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Synthesis, Characterization, and Ionic Conductivity of Alternating Copolymers Containing Organo-λ^5-phosphazenes with Polyether Side Chains

Martin Pomerantz,* Ganapathy Krishnan, Mark W. Victor,[1] Chang Wei, and Krishnan Rajeshwar*

Center for Advanced Polymer Research, Department of Chemistry, Box 19065, The University of Texas at Arlington, Arlington, Texas 76019-0065

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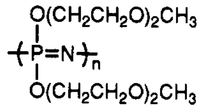
The synthesis and characterization of four polymers containing both organic ($-CH_2CH_2-$ and p-C_6H_4) and λ^5-phosphazene groups in the backbone along with polyether side chains on the phosphorus atoms (**3a–d**) are described. Ac impedance measurements on pressed pellets doped with lithium triflate have provided ionic conductivities of 3.5×10^{-6} S cm^{-1} for **3a** and 2.0×10^{-6} S cm^{-1} for **3c** at 22 °C (**3a** and **3c**; O:Li$^+$ = 5:1). These values are considerably larger than that of PEO–Li-triflate at room temperature, a factor of about 10 lower than that of MEEP–Li–triflate at 30 °C,[11] and only a factor of about 5 lower than that of cross-linked MEEP–Li–triflate at room temperature.[12]

Introduction

Since the discovery of high ionic mobility in complexed poly(ethylene oxide) (PEO) by Wright et al. in 1975,[2,3] intense interest has been generated in the use of polymeric materials as solid electrolytes.[4–7] Among the most important potential uses of these polymer solid electrolytes (PSE) are in lightweight, high-energy-density, solid-state batteries and fuel cells.[4,7] There are potentially a number of quite significant advantages of these PSE based devices over more traditional technology. Among these are that the polymers are lightweight, are solid rather than liquid, and can be fabricated into thin films. This translates, for example, to a battery with a high energy density since more active material can be packed into a given space.[4]

Unfortunately one of the major classes of PSEs being examined, polyethers such as poly(ethylene oxide) (PEO) and poly(propylene oxide), have fairly low room-temperature ionic conductivity.[4,8] Ion conductivity increases with temperature, but the dimensional stability decreases significantly. PEO shows good conductivity at temperatures above 70 °C, which is the melting point of the polymer. Below 70 °C ionic conductivity is poor because the polymer is in the crystalline phase[4,9] and conduction is dependent on the extent of amorphous domains.

Several years ago a polymer with an inorganic polyphosphazene backbone and short triether side chains (MEEP, **1**) was prepared and shown to have considerably better ambient ionic conductivity than the polyethers.[6,10,11]



$$\left(\overset{\displaystyle \mathrm{O(CH_2CH_2O)_2CH_3}}{\underset{\displaystyle \mathrm{O(CH_2CH_2O)_2CH_3}}{\mathrm{P}}}=\mathrm{N}\right)_n$$

1

It too suffers from dimensional stability problems, and so more recently there have been attempts to improve the mechanical properties by cross-linking.[12,13] Other attempts at improving the dimensional stability while maintaining the good ionic conductivity have involved the use of molecular composites such as those between MEEP and PEO[14–16] and between MEEP and tetraethoxysilane polymerized in situ.[17]

Other properties required in these polymers in order to make them good ion conductors are appropriate coordination sites (e.g., oxygen or nitrogen) for the ion (e.g., Li$^+$) being transported, an amorphous, or at least minimally crystalline morphology, and a low glass transition temperature, T_g.[4,18]

As a result of our longstanding interest in the chemical and physical properties of organo-λ^5-phosphazenes[19–27] and in polymers whose backbones contain both phosphazene

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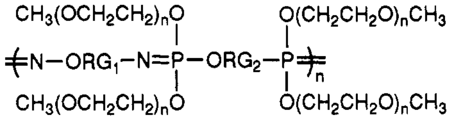
and organic spacer groups,[28] it was decided to synthesize and study a new class of polymers as possible ionic conductors (PSEs). This new class of polymers contain both phosphazene and organic spacer groups in the backbone and pendant polyether side chains attached to the phosphorus atoms as shown in the general structure **2**, where ORG_1 and ORG_2 are the organic spacer groups.



