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Polymer dynamics in 3PEG–$LiClO_4$–TiO_2 nanocomposite polymer electrolytes

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(Received 20 September 2002; accepted 5 December 2002)

The microscopic polymer dynamics in nanocomposite polymer electrolytes has been investigated using quasielastic neutron scattering experiments. Four samples based on the fully amorphous copolymer trihydroxy poly(ethylene oxide-co-propylene oxide) (3PEG) were investigated: 3PEG, 3PEG 1.5 mol/kg $LiClO_4$, 3PEG 1.5 mol/kg $LiClO_4$ 10 wt % TiO_2, and 3PEG 1.5 mol/kg $LiClO_4$ 20 wt % TiO_2. In addition to a slow relaxation giving rise to elastic scattering, at least two dynamical processes were observed: a fast, local chain motion and a slower diffusive segmental motion. No changes of the quasielastic peak widths could be observed between the filled or unfilled composites; however, the elastic scattering of the sample was found to increase upon addition of the filler to the polymer electrolyte. The results indicate the presence of a roughly 5-nm-thick immobilized polymer layer (~5 vol %) around filler particles, while the dynamics of the bulk polymer (~95 vol %) is not influenced by the filler. The results imply that the ionic conductivity increase observed in the nanocomposite polymer electrolyte cannot be attributed to enhanced polymer dynamics. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1540980]

I. INTRODUCTION

Solid polymer electrolytes (SPEs) are being considered for use in various electrochemical applications. One promising area is that of all solid state lithium batteries. Many SPEs are based upon poly(ethylene oxide) (PEO), which suffer from relatively low ionic conductivities at room temperature and therefore are unoptimized for practical use in batteries.[1] One reason for the low conductivity is that PEO is semicrystalline, and the ion conduction, which generally is governed by the polymer chain motion, predominately takes place in the amorphous phase. In order to improve the conductivity of the electrolyte many approaches have been utilized, the most common being to add low molecular weight solvents to increase the mobility of the polymer chain and the ionic species. However, the use of such liquids is not optimal on large scales due to possible safety problems of liquid leakage and compatibility with the electrodes.

Recently, a new approach has been taken to improve the conductivity of SPEs through the use of nanosized fillers.[2,3] These SPEs have since become known as nanocomposite electrolytes. In terms of practical applications, these systems have substantial advantages over their gel counterparts, due to improved mechanical properties and better stability at the electrode–electrolyte interface.

The semicrystalline PEO_8:$LiClO_4$ system has been extensively studied using nanosized SiO_2, TiO_2, or Al_2O_3 as fillers.[2–6] Croce *et al.* showed that the conductivity around the melting point of PEO is increased by a factor of approximately 10 on the addition of nanoparticulate TiO_2 and Al_2O_3, compared to the corresponding unfilled polymer electrolyte.[2] It has been shown that the degree of crystallinity is decreased in the filled samples.[2,4,5] However, reduced crystallinity cannot solely explain the conductivity increase. Other effects, for instance interface diffusion or filler induced changes of the polymer structure or dynamics, may therefore also contribute to the conductivity enhancement.

In order to discriminate between the effect of the nanoparticle filler on the crystallinity and other effects, such as changes of polymer dynamics, we have chosen to investigate another system based on the completely amorphous polymer trihydroxy poly(ethylene oxide-co-propylene oxide) (3PEG). The 3PEG system has been studied earlier using spectroscopic and dielectric measurements.[3,6,7] It was shown conclusively that the conductivity was increased when filler was added to 3PEG 1.5 mol/kg $LiClO_4$ polymer electrolytes.[3] Using Raman spectroscopy significant changes were ob-

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served in the polymer conformations on the addition of the filler. The intensity in the D-LAM region was suppressed by addition of TiO_2 filler, which was interpreted as the result of reduced segmental flexibility of the polymer chains.[7] A weak shift in the position of the symmetric stretching vibration of the ClO_4^- was also noted, which suggested coordination of the anion to the filler,[6] results that have been supported by molecular dynamics (MD) simulations by Kasemagi *et al.*[8] In samples containing lithium triflate ($LiCF_3SO_3$) no change in the ion pairing peak was observed, which suggests that the addition of filler does not change the relative number of conducting ions.[6] Positron annihilation lifetime spectroscopy has shown that the addition of TiO_2 particles can increase the number of free volume sites within the electrolyte.[7] These results show that there are structural changes within the electrolyte on the incorporation of the filler. The authors of Ref. 7 suggest that the conductivity increase in amorphous polymer nanocomposite systems is due to increased ionic conductivity in an interphase layer close to the filler surfaces.

