## The dynamics in polyethyleneoxide–alkali iodide complexes investigated by neutron spin-echo spectroscopy and molecular dynamics simulations

## B. Mos and P. Verkerk

Interfacultair Reactor Instituut, Delft University of Technology, 2629 JB Delft, the Netherlands

S. Pouget

Institut Laue Langevin, F-38042, Grenoble, France

A. van Zon, G.-J. Bel, and S. W. de Leeuw

Department of Applied Physics, Delft University of Technology, 2628 CJ Delft, the Netherlands

C. D. Eisenbach

Institut für Technische Chemie II, Universität Stuttgart, D-70569 Stuttgart, Germany

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We determined the self part of the intermediate scattering function in liquid polyethyleneoxide (PEO) and PEO–alkali iodide complexes by means of neutron spin-echo spectroscopy and molecular dynamics (MD) computer simulations. We present the first accurate quantitative results on the segmental dynamics in the time range up to 1 ns and the wave-vector range from a few nm<sup>-1</sup> to approximately 20 nm<sup>-1</sup>. We investigate the influence of polymer chain length, salt concentration, and cation type. We find that the neutron data and MD data for pure PEO agree very well. A relatively small concentration of dissolved salt (1 metal ion per 15 monomers) leads to a slowing down of the segmental motions by an order of magnitude. Here, the MD simulations agree qualitatively. Increasing the chain length from 23 to 182 monomers has no significant effect except at the highest salt concentration. Similarly, changing the cation from Li to Na hardly makes any difference. The Rouse model does not adequately describe our data. © 2000 American Institute of *Physics*. [S0021-9606(00)51525-6]

Amorphous polymer electrolytes provide an environment-friendly alternative for liquid electrolytes used in batteries, fuel cells, electrochemical displays, and chemical sensors.<sup>1</sup> A polymer electrolyte is a complex of a polar polymer with a metal salt. In order to optimize performance of applications, it is of fundamental importance to understand the mechanism of ion transport, which is closely coupled to the segmental motions of the polymer chain. The systems most studied are poly(ethyleneoxide) (PEO) and poly(propyleneoxide) (PPO) salt complexes.

From Brillouin light scattering of PPO-salt systems<sup>2</sup> and MD simulations of PEO-NaI systems<sup>3</sup> it appears that the Na<sup>+</sup> ions form crosslinks between different oxygen atoms within a polymer chain, which causes slowing down of movement of polymer segments. Quasielastic neutron scattering measurements on the PPO-LiClO<sub>4</sub> complex have confirmed this effect, but because of the limited energy resolution it was impossible to obtain quantitative results for the effect of solvated salt on the structural relaxation.<sup>4</sup> Londono et al.<sup>5</sup> have performed neutron diffraction with isotopic Li substitution in combination with MD simulations in order to determine the partial pair distribution function  $g_{\text{Li},0}(r)$ . They obtained a Li-O coordination number of about 3.5 for PEO-LiI (O:M=5, which is the number of ether oxygens of the polymer chain per metal ion), confirming crosslinking between cations and ether oxygens. It has been shown that the conductivity characteristics for PPO-Li salt and PPO-Na salt are very similar.<sup>6</sup> Therefore, we expect that the influence of Li and Na on the polymer dynamics in PEO is similar.

Until today, no quantitative results were available on the local dynamics of the backbone segments of the polymer nor on the influence of various parameters such as salt concentration, polymer chain length, and different ions. Neutron spin echo (NSE) is the technique of choice regarding energy resolution and wave-vector range, which both fit perfectly with the scale of the local dynamics of the polymer chains. In addition, state-of-the-art supercomputers provide a means to simulate polymer electrolytes on a comparable scale in time and space. We used a combination of both techniques to investigate the dynamics of PEO/alkali iodide complex. The polymer chain length in the simulations was practically the same as in part of the NSE measurements.

A disadvantage of NSE is the reduction of the signal from hydrogenous samples by 2/3 due to the incoherent scattering and spin flip (the coherent and incoherent scattering cross sections for H are  $\sigma_{coh}=1.76$  b and  $\sigma_{inc}=80.3$  b). Usually this is avoided by using deuterated, coherently scattering samples (for D:  $\sigma_{coh}=5.59$  b and  $\sigma_{inc}=2.05$  b) and one measures the total intermediate scattering function F(k,t) instead of the self part  $F_s(k,t)$ , as in the case of incoherently scattering samples. However, we used the increased count rate in the new C configuration of IN11 at ILL<sup>7</sup> with a multidetector (41 cells) covering 30°. Thus, there was no need for deuteration and we were able to measure  $F_s(k,t)$  in ten different

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samples (including three runs for resolution correction and one for background correction).