$$\left[N-ORG_1-N=\overset{O(CH_2CH_2O)_nCH_3}{\underset{CH_3(OCH_2CH_2)_nO}{P}}-ORG_2-\overset{O(CH_2CH_2O)_nCH_3}{\underset{O(CH_2CH_2O)_nCH_3}{P}} \right]_n$$

2

In principle, these spacer groups could be modified and changed in order to prepare polymers with better physical and mechanical properties while maintaining the excellent ionic conductivity of MEEP. Very few polymers of this type having both P=N and other groups in the backbone have been reported and none with polyether side chains. There are two papers where both ORG_1 and ORG_2 are completely organic[28,29] and only a few reports where ORG_2 is organic and where ORG_1 contains inorganic atoms,[30–34] and a recent paper describes a polymer with two P=N and one C=N group in the backbone repeat unit.[35]

Experimental Section

General Methods. Thermal analyses were performed on a du Pont 9900 thermal analysis instrument employing a Model 951 thermobalance for TGA measurements. All experiments were performed in a static air atmosphere. IR spectra were recorded on a Biorad-Digilab FTS-40 Fourier transform instrument in the diffuse reflectance mode using finely powdered mixtures of compound with KBr. GPC analysis was performed using a Waters system with a Model 510 pump, a Model 490 UV, and a Model 410 refractive index detector using water as eluent. The columns were Waters Ultrahydrogel 500-, 250-, and 2000-Å GPC columns in series. The standards used for GPC analysis were poly(ethylene glycol) and poly(ethylene oxide) samples with molecular weights ranging from 440 to 763 200; all samples were filtered through a 0.45-μm filter. NMR spectra were recorded on a Bruker MSL 300 spectrometer at 121.5 MHz for ^{31}P and 75.5 MHz for ^{13}C with TMS or methanol as internal reference or H_3PO_4 as external reference. Elemental analyses were performed by Texas Analytical Laboratories, Stafford, TX. The polyether alcohols, 2-(2-methoxyethoxy)ethanol, MPEG-350, MPEG-550, and MPEG-750 (Union Carbide-CARBOWAX Methoxy Polyethylene Glycols) were dried azeotropically three times with benzene/ethanol (100 mL/50 mL) and two times with benzene (100 mL) and stored over alumina (basic type WB-5). Toluene was dried and distilled over sodium. Dioxane was distilled from lithium aluminum hydride and stored over 4-Å molecular sieves. Methanol was refluxed with magnesium metal and distilled and stored over 4-Å sieves. 1,2-Bis(dichlorophosphino)ethane (4) was a commercial sample which was stored and weighed in a drybox.

Preparation of Chloropolymer 6. 1,2-Bis(dichlorophosphino)ethane (**4**, 2.3 g, 9.9 mmol) was weighed in a drybox into a 100-mL three-necked flask. To this was added 100 mL of anhydrous toluene, and the solution was stirred under a stream of nitrogen. 1,4-Diazidobenzene[29] (**5**, 1.58 g, 9.9 mmol) dissolved in anhydrous toluene (30 mL) was added dropwise through an addition funnel. After the addition was complete, the mixture was stirred at room temperature overnight and then refluxed for 4.5 days during which time a tan-colored precipitate formed. The mixture was cooled, and the solvent removed to give a tan-colored powder which was dried under vacuum and stored in a drybox, yield = 2.83 g (94%). DRIFT IR (KBr) $\bar{\nu}$ (cm^{-1}) 1609, 1511, 1404, 1215, 980, 951, 828, 734, 547, 520.

General Procedure for the Synthesis of the Polymers 3a–d. The polyether alcohol was dissolved in anhydrous dioxane (5–10 mL) in a three-necked round-bottomed flask, to which was attached an addition funnel, a condenser, and a drying tube. A constant stream of argon was maintained. An equivalent amount of sodium was added, the mixture was heated gently, and the resulting alkoxide solution turned brown in color. The chloropolymer **6** was added to the alkoxide solution followed by an additional 45–50 mL of dioxane, and the resulting mixture was refluxed, under argon, for 10–12 days. During this period the color of the reaction mixture turned from tan to dark brownish-black. The solvent was removed under reduced pressure and water (10–15 mL) was added to dissolve the product. This solution was then transferred to a dialysis membrane (Spectropor, MW cutoff 3500) and dialyzed against water (eight changes, 5 days) and then against methanol (four changes, 3 days). The solution in the dialysis tube was then transferred to a flask, and the methanol was removed under reduced pressure to provide the product polymer **3a–d**, which was dried under vacuum in a desiccator. All the polymers synthesized were brownish-black powders.