In order to clarify the role of the filler for the polymer dynamics, in this work we have performed quasielastic neutron scattering (QENS) on nanocomposites based on 3PEG. QENS is a technique suitable for the study of polymer dynamics on time scales of the order 10^{-11}–10^{-10} s. QENS is particularly suitable for studying the self-motion in hydrogen-containing samples, since the scattering from such samples is almost completely incoherent due to the large incoherent cross section of hydrogen. The obtained incoherent structure factor is directly related to the motions of hydrogen atoms and can be compared to theoretical models. A few polymer electrolyte systems have been investigated in the past by means of QENS.[9–17] In poly(propylene oxide) (PPO) two dynamical processes have been identified, one which is associated with the rotational motion of methyl side groups, the other which is assumed to arise from local segmental motion of the polymer chains. It was found that the introduction of salt slowed down the segmental motion but left the rotational motion of the methyl group more or less unaffected.[10] Similar behavior was later observed in PEO-based systems in the molten state.[14] There is, to our knowledge, no reported QENS study on a nanocomposite polymer electrolyte to date. However, a nanocomposite polymer system without any salt has been investigated by Arrighi *et al.*, who studied poly(dimethyl siloxane) filled with 20 nm SiO_2 particles.[18,19] Their results showed that the mobility of polymer chains close to the filler particles (roughly within 5 nm) was restricted, while polymer chains further away were unaffected by the filler.

The aim of this work is to test the hypothesis that the local polymer dynamics, and hence the ionic conductivity, in a fully amorphous polymer electrolyte is influenced by the addition of a nanoparticulate filler. We have synthesized four systems: an unsalted cured amorphous polymer 3PEG, 3PEG 1.5 mol/kg $LiClO_4$, 3PEG 1.5 mol/kg $LiClO_4$ 10 wt % TiO_2, and 3PEG 1.5 mol/kg $LiClO_4$ 20 wt % TiO_2, to carefully examine the changes of the chain dynamics occurring within the electrolyte using quasielastic neutron scattering.

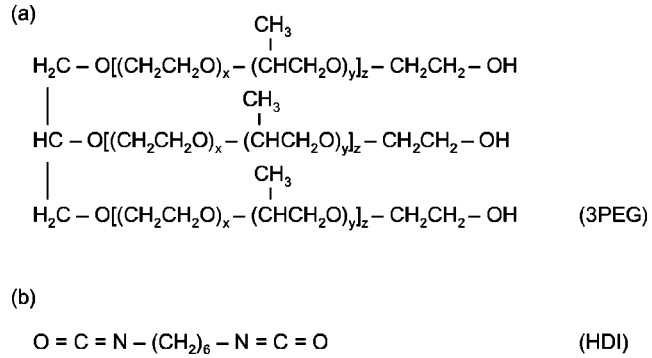

FIG. 1. Chemical structure of (a) 3PEG and (b) hexamethylene diisocyanate (HDI). After curing cross-links between the end groups in 3PEG are formed.

II. EXPERIMENT

We have used the fully amorphous copolymer trihydroxy poly(ethylene oxide-co-propylene oxide) (3PEG) with an ethylene/propylene group ratio of 3:1. Figure 1(a) shows the chemical structure of 3PEG. The polymer was prepared by dissolving it in hot distilled water, followed by the addition of dichloromethane. After separation of the two phases, the polymer phase was kept and washed a further two times with dichloromethane. Following this, the clean polymer was rotorary evaporated to remove any excess water and dichloromethane. A small amount of the polymer was then vigorously dried before characterization using gel permeation chromatography, which found the polymer to have an average molecular weight of 7000 g/mol. Lithium perchlorate (Aldrich, 98%+) was dried at 80 °C under vacuum for one week prior to dissolution in the polymer at 1.5 mol/kg, using high temperature and vigorous stirring. The resulting polymer–salt complexes were then dried at elevated temperature under vacuum for two weeks. Degussa P25 Titandioxid (TiO_2) with nominal particle diameter 21 nm was

