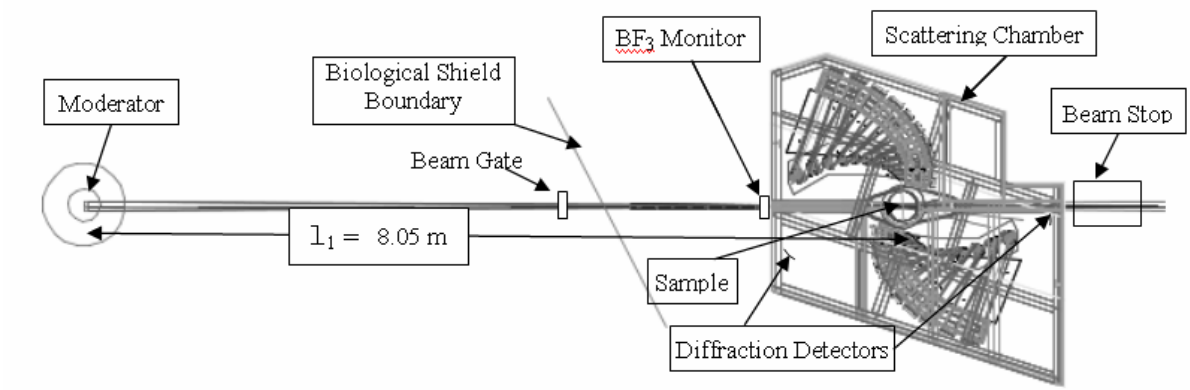

Fig. 1. A schematic layout of QENS (ANL/IPNS). Neutron scattering experiments have been performed on th QENS spectrometer (ANL/IPNS). An average energy resolution (FWHM) varying from 80 μeV (elastic) to 4-5% of the energy transfer (inelastic, up to ~200 meV neutron energy loss) is maintained over a wide range of wavevectors from 0.3 to 2.5 $Å^{-1}$. The diffraction patterns (total scattering) from 0.05 to 30 $Å^{-1}$ are measured concurrently by two additional detector clusters.

Signal from those detectors are directly related to $S(Q,\omega)$ the dynamical structure factor of the sample. In parallel, the white neutron intensity scattered by the sample is recorded by two diffraction detectors banks allowing the sample static structure factor to be measured in the range [0.01 $Å^{-1}$,30 $Å^{-1}$]. Installation of super mirror funnel guide has resulted in an increase of flux of a factor 2.5 in the Quasi-elastic region. Detail description of the instrument will be found elsewhere [[10]] but we want to insist in this paper on the ability of this instrument to measure at the same time, local (few Å) sample dynamics in the piscosecond time range and sample structure (diffraction and small angle scattering). The later is in our opinion particularly important to (i) draw a clear and direct correlation when dynamical event(s) are correlated to phase transition(s) and (ii) for confining media in-situ characterization in study like the present one, where dynamical changes are induced by confinement.

DISCUSSION

In an incoherent inelastic neutron scattering experiment, the decrease as a function of Q of the integrated quasi-elastic intensity is related to the atomic mean-square displacement, $<u^2>$, of the atoms under scrutiny (i.e. in the present case, the PEO polymer protons). As shown by the $<u^2>$ temperature dependence of PEO bulk and confined (Table 1), confinement induces a striking decrease of the polymer mobility.

T (K)	$<u^2>$ Bulk PEO (Å^2)	$<u^2>$ Vycor confined PEO (Å^2)
150	0.025 ± 0.004	0.032 ± 0.004
298	0.078 ± 0.004	0.082 ± 0.005
333	0.105 ± 0.005	0.101 ± 0.005
363	0.202 ± 0.005	0.142 ± 0.006

Table 1. Influence of confinement on PEO mean-square displacement, $<u>^2$, as measured by incoherent inelastic neutron scattering. The melting transition of PEO at 335 K, is strongly affected by confinement: the lower $<u>^2$ of confined PEO compared to bulk at 363 K is to be interpreted as a consequence of strong slowing down of the polymer dynamics.