Polymer 3a. The general procedure given above was employed with the following amounts of starting materials: 2-(2-methoxyethoxy)ethanol, 3.60 g, 30 mmol; sodium, 0.70 g, 30 mg atom; chloropolymer **6**, 0.90 g, 3 mmol; and dioxane, 50 mL. The product obtained after dialysis was a brownish-black powder, yield = 0.230 g (11.4%). DRIFT IR (KBr) $\bar{\nu}$ (cm^{-1}) 1512, 1279, 1212 (P=N),[36] 1052, 914, 832. ^{31}P NMR (D_2O) δ 1.44 (very small), 16.04 (br), 18.47 (br), 18.86 (br), 21.22 (br), 22.47 (br), 22.9 (br), 25.0 (br), 25.16 (s), 26.20 (s), 27.1 (br), 28.02, 28.72. ^{13}C NMR (D_2O) δ 14.22, 21.59 (br), 23.14, 23.29, 58.17, 66.11, 69.59 (br), 71.09, 117.91, 120.20 (br), 121.06 (br), 127.9 (br). Anal. Calcd for $C_{28}H_{52}N_2P_2O_{12}$ per repeat unit: C, 50.13; H 7.82; N, 4.18; P, 9.24. Found: C, 50.21; H, 7.86; N, 4.22; P, 9.33.

Polymer 3b. The general procedure given above was employed with the following amounts of starting materials: Union Carbide MPEG-350, 2.55 g, 7.3 mmol; sodium, 0.16 g, 7.0 mg atom; chloropolymer **6**, 0.500 g, 1.0 mmol; and dioxane, 55 mL. The product obtained after dialysis was a brownish-black powder, yield = 0.10 g (6.5%). DRIFT IR (KBr) $\bar{\nu}$ (cm^{-1}) 1609, 1512, 1378, 1280, 1195 (P=N),[36] 1059, 925, 832, 719, 519. ^{31}P NMR (D_2O) δ 21.58 (br), 23.83 (br), 24.92, 26.17, 28.4 (br). ^{13}C NMR (D_2O) δ 69.8. Anal. Calcd for $C_{68}H_{132}N_2P_2O_{32}$ per repeat unit: C, 52.62; H 8.58; N, 1.81; P, 3.99. Found: C, 52.40; H, 8.54; N, 1.86; P, 4.03.

Polymer 3c. The general procedure given above was employed with the following amounts of starting materials: Union Carbide MPEG-550, 16.5 g, 30.0 mmol; sodium 0.70 g, 30 mg atom; chloropolymer **6**, 0.810 g, 2.4 mmol; and dioxane, 60 mL. The product obtained after dialysis was a brownish-black powder, yield = 0.230 g (4.0%). DRIFT IR (KBr) $\bar{\nu}$ (cm^{-1}) 1607, 1511, 1457, 1360, 1282, 1195 (P=N),[36] 1099, 941, 834, 744, 517. ^{31}P NMR (D_2O) δ 1.00 (br, very small), 16.31 (br), 18.81 (br), 20.68 (br), 22.59, 23.16, 24.47, 25.08, 25.23, 26.08, 26.19, 26.90 (br), 27.77, 27.93, 28.34, 28.50, 28.71, 28.94, 29.52. ^{13}C NMR (D_2O) δ 21.44, 58.20, 60.51, 64.75, 69.61, 69.73, 71.10, 71.83, 118.45 (br), 128.48

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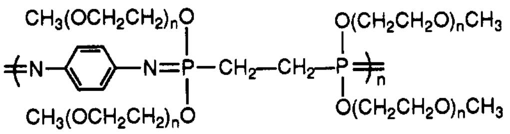
(br). Anal. Calcd for $C_{108}H_{212}N_2P_2O_{52}$ per repeat unit: C, 53.30 H 8.79; N, 1.15; P, 2.55. Found: C, 53.12; H, 8.63; N, 1.08; P, 2.61.