All PEO-salt complexes were prepared in the same way. We mixed the dry PEO and salt, added methanol, and heated the mixture up to 60 °C inside a desiccator under nitrogen atmosphere dissolving all PEO and salt. Next, the temperature of the mixture was increased until it started to boil, and under reduced pressure the methanol was evaporated. After a few hours the pressure had dropped to 1  $\mu$ bar, and the fluid temperature was set at 150 °C. This state was kept under the same pressure for 24 h in order to remove methanol and water traces. The pure PEO samples were dried in the same way. After quick transfer of the samples to a glovebox, they were loaded into the sample cells under reduced pressure, while the sample remained liquid with a low viscosity at a temperature of 120 °C. The sample cells were sealed with Stycast to prevent sample contamination with water vapor and were tested for leaks. In such a way the following samples were made: PEO  $(-CH_2-CH_2-O_n)_n$ , PEO-LiI (O:M=15), and PEO-LiI (O:M=25) with PEO chain lengths n of 23 and 182 monomers, and PEO-NaI (O:M =15) with n=23. The PEO, LiI, and NaI were obtained from Aldrich Corporation.

The aluminum sample cell has an inner thickness of 0.2 mm with one 1 mm window and one 2 mm window.  $F_s(k,t)$  was measured at a temperature of 70 °C in a time range of 4–970 ps, and a wave-vector range  $3.7 < k/\text{nm}^{-1} < 15.3$ . The k range was obtained by choosing an incident neutron wavelength of 0.5 nm, and multidetector angles of  $17^\circ-47^\circ$  and  $45^\circ-75^\circ$ . Three samples, PEO–LiI (O:M=50, n=182), PEO (n=23), and PEO–LiI (O:M=15, n=23) were also measured at a temperature of 2 K for resolution correction, and they proved to be consistent.

At 70 °C all samples were in the liquid state (see Ref. 1, p. 17), and all salt is also dissolved at this temperature, so a well-defined system is obtained. Thus, complications in the data analysis due to (partial) crystallinity of the samples are avoided. It turned out that at this temperature the relaxation times for all samples fell within the time window of the spectrometer.

The experimental data were corrected for resolution by dividing by the average over the resolution runs and were normalized by dividing by  $F_s(k,t=0)$ . In order to improve the statistics all data were averaged over ten detector cells, where  $F_s(k-\Delta k/2\cdots k+\Delta k/2,t)$  ( $\Delta k \approx 1.5 \text{ nm}^{-1}$ ) is approximately linear. Examples of the experimental  $F_s(k,t)$  are given in Fig. 1.

In our simulations, we used a modified version of the model used by Neyertz *et al.*,<sup>8</sup> where the main difference concerns the use of united atoms. In all configurations, the polymer chains have a length of 25 monomers which, including the CH<sub>3</sub> end groups, lead to a total length of 80 sites. Intramolecular interactions are modeled with valence angle and torsion angle potentials, using the same numerical details as in Ref. 8. Since a united atom model is assumed, the nonbonded interactions of Ref. 8 can no longer be used. This interaction is therefore replaced by a Lennard-Jones interaction potential, the numerical details of which can be found in Ref. 9. The long-range Coulomb interaction is calculated



FIG. 1. Measured  $F_s(k,t)$  at  $k=10.3 \text{ nm}^{-1}$  for PEO (circles), PEO-LiI (O:M=25) (squares), PEO-LiI (O:M=15) (triangles), with their accompanying fits (solid lines), all for n=23, and  $F_s(k,t)$  of PEO (n=25) from MD simulations (dashed line).

with the use of a PPPM method, see Ref. 10, where it is shown that this technique gives the same results as the Ewald summation, but scales as  $\bigcirc(N)$ . The charges of the sites in the polymer backbone are -0.348 (O) and 0.174 (CH<sub>2</sub>), and are located at the backbone position of the corresponding site.

Starting configurations were made by using a pivot Monte Carlo algorithm with a Metropolis acceptance criterion.<sup>3</sup> After this, the polymers were put in a computational cubic box with a length of 3.82 nm. In the case of the PEO-NaI systems, the Na<sup>+</sup> and I<sup>-</sup> ions were added at random positions. The systems simulated are PEO (32 chains), PEO-NaI O:M=27.8 (31 chains and 29 ion pairs), and PEO-NaI O:M=8.67 (29 chains and 87 ion pairs). The corresponding densities are 1121, 1215, and 1404 kg/m<sup>3</sup>, respectively, which should be compared with the experimentally determined densities of 1110 and 1300 kg/m<sup>3</sup> for, respectively, PEO and PEO-NaI O:M=15, while the pressure was approximately 500 bar for the three systems. Excluded volume is gradually "switched on" starting from a truncated Lennard-Jones interaction. After this, the system is equilibrated for 1 ns at 70 °C. The bond lengths are fixed using a constraint dynamics algorithm,<sup>11</sup> and the temperature is regulated via a Nosé-Hoover thermostat.<sup>12</sup> After equilibration,  $F_s(k,t)$  as the Fourier transform of the self part of the Van Hove correlation function and  $\langle \Delta r^2(t) \rangle$  are calculated for 500 ps. To improve statistics, successive measurements are performed every 10 ps, using a time window of 350 ps.