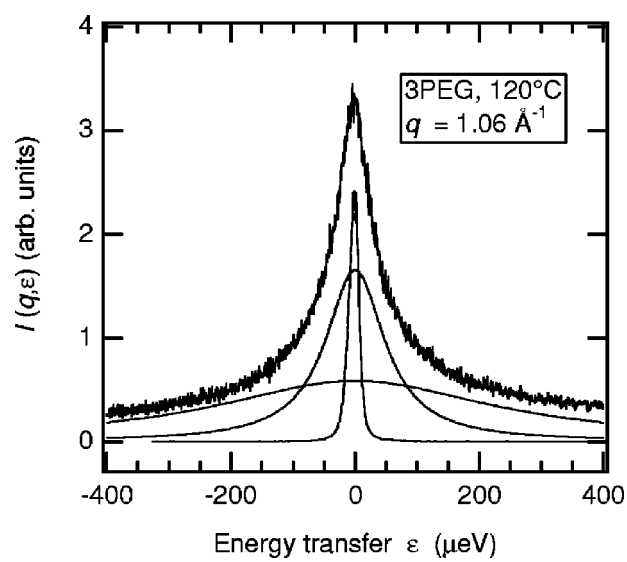

FIG. 2. Measured dynamic structure factor $I(q,\epsilon)$ for 3PEG at 120 °C and $q=1.06$ Å. Also shown is the instrument resolution (unnormalized) and two Lorentzians (unnormalized) obtained from curve fitting as discussed in the text.

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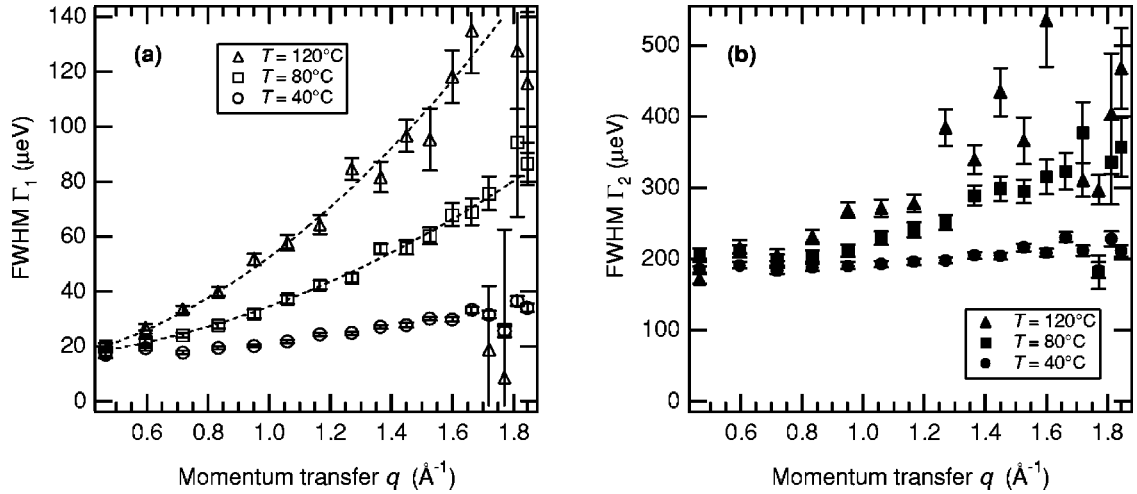

FIG. 3. FWHM Γ_j of (a) the narrow component and (b) the broad component vs momentum transfer q for 3PEG. Dashed lines show fitted q^2 curves.

dried at 250 °C under O_2/Ar gas mixture for 24 h, prior to being used in the composite electrolytes at 10 and 20 wt %, respectively.

Curing of the pure polymer, polymer–salt complex, and the composites, resulting in cross-links between polymer end groups, took place in an argon filled glove box using stoichiometric amounts of hexamethylene diisocyanate (Aldrich, used as received) and a drop of Thorcat535 catalyst (Thor, used as received). The chemical structure of hexamethylene diisocyanate is shown in Fig. 1(b). The samples were then cast onto a dry, degassed Teflon sheet with a depth of 0.5 mm for curing at 50 °C. Replicate samples were made in all cases with those showing the least number of bubbles used in the experiments. Flat aluminium cans containing the samples of thickness 0.6 mm were then sealed in the glove box.