Polymer 3d. The general procedure given above was employed with the following amounts of starting materials: Union Carbide MPEG-750, 21.8 g, 29 mmol; sodium, 0.67 g, 29 mg atom; chloropolymer **6**, 1.00 g, 2.9 mmol; and dioxane, 60 mL. The product obtained after dialysis was a brownish-black powder, yield = 0.070 g (1.0%). DRIFT IR (KBr) $\bar{\nu}$ (cm^{-1}) 1611, 1511, 1467, 1345, 1281, 1245, 1112, 942, 842, 744, 718, 511. ^{31}P NMR (D_2O) δ 0.46 (br, very small), 23.0 (br), 25.43 (br). ^{13}C NMR (D_2O) δ 23.30, 58.23, 60.54, 69.76, 71.16, 71.90, 120.5 (br). Anal. Calcd for $C_{140}H_{276}N_2P_2O_{68}$ per repeat unit: C, 53.58 H 8.87; N, 0.89; P, 1.98. Found: C, 53.21; H, 8.56; N, 0.91; P, 2.19.

Ac Impedance Measurements. Ac impedance spectra were obtained using a Solartron Model 1250 frequency response analyzer and a Solartron Model 1286 electrochemical interface. Impedance spectra were analyzed by using custom software on a Hewlett-Packard Series 300 desktop computer. The samples for conductivity measurements were prepared by dissolving the polymers **3a** and **3c** and lithium triflate (oxygen:metal = 5:1) in water (3 mL). The solution was then poured into a Teflon dish and the water was slowly removed in a vacuum oven at 30 °C for 24 h; the polymer/salt mixture was dried for about 40 h at 40 °C in the vacuum oven and finally stored in a vacuum desiccator until used. The material was finely ground, pressed into a pellet using an IR die (2000 psi) and the pellet was attached to copper lead wires using CP-2000-TP electrically conductive paint (Delta Technologies, Stillwater, MN). The thickness and diameter of the pellets were measured using a micrometer with a digital display. The pellets were also stored in a vacuum desiccator when not being studied. A two-electrode configuration was used for the experiments and a Faraday cage was employed to minimize electrical noise during the measurements. The dc bias potential was 0 V, and the superimposed sinusoidal signal had an amplitude of 50 mV. The impedance data were collected at eight frequencies per decade in each scan over a frequency range 100 mHz to 65 kHz.

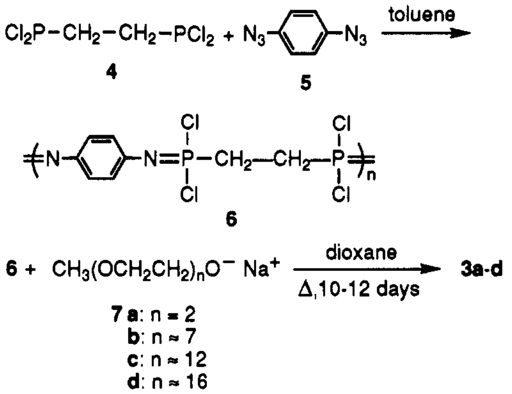
Results and Discussion

The molecules prepared for this study are shown in structure **3** where $n = 2$ (**3a**), n = ca. 7 (**3b**), n = ca. 12 (**3c**), and n = ca. 16 (**3d**). The latter three molecules do not have a definite value for n since the polyether alcohols used to make these compounds were commercial substances (Union Carbide-CARBOWAX Methoxy Polyethylene Glycols, MPEGs) with a distribution of molecular weights, as explained below. The synthesis, shown in Scheme I, involved the Staudinger reaction[37] between 1,2-bis(dichlorophosphino)ethane (**4**) and 1,4-diazidobenzene (**5**)[29] to produce the chlorinated polymer **6**. This in turn was reacted with a large excess of the sodium salt of the appropriate polyethylene glycol monomethyl ether **7a–d** to give the desired polymers **3a–d**. It has previously been shown by Lysenko et al.[38] that the P–Cl bonds of a λ^5-phosphazene could be replaced by P–OR bonds by the action of alkoxides. It should also be noted that the polyethylene glycol monomethyl ethers employed were (a) pure diethylene glycol monomethyl ether (n = 2), (b) Union Carbide MPEG-350 which has an average molecular weight of 350 and a distribution of 335–365 ($n \approx 7$), (c) Union Carbide MPEG-550 which has an average molecular weight of 550 and a distribution of 525–575 ($n \approx 12$), and (d) Union Carbide MPEG-750 which has an average molecular weight of 750 and a distribution of 715–785 ($n \approx 16$).