After 200 ps, however, the system phase separates. This is partly due to insufficient screening as a result of the neglect of polarization. This phase separation was also observed in the original model,<sup>13</sup> although at a higher temperature. To overcome this problem, both Na and I charges were lowered (by an equal amount in order to preserve charge neutrality) until the salt dissolves. This was reached at partial charges of 0.5 *e*. We found that these modifications have little influence on the first coordination shell around the Na and I ions.

These observations indicate that using a united atom model and reduced charges has no significant effect on the 6



FIG. 2. Relaxation time  $\tau$  as a function of k for PEO (n=23, stars), PEO-LiI (O:M=25, n=23, open squares), PEO-LiI (O:M=15, n=23, triangles, n=182, solid squares), according to measurements, and PEO (n=25, dashed line), PEO-LiI (O:M=8.67, n=25, dotted line), according to MD simulations. The thin solid lines are power law fits.

structural properties of the system. Moreover, this paper focuses on the dynamics of the polymer backbone and simplified models allow the study of longer time scales, where the local structure is not of great importance. Therefore, we do not expect that small structural differences have a significant effect on the dynamical properties of this system.

For polymer melts of low molecular mass, the Rouse model gives a good description of the dynamics<sup>14</sup> as long as the scale is nonlocal. The self part of the intermediate scattering function is given by<sup>15</sup>

$$F_s(k,t) = \exp[-\sqrt{t/\tau(k)}], \qquad (1$$

in which *t* is the time and  $\tau(k) = \tau_0 k^{-4}$  with

$$\tau_0 = \frac{3\pi\zeta}{k_B T b^2},\tag{2}$$

where  $k_B$  the Boltzmann constant, *T* the temperature,  $\zeta$  the friction coefficient, and *b* the size of a rigid unit in the Rouse model. It was shown by nuclear magnetic resonance (NMR) measurements that *b* is approximately 0.4 nm and independent of the salt concentration in PEO–LiCF<sub>3</sub>SO<sub>3</sub> complexes above the glass transition temperature  $T_g$ .<sup>16</sup>

In order to test the validity of the Rouse model, experimental as well as simulation data were fitted for each k with a more general model: a stretched exponent in the form

$$F_{s}(k,t) = \exp[-\{t/\tau(k)\}^{\beta(k)}].$$
(3)

This expression was previously found to be consistent with measurements<sup>17</sup> and simulations.<sup>18</sup> In Fig. 2 the resulting  $\tau$ 's are given. It was shown by Colmenero *et al.*<sup>19</sup> and more recently by Arbe *et al.*<sup>20</sup> that a power law

$$\tau(k) = \tau_0 (k_0 / k)^{\nu}, \tag{4}$$

with  $\tau_0$  a characteristic time of the relaxation at wave vector  $k_0$ , gives a good description of neutron backscattering measurements. For convenience we choose  $k_0 = 10 \text{ nm}^{-1}$ . One way to understand this is by using the Gaussian approximation, which states that  $F_s(k,t)$  can be written as  $F_s(k,t) = \exp(-k^2 \langle r^2(t) \rangle / 6)$ , where the mean square displacement  $\text{MSD} = \langle r^2(t) \rangle$  is proportional to  $t^\beta$  for polymers. Comparing



FIG. 3. Stretched exponent factor  $\beta$  as a function of the salt concentration (M:O) for PEO–LiI (n=23) (dashed line, circles), PEO–LiI (n=182) (dotted line, squares), PEO–NaI (n=23) (dash-dotted line, black dots), and MD simulations of PEO–NaI (solid line, crosses).

this expression with Eq. (3) leads to Eq. (4) with  $\nu = 2/\beta$ , if  $\beta$  is *k* independent. In the case of ideal Rouse dynamics, the mean square displacement is proportional to  $\sqrt{t}$ . As a result,  $\beta = 0.5$  and  $\tau \propto k^{-4}$ . However, from simulations of more realistic polymers it is known that  $\beta$ , obtained from the MSD and the Gaussian approximation, is somewhat higher, around 0.63.<sup>18,21</sup> In the case of PEO,  $\beta$  obtained from the MSD is 0.65 and independent of the NaI concentration; see Fig. 3.