Quasielastic neutron scattering were performed at the IRIS backscattering spectrometer at the ISIS spallation source, Rutherford Appleton Laboratory, UK.[20,21] Pyrolytic graphite analyzers (PG002) were used, giving a momentum transfer (q) range of 0.3–1.8 Å^{-1}, and an energy transfer (ϵ) range of $\pm$0.4 meV with resolution 15 μeV [full width at half maximum (FWHM)]. The 51 detectors, each corresponding to a particular q-value, were grouped into 17 groups of 3 detectors per group. The measured raw counts were converted to experimental dynamic structure factor $I(q,\epsilon)$ using the IDA routine package.[22] No absorption corrections were made on the data presented here since only peak widths and relative intensities are analyzed, on which absorption has no or little influence. Multiple scattering corrections were not applied, which might be a problem because of the rather strongly scattering samples (sample transmission ~70%). However, since we in this study only make relative comparisons, multiple scattering effects should be of less importance for the results. Measurements were performed at temperatures in the range 20–120 °C, that is well above the glass transition temperature (−37 °C), but below the decomposition temperature (around 200 °C) of the samples.[3]

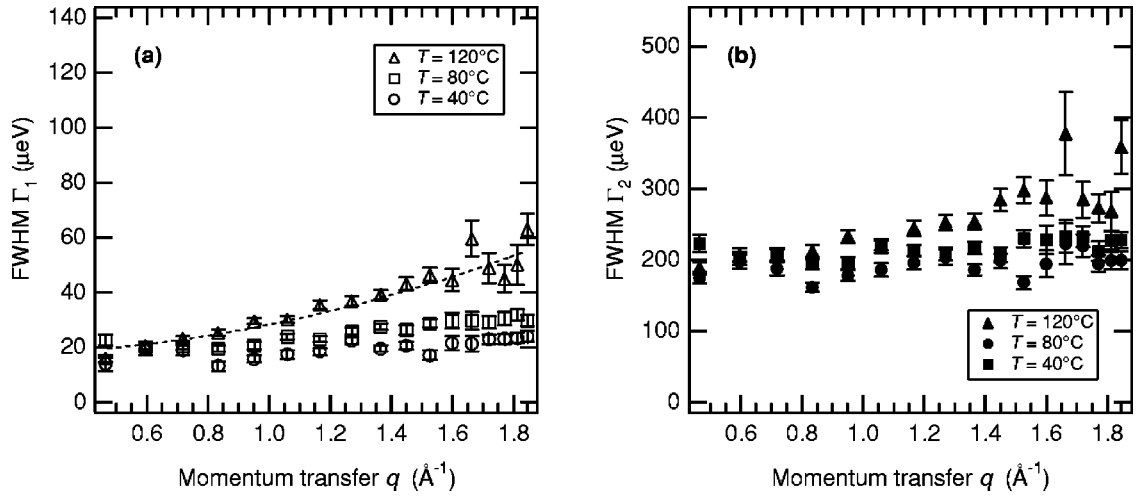

FIG. 4. FWHM Γ_j of (a) the narrow component and (b) the broad component vs momentum transfer q for 3PEG 1.5 mol/kg $LiClO_4$. The dashed line shows a fitted q^2 curve.

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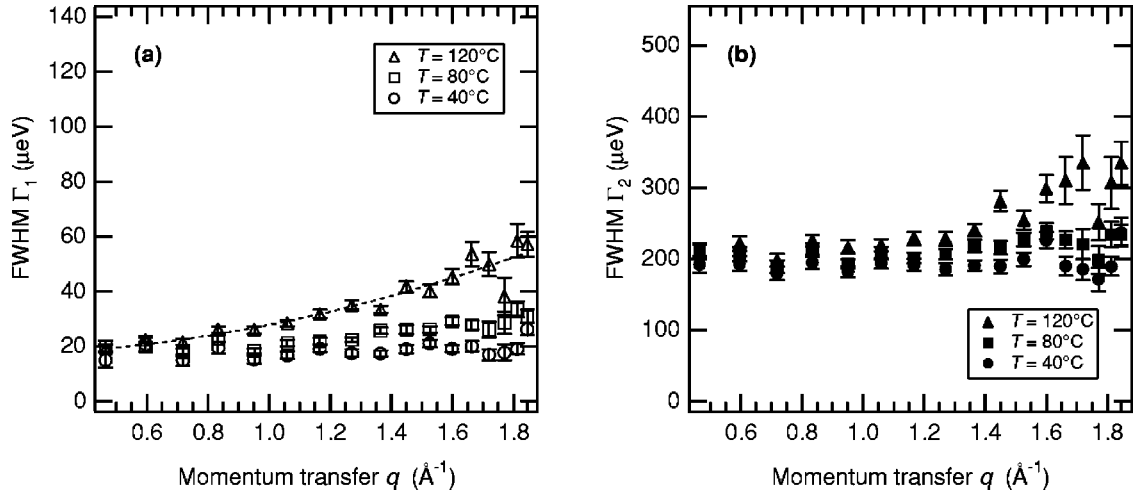

FIG. 5. FWHM Γ_j of (a) the narrow component and (b) the broad component vs momentum transfer q for 3PEG 1.5 mol/kg $LiClO_4$ with 10 wt % TiO_2 filler. The dashed line shows a fitted q^2 curve.

