

## Structure of Liquid PEO-LiTFSI Electrolyte

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The structure of a polymer electrolyte,  $\text{P(EO)}_{7.5}\text{LiN(SO}_2\text{CF}_3)_2$ , has been determined by neutron diffraction with isotropic substitution. The Li ions are bonded on average to five ether oxygens belonging to pairs of PEO coils. These are arranged with a considerable degree of extended-range order providing pathways for the Li ion conduction. The lack of ion pairing in this system below 4.8 Å is reminiscent of that observed in the remarkable structure of  $\text{P(EO)}_6\text{LiAsF}_6$  and implies that anions and cations are free to migrate independently.

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The mechanism of ionic conduction in lithium polymer electrolytes is not fully understood, although it remains a central issue for the full exploitation of these materials [1] in vehicle propulsion and consumer batteries [2]. An important part of this understanding concerns the location and distribution of the lithium ions relative to the polymer coils and the compensating anions. So far, most structural work on polymer electrolytes has been focused on crystalline phases, including  $\text{P(EO)}_6\text{LiAsF}_6$ ,  $\text{P(EO)}_3\text{LiN(SO}_2\text{CF}_3)_2$  [ $\text{P(EO)}_3\text{LiTFSI}$ ], and  $\text{P(EO)}_3\text{LiCF}_3\text{SO}_3$  [3–5]. While these results have given significant insights, ionic conduction in these materials is known to occur principally in their amorphous phases [6]. Therefore, information is needed about the structure of the disordered phases, particularly regarding the way in which the lithium ions are bonded to the polymer coils, the number of coils involved, the degree of cation-anion pairing, and the organization of the polymer coils in ways which might promote or hinder ion transport.

While considerable structural information has been inferred from optical, electrochemical, and NMR measurements in the amorphous phase, direct structural investigations have been limited to systems with LiI [7] as the salt or PPO [8] as the polymer. We have determined the structure of  $\text{P(EO)}_{7.5}\text{LiTFSI}$ , a polymer electrolyte whose conductivity [9], phase diagram [10], and chemical safety and stability make it a promising candidate for battery applications. The EO:Li ratio is close to the maximum conductivity and is within the crystallinity gap for low to medium molecular weight polymers and close to the eutectic composition (9:1) for high molecular weight polymers [10]. Only the 3:1 crystalline structure is known [4], and there is no crystallographic information on the 6:1 composition. The technique we used—neutron diffraction with isotopic substitution (NDIS) [11]—allows a direct

determination of the structure around the isotopically substituted element, in this case Li, and provides information about longer-range structural correlations. We propose here a structural representation for the polymer electrolyte where the  $\text{Li}^+$  ions are bonded on average to five ether oxygens belonging to pairs of PEO coils which interlock to form cylinders arranged in a 2D dense random packing, with the  $\text{TFSI}^-$  anions occupying the spaces between them. This picture implies a retention into the liquid state of a high degree of extended-range order (ERO) similar to that reported by Bruce and co-workers in crystalline  $c\text{-P(EO)}_6\text{LiAsF}_6$  [3], and explains the relatively high conductivity of this electrolyte [9]. Li conduction must occur by breaking and remaking of the five Li-O bonds, as observed in the molecular dynamics (MD) study of  $\text{P(EO)}_x\text{LiI}$  [12]. These processes are accompanied by fast relaxation of the local polymer chain structure observed in recent quasielastic neutron scattering measurements [13].

$\text{P(EO)}_{7.5}\text{LiTFSI}$  films of 1 mm thickness were prepared by stepwise evaporating deuterated acetonitrile solution (Aldrich) mixed with deuterated polyethylene oxide ( $d\text{-PEO}$ ) and  $^6\text{LiTFSI}$  ( $^7\text{LiTFSI}$ ) in a high vacuum oven for three days; the final drying stage was completed at 100 °C and  $10^{-6}$  torr. The  $d\text{-PEO}$  (Polymer Source, Inc.) had an  $M_w$  of  $52 \times 10^3$ ,  $^2\text{H}$  enrichment of 99.8% and polydispersity of 1.06. The salts were synthesized from HTFSI and  $^6\text{LiOH}$  ( $^7\text{LiOH}$ ) with an isotopic metallic enrichment of 96% (98%). The films were loaded, in an Ar glove box, into flat cells with vacuum-sealed vanadium windows. Care was taken to synthesize chemically identical samples containing  $^6\text{Li}$  and  $^7\text{Li}$  salts. Time-of-flight neutron scattering experiments were carried out on SANDALS at ISIS, with a wavelength range of 0.065 to 2.5 Å and scattering angle range of 7.0° to 36.5°. The samples were run at room temperature, at which

P(EO)<sub>7.5</sub>LiTFSI is in the liquid phase [10]. Data were checked for detector stability and corrected for instrumental background, container scattering, multiple scattering, and absorption, and normalized to scattering from a vanadium plate mounted on the same holder. Self-scattering was subtracted with a polynomial fitting procedure [14], and the resulting interference scattering, averaged over all detector groups for a scattering vector  $Q$  range of 0.2 to 40  $\text{\AA}^{-1}$ , was divided by the squared mean scattering length  $\langle b \rangle^2$  to give the average structure factor  $S(Q)$ .