This information can be considered as a sum-up of the dynamical effect of confinement, but detailed analysis of the energy dependence of the neutron intensity scattered at each angle (i.e. Q) can provide a much more detailed information.
Visual inspection of a susceptibility representation of PEO QENS data allows identifying two distinct independent dynamical contributions in the system. A broad Q independent excitation is observed at relatively high quasi-elastic energy transfer around 3-5 meV. An additional very dispersive low energy excitation, associated to polymer segmental dynamics, is also identified.
Such local relaxation of polymer melts is known to be satisfactory described by a Kohlraush-Williams-Watts (KWW) or (stretched exponential) function. For the sake of simplicity, the broad excitation will be supposed to be due to a single correlation time τ_0 and will therefore take the functional form of a Lorentzian line of, $\Gamma r = 1/\tau_0$ HWHM. The related total dynamical structure factor as measured by inelastic neutron scattering is therefore:

$$S(Q,\omega) = \frac{I_1(Q)}{\pi}\int_0^{\infty} e^{-\left(\frac{t}{\tau(Q)}\right)^{\beta}} e^{iQr.\omega t}dt + \frac{I_2(Q)}{\pi}\frac{\Gamma_r(Q)}{\Gamma_r(Q)^2+\omega^2} \qquad (1)$$

where τ is a Q dependant relaxation time, $\beta < 1$ is the "stretch exponent" that controls the extension of the decay process in time (t), Q is the scattering vector and ω is the energy transfer from/to neutron to/from sample.
Numerical adjustment of Eq.1 to experimental data is satisfactory in the range -1.5 meV up to 10 meV and allows extracting numerical values of the parameters involved.

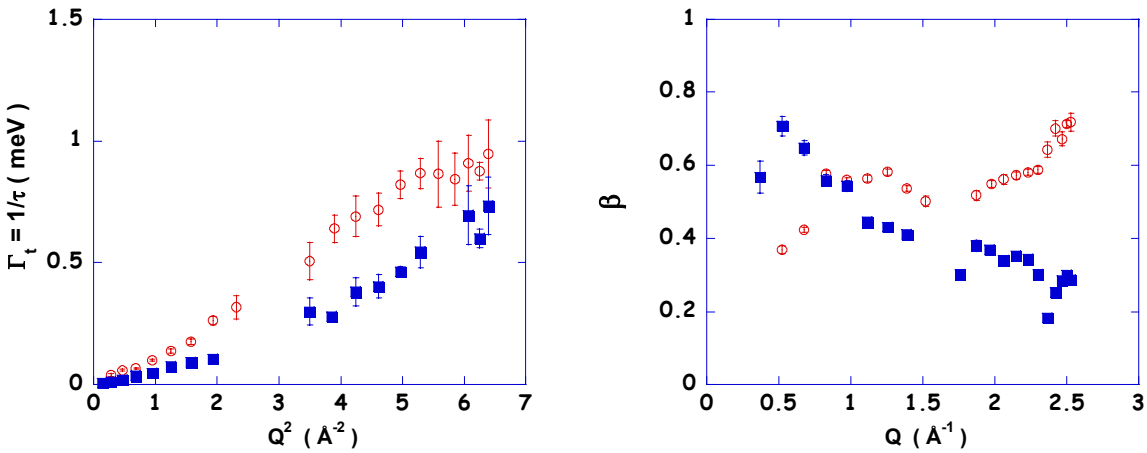

Fig.2. Q dependence of the correlation time, τ (left) and exponent β (right) of Eq.1 for bulk (o) and Vycor confined (■) PEO at T = 373 K.

The trend observed by the analysis of atomic mean square displacements (Table. 1) is confirmed: upon confinement, the correlation times associated with polymer segmental dynamics are significantly increased over the whole Q range (Fig.2). A significant change is also observed in the Q behaviour of the stretched exponent. In the case of bulk PEO, β is fairly Q independent at an average value of 0.58, but upon confinement it becomes strongly Q dependant and at high Q becomes smaller that the stretched exponent of the bulk. This strongly suggests that the distribution of correlation times describing the local polymer dynamics significantly broadens upon confinement. Γ_r is found fairly Q independent in bulk and confined PEO and is found to be almost not affected by confinement.