III. RESULTS

Figure 2 shows a typical spectrum $I(q,\epsilon)$ taken of 3PEG at 120 °C and $q=1.06$ Å^{-1}. All spectra were fitted using the IDA routine QUASI_LINES, which utilizes Bayesian analysis to fit a sum of the elastic intensity and 1–3 Lorentzians convoluted with the resolution function,

$$I(\epsilon)=\left[A_0\delta(\epsilon)+\sum_{j=1}^{N}A_j\frac{w_j}{\pi(\epsilon^2+w_j^2)}\right]\otimes r(\epsilon)+b(\epsilon)+\sigma(\epsilon), \quad (1)$$

to experimental data $I(\epsilon)$ for each q-value.[22,23] Here, $r(\epsilon)$ is the instrumental resolution function, $b(\epsilon)$ is the background, and $\sigma(\epsilon)$ noise. Each Lorentzian is described by the amplitude A_j and width w_j (the FWHM is $\Gamma_j=2w_j$). The number of Lorentzians, N, is either 1, 2, or 3. It was found that two Lorentzians were needed to fit the data satisfactorily. The two components will hereafter be called the narrow and the broad component, respectively. Their microscopic origin is discussed later. The two Lorentzian components and the instrumental resolution function are shown in Fig. 2.

Figure 3 shows the obtained FWHM versus momentum transfer q at different temperatures for pure 3PEG. The narrow component is shown in Fig. 3(a), while Fig. 3(b) shows the broad component. The FWHM of the narrow component increases with increasing q and is clearly temperature dependent. The broad component, on the other hand, is almost q-independent, and its temperature dependence is much weaker. The FWHM data obtained from the 3PEG 1.5 mol/kg $LiClO_4$ sample is shown in Fig. 4. The behavior is similar to that of the unsalted 3PEG. The FWHM of the narrow component is, however, smaller, which means that the corresponding process(es) is slower. The broad component is more or less unaffected. Upon addition of 10 wt % TiO_2 there is no significant change in the FWHM, either for the narrow or the broad component, as can be seen by comparing Figs. 4 and 5. Figure 6 shows that neither can any

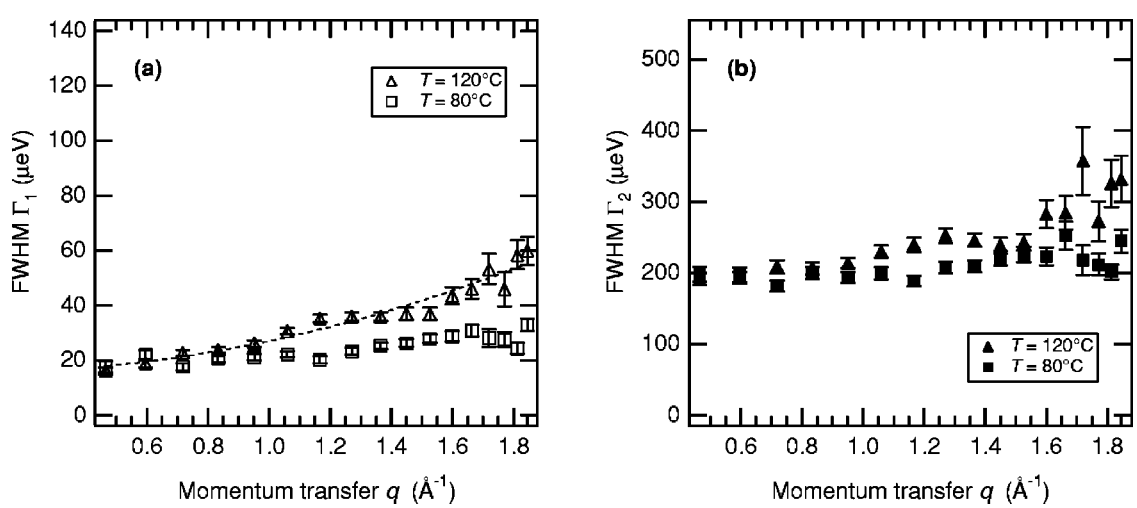

FIG. 6. FWHM Γ_j of (a) the narrow component and (b) the broad component vs momentum transfer q for 3PEG 1.5 mol/kg $LiClO_4$ with 20 wt % TiO_2 filler. The dashed line shows a fitted q^2 curve.