3 a: n = 2
b: n ≈ 7
c: n ≈ 12
d: n ≈ 16

Scheme I



The chlorinated polymer **6** was a tan-colored solid and insoluble in common organic solvents such as tetrahydrofuran, diethyl ether, nitromethane, acetonitrile, dimethyl sulfoxide, dioxane, sulfolane, hexamethylphosphoric triamide or dimethylformamide and was very air sensitive. It showed IR bands (diffuse reflectance FTIR, DRIFT) at 1609 and 1511 (aryl ring), 1404 (P–CH_2),[36] 1215 (P=N),[36] 828 (para-disubstituted aryl), and 547 and 520 cm^{-1} (P–Cl).[36]

The polymers **3a–d** were purified by dialysis (MW cutoff 3500) against water and then methanol and dried. They were very dark, brownish-black solids and were produced in rather low yield. They appeared to be water soluble, however polymers **3b** and **3d** were less soluble than the other two. Carbon, hydrogen, nitrogen, and phosphorus elemental analyses agreed in each case with the calculated values. ^{31}P NMR spectra (D_2O) showed peaks between δ 16 and 29, where one would expect these types of phosphorus atoms to resonate.[39] In **3a** sharp peaks appeared at δ 25.2, 26.2, and 28.7, while in **3b** they were at δ 24.9 and 26.2, and in **3c** there were a number of relatively sharp peaks with the major ones being at δ 25.2, 26.2, and 28.7. In **3d** there appeared to be less "fine structure" with the major, somewhat broad, peaks at δ 23.0 and 25.4. Carbon-13 NMR spectra were obtained for three of the four polymers. Polymers **3a**, **3c**, and **3d** showed the methylenes attached to the phosphorus atoms at δ 21–23 as broad multiplets. All three polymers showed the OCH_3 carbon atoms as relatively sharp bands at δ 58.2 for **3a** and 58.2 and 60.5 for both **3c** and **3d**. Polymer **3a** showed its OCH_2 carbon atoms at 66.1, 69.6, and 71.1 while **3c** and **3d** had nearly the same bands at δ 69.7, 71.1, 71.9 and 69.8, 71.2, 71.9, respectively, with the largest peak in both cases being the one at δ 69.7 and 69.8. In all three cases (**3a**, **3c**, and **3d**) the aromatic resonances appeared as broad multiplets between δ 112 and 130. Compound **3b** was not soluble enough to get a complete spectrum, but it did show one peak above baseline noise at δ 69.8.

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Thermogravimetric analysis (TGA) in air showed that polymer **3d** was stable up to about 220 °C, then it lost weight very slowly until at about 300–350 °C it rapidly lost nearly 40% of its weight and then again gradually lost weight up to 700 °C (60% weight loss). The other three polymers **3a–c** began showing some weight loss at about 75–100 °C and by 500 °C they had lost about 40–50% of their weight. The weight loss of polymer **3a** was only about 2% below 100 °C and, since all samples were dried for at least 24 h and stored in a vacuum desiccator, it seems unlikely that the weight loss of these three polymers below 100 °C is due to solvent loss.

Attempts to examine the molecular weights proved rather interesting. Three Waters Ultrahydrogel aqueous GPC columns of 500, 250, and 2000 Å in series were employed. These were suitable for molecular weights up to about 2 000 000. Twelve poly(ethylene glycol) and poly(ethylene oxide) standards ranging in molecular weight (MW) from 440 to 763 200 were used. The GPC was done using aqueous solutions which had been filtered through 0.45-μm filters. For all four polymers there was a very large peak with a retention time of 12–13 min whereas the standards had retention times ranging between 35.35 min for MW = 440 and 20.95 min for MW = 763 200. These polymer peaks would therefore be equivalent to molecular weights of many hundreds of millions, clearly an absurd result. One of the polymers **3c** was then examined using laser light scattering. The result showed that the material was in fact a colloidal dispersion and was polydispersed with an average effective diameter of 145 nm. This result coupled with the GPC results indicate that the polymers must be highly aggregated and that particles of this size must be capable of getting through the interstices of the GPC columns which have nominal particle size of 5 μm.