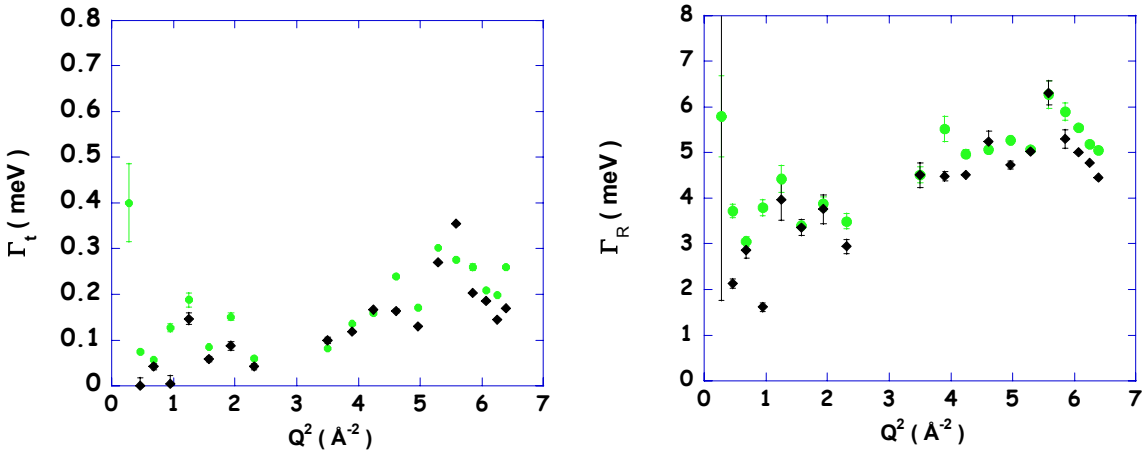

Fig.3. Q dependence of the correlation time, τ (left) andΓ_r (right) of Eq.1 for bulk (●) and Vycor confined (♦) PEOLiTFSI at T = 373 K.

As shown by the very small values of Γ_t shown on Fig.3 as compared to the corresponding values of Fig.2, PEO chains cross-linking induced by Li^+ ions in the PEOLiTFSI system dramatically slows the polymer dynamics down. As in the case of pure PEO, Γ_r is found fairly Q independent in this system and almost not affected by confinement.

As we have seen above, such a KWW-based analysis satisfactorily describes local (above 0.3 $Å^{-1}$) short times (ps) data, and parameters extracted by such an analysis enable to quantitatively compare the dynamical behaviour of different samples. As opposite to long times (nanosecond) and on relatively large scale (Q< 0.2 $Å^{-1}$) [11] where stretched exponentials can be linked to some theoretical development (Rouse model [12]), in the Q range and time scales accessed on QENS, no theoretical basis comes to support such functional forms leading to a rather limited analysis.

As state in the introduction, we want to propose in this paper an alternate to the use of the KWW function for data treatment of polymer melts. In the high Q range (Q< 0.2 $Å^{-1}$) we are dealing with in the field of time-of-flight inelastic neutron scattering experiments, detailed information on the polymer local dynamics are needed.
2D ^{13}C solid state NMR experiments have shown [13] that PEO conformational transitions have to be described as helical jump (HJ) motions. This process involves a rotation of a given monomer by a 180° angle coming along with a concomitant chain translation of one monomer unit.
The autocorrelation function of the motion follows [14]:

$$G^{HJ}(t) = e^{-t/\tau_1}.I_0(t/\tau_1) \tag{2}$$

where HJ stands for helical Jump, $1/\tau_1$ is the rate of the conformational change and I_0 is the modified Bessel function of the first kind of order 0.
Quasi-elastic neutron scattering enables to access polymer conformational changes. In the case of incoherent (isotropic) samples, one actually measure the incoherent dynamical structure factor, $S_{inc}(Q,\omega)$, the Fourier transform over space, r, and time, t, of the self correlation function $G_s(r,t)$ of the nuclei under investigation. If this particle does not experience a perfectly ergodic dynamics, $G_s(r, t = \infty)$, the long time tail of $G_s(r,t)$ is non-null and $S_{inc}(Q,\omega)$ presents an elastic component, $\delta(\omega)$. $S_{inc}(Q,\omega)$ takes the general form [15], here labelled *loc* since it is related to local conformational change:

$$S_{inc}^{Loc}(Q,\omega) = \frac{1}{\pi}\int_0^{\infty} G_s(r,t).e^{iQr.\omega t}dt = A_0(Q).\delta(\omega) + \left(1 - A_0(Q)\right).D(Q,\omega) \tag{3}$$