The  $S(Q)$ 's measured for the <sup>6</sup>Li and <sup>7</sup>Li samples (Fig. 1) have identical features but a small intensity variation arising from the different Li scattering lengths (2.01 and  $-2.22$  fm, respectively) for the two samples. The strong peak at  $Q = 1.5 \text{\AA}^{-1}$  reflects the *intermediate-range order* (IRO) of the polymer network: It is similar to the first sharp diffraction peaks observed in many network and molecular liquids [15]. The peak at  $Q = 0.57 \text{\AA}^{-1}$ , highlighted in the inset of Fig. 1, reflects the *extended-range order* [16] appearing in the electrolyte. These two features will be discussed later.

The average pair distribution function shown in Fig. 2 is derived from  $T(r) = \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} [S(Q) - 1] Q \times \sin(Qr) M(Q) dQ + 4\pi\rho_0 r$ , where  $M(Q)$  is a modification function that reduces termination errors in the transform,  $\rho_0 = 0.118 \text{\AA}^{-3}$  is the total number density,  $Q_{\min} = 0.2 \text{\AA}^{-1}$ , and  $Q_{\max} = 40 \text{\AA}^{-1}$ .  $T(r)$  was fitted by a series of Gaussian functions to provide average bond distances and coordination numbers for the polymer host:  $r(\text{C-H}) = 1.10 \pm 0.02 \text{\AA}$ ,  $r(\text{C-O, C-C, not resolved}) = 1.44 \pm 0.02 \text{\AA}$ , and  $r(\text{H-H}) = 1.75 \pm 0.03 \text{\AA}$ . The value of 1.9 obtained for the C-H coordination number provides a check on the data normalization procedure. Our results are consistent with those from other molten polyelectrolytes [8] and from pure PEO [17]. However, no information can be inferred about the Li environment

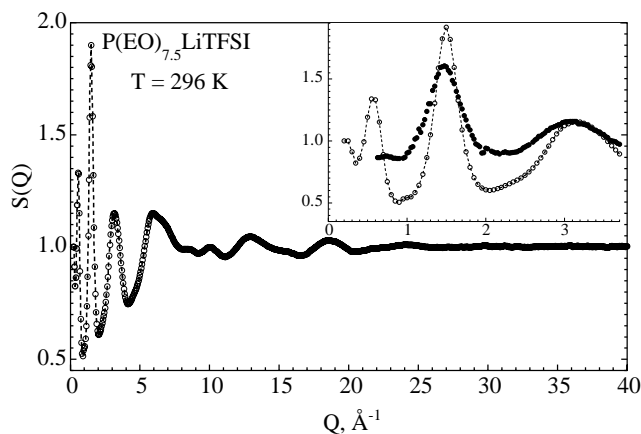


FIG. 1. Neutron weighted average structure factor  $S(Q)$  for liquid P(EO)<sub>7.5</sub>LiTFSI at  $T = 296$  K. Inset: Low- $Q$  region of  $S(Q)$  for the electrolyte and liquid PEO at  $T = 363$  K from Ref. [17].

from Fig. 2, making it necessary to rely on the powerful NDIS technique, as shown below.

The structural environment about a  $\text{Li}^+$  ion is obtained from the first-order difference,  $S_{\text{Li}}(Q) = [\langle b \rangle_6^2 S_6(Q) - \langle b \rangle_7^2 S_7(Q)] / (\langle b \rangle_6^2 - \langle b \rangle_7^2)$ , where the subscripts 6 and 7 refer to samples containing <sup>6</sup>Li and <sup>7</sup>Li, respectively. The corresponding pair distribution function  $T_{\text{Li}}(r)$ , calculated with  $Q_{\max} = 20 \text{\AA}^{-1}$ , is shown in Fig. 3. The peak at  $2.10 \pm 0.04 \text{\AA}$  can be unambiguously assigned to Li-O, and a coordination number of  $n_{\text{O}} = 4.9 \pm 0.5$  is derived from a Gaussian fit. Based on *ab initio* quantum chemical calculations (QC) [18,19], we assign the remaining peaks to various pair correlations and allocate the distribution of coordination numbers among the different correlations. Thus, the peak at  $3.05 \pm 0.05 \text{\AA}$  is assigned to both Li-C and Li-H correlations and a coordination number of  $19 \pm 2$  derived from two Gaussians with  $n_{\text{C}} = 10 \pm 2$  and  $n_{\text{H}} = 9 \pm 2$ . The peak at  $3.8 \pm 0.1 \text{\AA}$  is assigned to Li-H and second neighbor Li-O, and we derive similarly  $n_{\text{H}} = 17 \pm 3$ . Finally, based on MD results [12,20] the peak at  $4.85 \pm 0.5 \text{\AA}$  is assigned to Li-O with  $n_{\text{O}} = 17 \pm 4$ . These results make it possible to address some outstanding questions on the structure of amorphous polymer electrolytes.