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TABLE I. Fractional contribution of the elastic scattering to the total scattering, F, for different momentum transfers at $T=80\,°C$.

	F ($T=80\,°C$)			
	$q=0.60$ Å^{-1}	$q=0.83$ Å^{-1}	$q=1.06$ Å^{-1}	$q=1.27$ Å^{-1}
3PEG	0.244 ± 0.008	0.086 ± 0.007	0.037 ± 0.005	0.030 ± 0.004
3PEG–$LiClO_4$	0.511 ± 0.007	0.331 ± 0.008	0.223 ± 0.006	0.176 ± 0.007
3PEG–$LiClO_4$ 10 wt % TiO_2	0.538 ± 0.007	0.388 ± 0.006	0.249 ± 0.008	0.187 ± 0.007
3PEG–$LiClO_4$ 20 wt % TiO_2	0.558 ± 0.006	0.375 ± 0.007	0.263 ± 0.008	0.195 ± 0.007

significant change in dynamics be observed when 20 wt % filler is added.

So far, we have only considered the widths of the quasielastic scattering. Let us now consider the fractional contribution to the total scattering of the elastic scattering, F, calculated according to

$$F=\frac{A_0}{A_0+A_1+A_2}. \tag{2}$$

Tables I and II show values of F at different temperatures and momentum transfers. It is quite clear that the elastic scattering (F) increases when salt is added to the polymer, due to the slowing down of the dynamics as also observed above in the widths of the narrow component. When 10 wt % filler is added there is further increase of F. The increase is too large to be only due to elastic scattering from the fillers, since the filler only contributes to 0.25% of the total scattering cross section. Therefore, the increase indicates that some of the polymer is immobilized and hence causes the extra elastic scattering. The immobilization may be due to polymers interacting strongly with the filler surfaces. However, increasing the filler content to 20 wt % leads only to small or negligible increases of F, as seen in Tables I and II. An explanation for this might be that the particles aggregate more in the 20 wt % sample than in the 10 wt % sample, so that the total filler surface area does not increase substantially.

IV. DISCUSSION

Let us first discuss the microscopic origin of the different dynamical processes, which are seen in our data as an elastic contribution to the total scattering, as well as the broad and the narrow component in the quasielastic scattering.

The broad quasielastic component is probably due to some type of fast, local chain motion. From the weak temperature dependence and the absence of any q-dependence, one may at first suspect that the component is due to methyl group rotation, but it has to be of other origin. First, there are relatively few methyl groups in the present samples (around one out of six hydrogen atoms belongs to methyl groups) so the contribution to the total scattering from rotating methyl groups is fairly low. However, the amplitudes A_1 and A_2 (in Eq. (1)) are comparable, which indicates that the broad component is not due to any methyl group rotation. Second, the residence time, calculated according to[24]

$$\tau=\frac{6\hbar}{\Gamma}, \tag{3}$$

obtained using $\Gamma=200\ \mu$eV, turns out to be too short (20 ps). Previously, values of τ of around 100–150 ps have been obtained for the methyl group motion in PPO[11] (note that τ_r in Ref. 11 equals $\tau/3$). Although the time scales of the methyl group rotation are not necessarily the same in different systems, there is no reason to believe that the methyl group rotation should be substantially faster in the present system than in PPO. The process causing the broad component is therefore likely (considering both the amplitudes and calculated residence times) to be related to some type of fast, local chain motion. A q-independent process on roughly the same time scales as observed here has earlier been observed in PEO–$LiClO_4$ (Ref. 14) and PPO (Ref. 25). In the former case it was attributed to rapid conformal fluctuations, with largely rotational character, of chain segments,[14] and in the latter to fast, local motion of hydrogens in the polymer backbone.[25] In view of the partly similar local chain structure in our system, it is likely that the process we observe is of the same nature as the ones observed in Refs. 14 and 25.