$D(Q,\omega)$ is related to the time dependence of the a particle dynamics. $A_0(Q)$ is called the Elastic Incoherent Structure Factor (EISF). The EISF is the Fourier transform over space of the $G_s(r, t = \infty)$ loci. In the case of a particle diffusing inside a confining volume, $A_0(Q)$ is the form factor of this volume (sphere, cylinder…).
In the present polymeric system under investigation, $A_0(Q)$ will take into account the polymer local conformational motion geometry while a Lorentzian line ($\Gamma_0=1/\tau_0$ HWHM) will be the related to its time dependence $D(Q,\omega)$.
It should be noted that due to the combined effect of damping originating from the averaged dynamics of the neighboring chains and to the presence of the entanglements, the diffusion of the polymer chain as a whole, implied by the HJ motion, should not exceed few tens of Angstroms. Following the general confinement-related form, Eq.3, with the time dependence of Eq.2, such a localized diffusive motion takes the functional form:

$$S_{inc}^{Diff}(Q,\omega) = A_1(Q)\delta(\omega) + (1 - A_1(Q)) \,.\, S_{inc}^{HJ}(Q,\omega) \tag{4}$$

Where $S_{inc}^{HJ}(Q,\omega) = \frac{1}{\pi}\int_0^\infty G^{HJ}(t)e^{iQr.\omega t}dt$ and $A_1(Q)$ is a form factor (EISF) of the volume over which the diffusion takes place.

Beyond this atomic description of polymer dynamics, characteristic times associated to larger scale polymer viscoelastic properties have to be taken into account, by example by as a single time τ_2 leading to the Lorentzian:

$$L^{Glob}(Q,\omega) = \frac{1}{\pi}\int_0^\infty e^{-t/\tau_2}e^{iQr.\omega t}dt \tag{5}$$

If we suppose that the above different dynamical mechanisms are uncorrelated, the total dynamical structure factor accounting for the PEO dynamics is a convolution of Eq. 3, 4 and 5. The measure intensity takes then the form:

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = \left[B_1(Q).\delta(\omega) + B_2(Q).S_{inc}^{Glob}(Q,\omega) \otimes S_{inc}^{HJ}(Q,\omega) + B_0(Q).L_0(Q,\omega)\right] \tag{6}$$

where, B_0, B_1, B_2 are integrated intensities of the different dynamical contributions with $B_1(Q)=A_1(Q)*A_0(Q)$, $B_2(Q)=A_0(Q)*(1-A_1(Q))$ and $B_0(Q) = 1-A_0(Q)$ and $B_0+B_1+B_2=1$.

The model scattering function given by Eq. (2) accounts very well for the observed QENS spectra over the whole Q range and energies up to 10 meV. A key point of the present work is that QENS experiments access spatial information *via* the *Q* dependence of the correlation times.

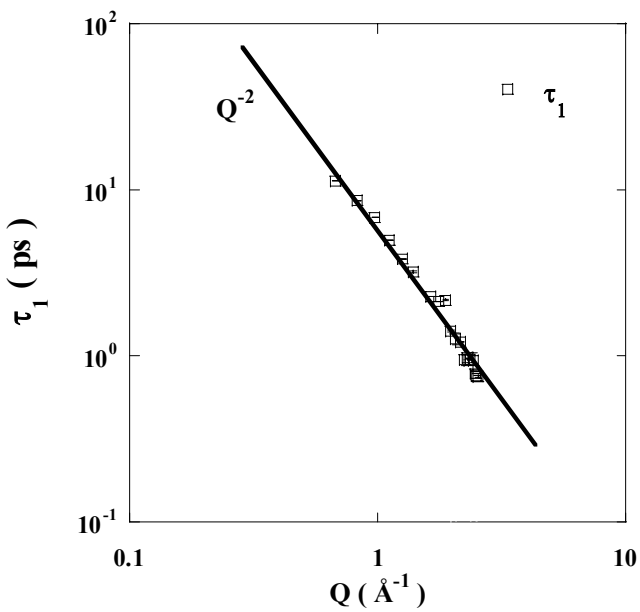

Fig. 4. Correlation time τ_1 derived from the fits of Eq. (6) to the QENS data; the straight lines indicate a Q^{-2} power-law behaviours. A monomeric friction coefficient, ξ_0 = 2.89 10^{-12} N.s.cm^{-1}, is derived from the τ_1 Q^2 dependence (see text).

$A_0(Q)$, easily extracted from B_1,B_2 and B_3, carries to the details of this geometry. $A_0(Q)$ is almost constant above 2.0 Å^{-1} at an unusually high value of about 0.5. Such a large EISF value at high *Q* is consistent only with a jump motion between two distinct sites: $EISF_{jump}$

= [1+sin($Q.d_{jump}$)/($Q.d_{jump}$)]/2. τ_0 accounts for the rather broad excitation of h/$\tau_0 \approx$ 5 meV HWHM clearly seen in a susceptibility representation of the QENS data.