The ionic conductivity of two of the samples (**3a** and **3c**) was measured by ac impedance spectroscopy. Polymers **3a** and **3c** were mixed with lithium trifluoromethanesulfonate (lithium triflate), where the oxygen:Li^+ ratio was 5:1. The samples were prepared as pressed pellets as described in the Experimental Section. Electrical contact was made on both sides of the pellets using conductive paint and the ionic conductivity was measured by ac impedance spectroscopy at 22 °C. Representative ac impedance data are shown in parts a and b of Figure 1 in the complex plane format for polymers **3a** and **3c**, respectively. The bulk resistances, R_b, were obtained from the ac impedance spectra as shown.[6] Replicate measurements yielded R_b values of 13.2 ± 0.5 kΩ for **3a** and 30 ± 2 kΩ for **3c**, respectively. These values coupled with the areas of the disks (1.33 and 1.32 cm^2, respectively) and their thicknesses (0.62 and 0.75 mm, respectively) yield conductivities of 3.5×10^{-6} S cm^{-1} for **3a** and 2.0×10^{-6} S cm^{-1} for **3c**. These conductivities are considerably larger than that of PEO complexed with lithium triflate, ca. 1×10^{-8} S cm^{-1} at room temperature.[40] Further, it is only a factor of about 10 lower than that of MEEP complexed with lithium triflate, $(2-3) \times 10^{-5}$ S cm^{-1} at 30 °C with a O:Li^+ ratio of 4–6:1.[11] Cross-linked MEEP complexed with lithium triflate is reported to have a room temperature conductivity of about $(1-2) \times 10^{-5}$ S cm^{-1},[12] which means that polymers **3a** and **3c** are only a factor of about 5 lower.

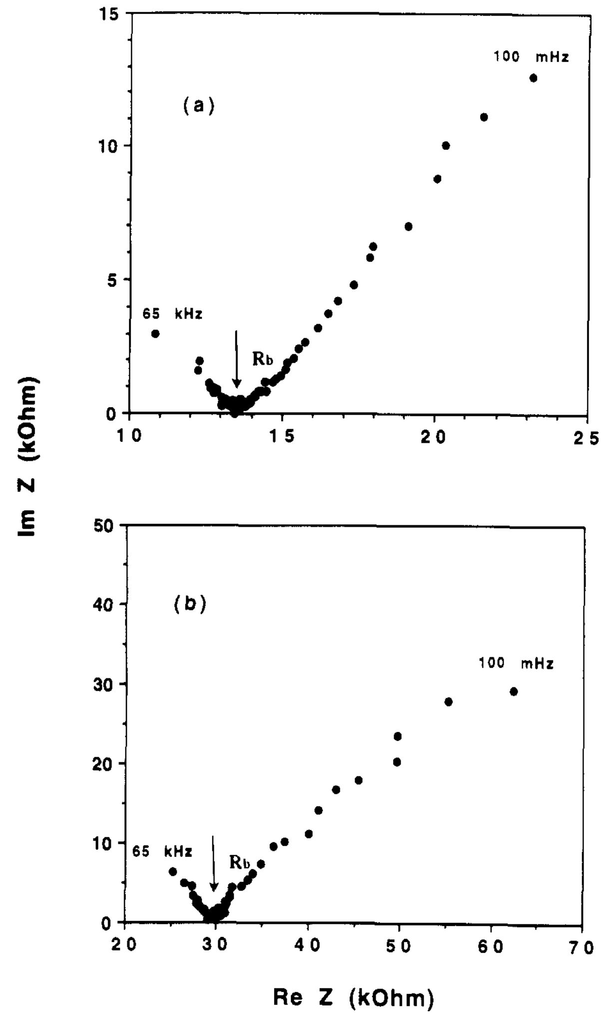

Figure 1. Complex plane plots of the impedance of (a) polymer **3a** and (b) polymer **3b**. The measurement frequency is shown as a parameter in each case, and the bulk resistance of the sample, R_b, was extracted as shown (cf. ref 6).

Even though these values for the conductivities are certainly not optimized as to the best Li^+:O ratio and polyether chain length, it is clear that these materials are rather good conductors.

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