The methyl group rotations may instead show up in the narrow quasielastic component, which could be composed of two parts: one process due to methyl group rotation and one with diffusive character. We denote the latter diffusive seg-

TABLE II. Fractional contribution of the elastic scattering to the total scattering, F, for different momentum transfers at $T=120\,°C$.

	F ($T=120\,°C$)			
	$q=0.60$ Å^{-1}	$q=0.83$ Å^{-1}	$q=1.06$ Å^{-1}	$q=1.27$ Å^{-1}
3PEG	0.118 ± 0.007	0.023 ± 0.004	0.009 ± 0.003	0.016 ± 0.002
3PEG–$LiClO_4$	0.313 ± 0.008	0.140 ± 0.007	0.073 ± 0.006	0.051 ± 0.005
3PEG–$LiClO_4$ 10 wt % TiO_2	0.359 ± 0.007	0.182 ± 0.006	0.087 ± 0.006	0.073 ± 0.005
3PEG–$LiClO_4$ 20 wt % TiO_2	0.336 ± 0.009	0.171 ± 0.008	0.101 ± 0.006	0.070 ± 0.005

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TABLE III. Calculated values of x and a_{immob} for filled samples, $T=80$ °C.

	3PEG–$LiClO_4$ 10 wt % TiO_2		3PEG–$LiClO_4$ 20 wt % TiO_2	
	x (%)	a_{immob} (nm)	x (%)	a_{immob} (nm)
$q=0.60$ Å^{-1}	5.5 ± 2.0	4 ± 1	9.6 ± 1.8	4 ± 1
$q=0.83$ Å^{-1}	8.5 ± 1.4	6 ± 1	6.6 ± 1.5	3 ± 1
$q=1.06$ Å^{-1}	3.4 ± 1.3	3 ± 1	5.2 ± 1.3	2 ± 1
$q=1.27$ Å^{-1}	1.3 ± 1.2	3 ± 1	2.3 ± 1.2	1 ± 0.5

mental motion, in order to discriminate it from the faster local chain motion (discussed earlier), which gives rise to the broad component. At low temperatures only the methyl group rotation with a q-independent width of about 20 μeV is observed. This corresponds to $\tau=200$ ps or $\tau_r=70$ ps, which is comparable to the times obtained in Ref. 11. When the temperature is increased the diffusive segmental motion starts to dominate, and a q^2 dependence of the width, which is characteristic for diffusion, is observed, as Figs. 3(a)–6(a) show. Note, however, that since the polymer in all samples is cross-linked and thus forms a network, there cannot be any long-range diffusion. The diffusive segmental motion must therefore be due to some sort of localized diffusion, for instance restricted motion of a few monomer units. This picture is consistent with the fact that the present experiment is performed at relatively large q, i.e., short length scales ($\lesssim 10$ Å) are probed. When salt is added the narrow component slows down. This behavior has been observed also in PPO-based electrolytes, and can be due to the formation of ionic cross-links between polymer chains, resulting in reduced diffusive segmental motion.[11,13] We note that the effect in the present system is small for low temperatures (40 °C) where methyl group rotation, which should be less influenced by the salt than the diffusive segmental motion, dominates. The broad component, however, is more or less unaffected by the presence of salt, which supports the hypothesis that it has to do with fast, local chain motions of a similar nature to the ones discussed in Refs. 14 and 25.

The elastic scattering is primarily due to polymer which is immobile on the time scales probed. The nanoparticle fillers contribute only to 0.25% of the total scattering. Some of the polymer is immobile already in the pure 3PEG, presumably due to the polymer cross-linking. Further immobilization occurs when salt and filler are added, as discussed earlier. Tables I and II show that the elastic scattering is stronger for smaller q-values than for larger. This is expected since for small q the motion becomes so slow that it cannot be resolved by the instrument and therefore contributes to the experimental elastic peak.

In summary, we suggest four dynamic microscopic processes: (i) slow relaxation of immobilized chain segments (slower than the instrument resolution and thus appearing as elastic), (ii) diffusive segmental motion of the bulk polymer, (iii) methyl group rotation, and (iv) fast, local chain motion.

Whatever the microscopic origin of the dynamics is, we have seen that the elastic scattering is affected by the introduction of filler. This indicates that upon addition of filler there is a drastic slowing down (or even an immobilization) of a small fraction of the polymer, presumably close to the filler surfaces, while the bulk of the polymer is essentially unaffected. These ideas would be consistent with the existence of an interphase layer near the filler, as suggested, for instance, in Refs. 4 and 7.