The correlation time, τ_1, follows a Q^{-2} power dependence (Fig.4) that, along with a Q independent corresponding intensity is characteristic of a translational diffusive motion. From a linear fit of the curve τ_1 *vs* Q^{-2} , we measure a diffusion coefficient D = 1.78 10^{-9} m^2/s. Present QENS measurement access proton average dynamics on a length scale of the order of a covalent bond. In the meV energy range such covalent bonds are rigid so that any proton translational diffusion coefficient can directly be associated to the diffusion coefficient of a single monomer considered as a single rigid body. We can therefore define, at temperature T, a monomeric friction coefficient ξ_0: $\xi_0=k_BT/D$, where k_B is the Boltzman constant. We find $\xi_0 = 2.89*10^{-12}$ N.s.m^{-1}. The monomeric friction coefficient plays a central role in polymer dynamics and is present in all theoretical expressions describing polymer dynamics from the short time semi-local scale (Rouse dynamics) up to the long time global scale (reptation).

Hall and Helfand (HH) [[16]] have derived a bimodal autocorrelation function to describe damped conformational changes along a polymer chain. Subsequently, Dejean de la Batie *et al.* (DLM) [[17]] showed that this autocorrelation function cannot account for the high value of the spin-lattice relaxation time T_1 observed in ^{13}C spin-lattice relaxation time experiments. To fully explain their data, they complemented the HH model with an additional kind of fast small-amplitude anisotropic motion that they identified with librations of C-H vectors leading to:

$$G(t) = (1-a).e^{-t/\tau_1}.e^{-t/\tau_2}.I_0(t/\tau_1) + a.e^{-t/\tau_o} \qquad (7)$$

In the first term, following [16], τ_1 is the correlation time associated with the correlated conformational jumps responsible for orientational diffusion along the polymer chain. τ_2 represents a damping (of that collective motion) consisting either of non-propagative isolated specific motions or of distortions of the chain with respect to its most stable local conformation. τ_0 corresponds to the correlation time of librations of C-H vectors inside a cone of half-angle θ and a is a geometrical factor that depends on (cosθ).

Let's first stress out the formal similarities between the DLM model and the model we propose. For the sake of comparison, we write this latter in Q space and in time (time Fourier transform of Eq. 5):

$$I(Q,t) = A_0(Q)A_1(Q) + A_0(Q)(1-A_1(Q))e^{-t/\tau_1}.e^{-t/\tau_2}.I_0(t/\tau_1) + (1-A_0(Q)).e^{-t/\tau_o} \qquad (8)$$

Despite a very similar formalism our results lead to a rather different interpretation of the PEO dynamics than that proposed by HH and DLM as an orientational propagation of conformational changes along the polymer chain. Such a collective excitation would not induce any protons physical translational diffusion and could therefore not account for the Q^{-2} dependence of τ_1 as measured on our hydrogenated (incoherently scattering) sample.

It should moreover be noted, as emphasized by Moe et al. [[18]], that the DLM Model in the form given in Eq. 7 does not seem to be the most suitable model to fit polymer melt data.

Those authors show that the best result is obtained by use of a sum of a fast component and a stretched exponential term similar to the model we used in the first part of this manuscript. Such a model has actually also been shown very valuable to fit PEO melt quasi elastic neutron scattering data by Triolo et al [19]. Nevertheless, in order to get a perfect fit to these data, those authors had to take into account a surprising and very small elastic contribution. The model we propose, Eq. 7 or 8 actually gives a physical basis to this elastic contribution as being due to the chain localisation at short times (ps) in a confining volume $A_1(Q)$.

CONCLUSION

Confinement induces a spectacular slowing down of the PEO dynamics above 335 K. At T=373 K, $(POE)_8$LiTFSI dynamics is significantly slower than in bulk PEO.
The analysis of a polymer melt QENS data proposed in this work leads to a promising appealing physical interpretation of local polymer dynamics that is generally lacking in the use of stretched exponential (KWW) functions. The core of our analysis is the determination by neutron scattering of a monomeric friction coefficient. Some more work has still to be done to validate the model we propose. It is in particular necessary to confirm that the monomeric friction coefficient numerical value we find in the case of PEO is in agreement with this quantity as measured by other techniques: rheology, PFG NMR and neutron spin echo.
If proven valid, such a model applied to the case of nano-confined polymer could be a route for estimating the monomeric friction coefficient (and therefore rheological properties) in physical environments where rheology is impossible.

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