An important issue concerning the Li-O coordination is the extent to which the five O's are ether oxygens (EO) of the polymer host or oxygens from the anions (AO). MacGlashan *et al.* [3] pointed out an increase in the cation coordination by the EO at the expense of AO with increasing salt content in crystalline electrolytes: e.g., in P(EO)<sub>1</sub>NaCF<sub>3</sub>SO<sub>3</sub> [21], P(EO)<sub>3</sub>LiTFSI [4], P(EO)<sub>3</sub>LiCF<sub>3</sub>SO<sub>3</sub> [5], and P(EO)<sub>3</sub>LiAsF<sub>6</sub> [3], the (EO, AO/F) coordination of the cation is (2,4), (3,2), (3,2), and (5,0), respectively. Second, spectroscopic studies of P(EO)<sub>x</sub>LiTFSI show that Li-TFSI pairing is absent for  $x > 7$  [22]. Third, the present work shows about 10 C and at least 20 H about each Li, and every EO monomer contains one O, two C, and four H atoms. These

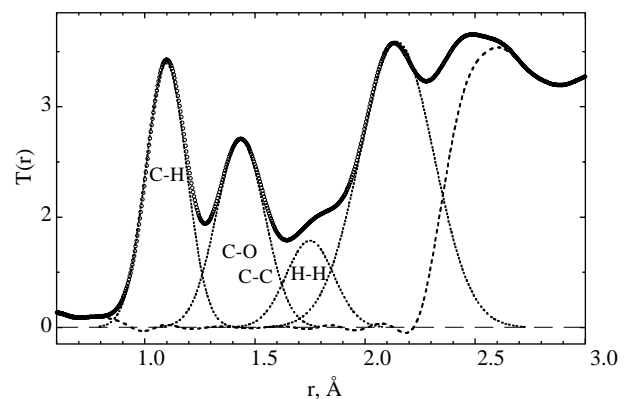


FIG. 2. Neutron weighted average pair distribution function for liquid P(EO)<sub>7.5</sub>LiTFSI. Circles: data; dotted lines: fitted Gaussians; dashed line: residual.

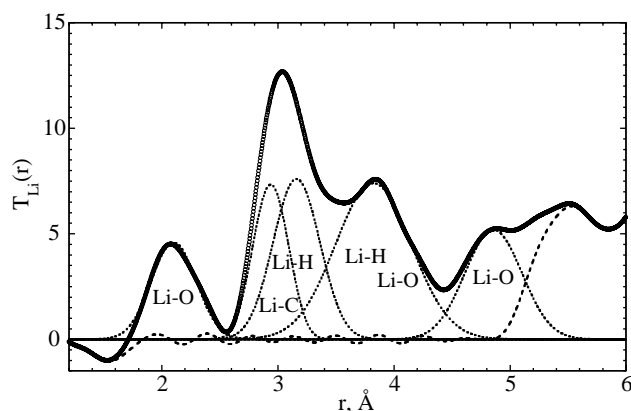


FIG. 3. Lithium difference pair distribution function for liquid  $P(\text{EO})_{7.5}\text{LiTFSI}$ . Circles: data; dotted lines: fitted Gaussians; dashed line: residual.

facts, taken together, support the conclusion that the five O coordinating to Li are all EO. In the case of  $P(\text{EO})_5\text{LiI}$ , the lower value of  $n_0$  ( $= 3.5$ ) [7] can be explained by the higher polarizability of  $\text{I}^-$  compared with  $\text{TFSI}^-$ , as manifested in the phase diagrams: The highest crystalline EO/Li ratio is three for  $\text{LiI}$  and six for  $\text{LiTFSI}$ , closely reflecting the coordination of  $\text{Li}^+$  by the EO. Following this argument,  $\text{LiCF}_3\text{SO}_3$  in a 3:1 complex and  $\text{LiClO}_4$  in a 6:1 complex can be expected to behave like  $\text{LiI}$  and  $\text{LiTFSI}$ , respectively: The x-ray results support such a conclusion [4,5].