The values obtained for  $\tau_0$  and  $\nu$  are given in Table I. We observe that  $\beta$  is, by good approximation, independent of k, and therefore  $\beta$  averaged over k is given in Table I. According to the neutron data,  $\tau_0$  increases dramatically when adding salt. For the highest concentration the polymer–sodium salt complex shows a larger value than for the polymer–lithium salt complexes. This might be related to the larger mass and diameter of Na<sup>+</sup> as compared to Li<sup>+</sup>. For the high salt concentration of O:M=15 the relaxation time is larger for the PEO–LiI complex with longer polymer chains. Apparently, here a more rigid network of cross-linked polymer chains is formed than in the case of the shorter chains. This effect is not seen for a concentration O:M=25.

TABLE I.  $\tau_0$ ,  $\nu$ ,  $\beta$  for different PEO-salt complexes. *n* denotes the number of monomers per chain.

Sample	п	$ au_0/\mathrm{ps}$	ν	β	βν
Experiment					
PEO	23	15.2(3)	3.27(5)	0.582(5)	1.90(5)
PEO	182	14.1(3)	3.38(6)	0.562(5)	1.90(5)
PEO25LiI	23	43(1)	3.71(5)	0.510(5)	1.89(5)
PEO <sub>25</sub> LiI	182	48(2)	3.85(7)	0.475(5)	1.82(5)
PEO15LiI	23	103(6)	3.6(1)	0.443(5)	1.62(6)
PEO <sub>15</sub> LiI	182	176(9)	3.3(1)	0.436(5)	1.44(6)
PEO <sub>15</sub> NaI	23	115(6)	3.89(8)	0.434(5)	1.69(5)
MD simulation					
PEO	25	13.2(3)	3.05(3)	0.612(6)	1.86(4)
PEO <sub>27.8</sub> NaI	25	19.4(4)	2.97(3)	0.623(6)	1.85(4)
PEO <sub>8.67</sub> NaI	25	33.7(5)	2.84(2)	0.628(6)	1.78(3)

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The MD simulations also show a rise in  $\tau_0$ , but it is not as nearly pronounced as that of the measurements. Experimentally,  $\nu$  hardly depends on the salt concentration; the increase in relaxation time is only expressed by an increase in  $\tau_0$ . It is also seen that  $\nu$  is independent on the chain length of the polymer as well as the type of cation. The MD simulations show a smaller value of  $\nu$  and also a trend that  $\nu$ decreases when the salt concentration increases. In the experiment the value of  $\beta$  starts at about 0.57 for the polymer, and steadily decreases for increasing salt concentration. Within the experimental error, all polymer–salt systems investigated have identical values for  $\beta$ . The MD simulations however, show no salt concentration dependency at all, and the value for  $\beta$  stays at around 0.62.

From these results it is concluded that the MD simulations are describing pure PEO very well. All fitting parameters,  $\tau_0$ ,  $\nu$ , and  $\beta$ , are in quantitative agreement with the measurements. With the introduction of salt to the system, significant deviations between measurements and MD simulations are seen. The most probable explanation is the reduction in the MD simulation of the Coulomb charge of the Na<sup>+</sup> and I<sup>-</sup> in order to take into account polarization interactions. It was shown earlier<sup>5</sup> and also in the present MD simulations that without this reduction NaI clustering occurs, which contradicts with measurements by Fauteux et al.,<sup>22</sup> and thus the polarization interactions should really be included in the MD simulation. This is a subject for further study, but it is worthwhile to note that a reduction of the ion charge by a factor of 1/2 might lead to a decrease of the relaxation time by an factor of approximately 5.

Furthermore, the measurements show that there is almost no difference between the relaxation of the pure polymer with long chains and the polymer with short chains in the measured k range. This is due to the fact that in the k range of our experiment, one observes only the local dynamics of the polymer.

According to the Rouse model  $\beta = 0.5$  and  $\nu = 4$ , while according to the Gaussian approximation  $\beta \nu = 2$ . Deviations from the Rouse model, observed in our experiments as well as our simulations, are due to the lack of inclusion of local dynamics of the polymer segments in the Rouse model. From MD simulations<sup>18</sup> it is known that at larger *k*, the microscopics of the polymer backbone in combination with the 7

cage effect, causes a crossover to  $\alpha$ -relaxation behavior. It is seen from the experimental as well as the MD data that  $\beta\nu$  is about 1.9 for pure PEO and here the Gaussian approximation is approximately valid up to  $k = 10 \text{ nm}^{-1}$ . The value of  $\beta\nu$ decreases with increasing salt concentrations, indicating that this approximation no longer holds in the PEO-salt complexes.

In summary, we have presented the first quantitative results on the segmental dynamics of PEO/alkali iodide complexes under the influence of polymer chain length, salt concentration, and type of cation using the new version of the ILL spin-echo spectrometer IN11C combined with state-ofthe-art MD simulations.

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