The thickness a_{immob} of the affected (immobilized) polymer layer can be estimated from the elastic scattering and

$$\frac{V^*}{V_{\text{pol}}}=\frac{p}{1-p}\frac{\rho_{\text{pol}}}{\rho_{\text{filler}}}\left(\left(1+\frac{a}{r}\right)^3-1\right), \tag{4}$$

where V^* is the polymer volume within a distance a from filler particles of radius r, V_{pol} is the total polymer volume, p is the mass fraction of the filler (here 0.1 or 0.2), and ρ_{filler} and ρ_{pol} the density of filler and polymer, respectively. Assume that polymer in a volume fraction x in the filled samples scatter 100% elastically, due to the immobilization in this volume, and that the rest of the polymer (with volume fraction $(1-x)$) has the same value of F as the unfilled polymer electrolyte. The fraction x can then be estimated from

$$x=\frac{F_{\text{filled}}-F_{\text{unfilled}}}{1-F_{\text{unfilled}}}. \tag{5}$$

Values of x are shown in Table III together with values of a_{immob} calculated using Eq. (4) (with $x=V^*/V_{\text{pol}}$ and assuming a particle diameter of 21 nm) for the temperature 80 °C. It can be seen that x is of the order 5% and a_{immob} of the order 4–5 nm.

An immobile layer thickness of around 4–5 nm is similar to what has been reported in Ref. 18, in which an adsorption layer with thickness of about 5 nm was found in PDMS-SiO_2 (40 wt % filler). Furthermore, MD simulations of a polymer melt with nanosized filler particles have shown that changes in the dynamics can be expected to occur within $2\langle R_g\rangle$, where $\langle R_g\rangle$ is the radius of gyration, from the filler surfaces.[26] In the present 3PEG systems $\langle R_g\rangle$ should be of the order 2 nm, which would imply changes of dynamics out to about 4 nm from the filler surface.[27] This is consistent with our results.

The present results, which show a significant immobilization of a layer of polymer close to the filler particle surface, suggest that the observed increase in ionic conductivity[3] cannot be attributed to a simple polymer dynamics mechanism only. It has been demonstrated earlier that the ionic mobility in bulk polymer electrolytes is directly related to segmental motion of the polymer chain.[28,29] The reported increase of the ionic conductivity on adding nanoparticle fillers must then have another origin than enhanced polymer dynamics, for instance formation of Li^+ conducting pathways at the filler surface, as suggested in Refs. 4 and 7.

V. CONCLUSIONS

Quasielastic neutron scattering experiments have been used to address issues related to the origin of enhanced conductivity in polymer electrolytes mixed with inorganic nanoparticles. Four samples have been investigated: 3PEG, 3PEG 1.5 mol/kg $LiClO_4$, 3PEG 1.5 mol/kg $LiClO_4$ 10 wt % TiO_2, and 3PEG 1.5 mol/kg $LiClO_4$ 20 wt % TiO_2. By fit-

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ting Lorentzians to the quasielastic spectra $I(q,\epsilon)$ two quasielastic components could be identified, one narrow (slow), which is attributed to diffusive segmental motion and most likely also methyl group rotation, and one broad (fast), which is attributed to fast, local chain motion. Judging from the widths of the Lorentzians, the fast process remains unchanged in all samples. The slow process is slowed down when salt is added, but no further changes of the peak widths are observed as the nanosized filler is added. The elastic scattering, on the other hand, is clearly affected upon addition of filler. The results suggest that there is an immobilized layer of polymer ($\sim$5 vol % of the total polymer) around filler particles, whose thickness is of the order 4–5 nm. The rest (bulk) of the polymer ($\sim$95 vol %) is largely unaffected by the presence of filler. This means that the observed conductivity increase in nanocomposite polymer electrolytes[3] is not generally caused by enhanced polymer dynamics.

ACKNOWLEDGMENTS

Professor P. Jacobsson is acknowledged for valuable discussions. Thanks to Degussa for provision of the ceramic powder used in this work. J.S. is a Royal Swedish Academy of Science Research Fellow supported by a grant from the Knut and Alice Wallenberg Foundation. A.S.B. would like to thank the Australian Nuclear Science and Technology Organization (ANSTO) for funding and the ISIS User Office for assistance with travel arrangements. This work was financially supported by the Swedish Research Council.

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