A second question is whether the EO's are on single or multiple polymer coils. While this cannot be answered by the present work, we may cite the crystallographic work [3], which shows cross-linking of neighboring chains by the cations at  $x = 6$ , but not at lower values of  $x$ . Second, the comprehensive MD study of liquid  $P(\text{EO})_x\text{LiI}$  by Muller-Plathe and van Gunsteren [12] finds cross-linking at  $x = 8$  but not at lower values of  $x$ . Third, recent QC calculations find that structures consisting of two coils are energetically favored over those involving only one coil [18]. These facts support the conclusion that Li is coordinated to pairs of EO coils.

The broad peaks observed at  $r = 4.85$  and  $5.5 \text{ \AA}$  may, at least partially, originate from correlations of  $\text{Li}^+$  with AO and other atoms, respectively. QC calculations of  $P(\text{EO})_8\text{LiClO}_4$  [19] show that a typical distance from a  $\text{Li}^+$  ion to an anion center for an EO coordination number of five can be about  $6.5 \text{ \AA}$ , so that Li-O distances around  $5 \text{ \AA}$  are possible, taking into account the Cl-O bond length of  $1.45 \text{ \AA}$  (the S-O bond length in the present case is  $1.44 \text{ \AA}$ ). In addition, the crystallographic study of  $P(\text{EO})_6\text{LiAsF}_6$  showed that the distance of a Li ion to the anion center is about  $6.4 \text{ \AA}$  [3], so that Li-F distances of  $5 \text{ \AA}$  are possible if the As-F bond length is  $1.6 \text{ \AA}$ . As suggested by both theoretical [22] and experimental [4,22] studies, the AO's are responsible for the  $\text{Li}^+$ -anion interactions. Since the negative charge on the  $\text{TFSI}^-$  is expected to be delocalized, it is reasonable to assume that

each  $\text{TFSI}^-$  provides on average four AO's to interact with a  $\text{Li}^+$  ion. The derived coordination number of about 17 implies that there are on average about four  $\text{TFSI}^-$  anions around each  $\text{Li}^+$  cation [23].

Information about both IRO and ERO may be inferred from the low- $Q$  region of  $S(Q)$ , shown for both the electrolyte and the pure polymer [17] in the inset of Fig. 1. The main peak at  $1.5 \text{ \AA}^{-1}$  present in both materials reflects the IRO of the polymer network. The  $Q$  value corresponds to a correlation length of about  $4 \text{ \AA}$ , the average spacing of the polymer chains. The peak at  $0.57 \text{ \AA}^{-1}$  present only in the electrolyte has a width of  $0.29 \text{ \AA}^{-1}$ , implying a high degree of ordering with a coherence length of  $20 \text{ \AA}$ . The appearance of ERO upon addition of salt to PEO is reminiscent of the situation in inorganic network glasses, where an ERO peak arises upon addition of modifier salts to vitreous silica and germania matrices [16,24]. In  $c\text{-}P(\text{EO})_6\text{LiAsF}_6$ , the first Bragg peak is observed at  $0.68 \text{ \AA}^{-1}$  corresponding to a plane spacing of  $d = 9.2 \text{ \AA}$ , the distance between cylinders comprising two PEO chains that enclose a column of Li ions. While in the crystal the cylinders make a lattice of square cells, each filled by a column of  $\text{AsF}_6$  anions, we may expect a similar arrangement in liquid  $P(\text{EO})_{7.5}\text{LiTFSI}$  but with the square lattice replaced by a 2D dense random packing and an average spacing of the cylinders of  $[4/\pi(1 + \eta)]^{1/2}d = 10.9 \text{ \AA}$ , assuming a 10% volume expansion  $\eta$  on melting. This arrangement would give rise to a peak at  $0.58 \text{ \AA}^{-1}$ , close to the value measured here.

The structure of liquid  $P(\text{EO})_{7.5}\text{LiN}(\text{CF}_3\text{SO}_2)_2$  proposed in the present work has a number of important implications for the ion transport mechanism. First, the absence of ion pairing, also found in the remarkable  $P(\text{EO})_6\text{LiAsF}_6$  crystal structure [3], implies that cations and anions are free to migrate independently enhancing the ionic conductivity. Second, the high degree of ERO in the liquid, with a coherence length of over  $20 \text{ \AA}$ , implies a significant measure of alignment of the cylinders comprising the polymer coils, providing pathways for  $\text{Li}^+$  transport along the cylinders. Moreover, the increased spacing of the cylinders relative to the  $c\text{-}P(\text{EO})_6\text{LiAsF}_6$  may facilitate transport of the anions between the cylinders, which is impossible in the crystal. Concerning the mechanism of  $\text{Li}^+$  conduction, this must occur by breaking and remaking the Li-O bonds, either one at a time or several at once. According to the MD results, both mechanisms are possible [12]. In either case, the disruption and formation of the bonds are accompanied by fast relaxation of the local chain structure that we have observed in recent quasielastic neutron scattering measurements [13].

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