Novel Polyanionic Solid Electrolytes with Weak Coulomb Traps and Controllable Caps and Spacers

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New chain polymers that contain weakly coordinating anionic groups at controllable anionic separations in a polyether backbone are described. The anions are mono-diacyl-capped orthoborate moieties. In this paper, the polyanionic electrolytes with mono-oxalato-capped and mono-malonato-capped orthoborate structures (called "polyMOBs" and "polyMMBs", respectively) are presented. After optimizing the anion separation, the conductivities of these lithium ion conducting polyanionic electrolytes are found to be high relative to those of most "dry" single-ion-conducting polymer electrolytes. A maximum ambient conductivity of almost 10^{-5} S cm^{-1} has been obtained for a solid polyMOB with 14 ethyleneoxy repeating units. The electrochemical "window" for these materials is in excess of 4.5 V. As prepared here, the polyMOB materials (but not the polyMMBs) contain some residual lithium bis(oxalato)-borate (LiBOB) as a side-product, which can be reduced but so far has not been eliminated. The effect of LiBOB content on conductivity is small, but it may cause the lithium ion transport number to be less than 1.0. These inexpensive, benign materials should be very suitable as electrolytes for electrochemical devices requiring single-ion conduction.

Introduction

Solvent-free polyether−lithium salt complexes have been extensively studied as solid polymer electrolytes (SPEs) during the past two decades, due to their potential applications in lithium/lithium ion rechargeable batteries, sensors, electrochromic display devices, and other electrochemical devices.[1,2] The most successful of these electrolytes is that developed by Armand and co-workers in which lithium bis(trifluoromethylsulfonyl)imide [$LiN(SO_2CF_3)_2$ or LiTFSI] is dissolved in poly(ethylene oxide) (PEO).[3] This complex has a specific conductivity of $10^{-4.3}$ S cm^{-1} at room temperature. The same result was claimed by Kerr and co-workers for LiTFSI when it is dissolved in different poly(ethylene glycol) containing polymers.[4] Recently, Fang and co-workers[5] prepared a PEO branched network polymer electrolyte based on the polymethylsiloxane system and the optimum conductivity of this polymer which contained $LiClO_4$ as ion source was $10^{-4.1}$ S cm^{-1} at room temperature. However, the conductivity of this "salt-in-polymer" electrolyte is unfortunately dominated by anionic motion because the lithium ions are strongly chelated by the basic ether oxygens in the chains. For example, transport numbers as low as 0.1 have been measured for the Li cations in these media,[6] and even in the favorable case of lithium imide, the transport number of Li^+ is estimated to be only 0.22.[7]

To improve the cation transport number of the PEO−salt complexes, the senior author and his group have utilized the chain polymers as a dilute component to impart "solidity"[8] to low-temperature melts of appropriate alkali cation salt mixtures. In the ideal case, the liquid formed is stable at ambient temperature and the cationic motion is decoupled from the anionic motion so that the conductivity is cationic, as in the popular "superionic glass" electrolytes.[9] Unfortunately, it has proven to be extremely difficult to find simple salts of lithium cations that have high chemical stability and also remain liquid at room temperature. Those that do, such as the unsymmetrical chlorofluorosulfonyl imide and its dichloro-equivalent,[10] prove to have very poor conductivities. An alternative to the latter approach, and in some ways a solution to its problems, is to make the anions serve simultaneously as anion and polymer, by joining them together in one long chain.[11] This is the approach taken in this paper.

An earlier and partially successful approach, which is an intermediate between the approaches mentioned above, has been to join the anions pairwise, by polymer segments, which make crystallization of the salt almost

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(1) *Polymer Electrolytes Reviews, Vols. 1 and 2*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science: London and New York, 1987 and 1989.
(2) Gray, F. *Electrolytes*: *fundamentals and technological applications*; VCH publishers Inc.: New York, 1991.
(3) Armand, M.; Gorecki, W.; Anréani, R. In *Second International Symposium on Polymer Electrolytes*; Scrosati, B., Ed.; Elsevier: London and New York, 1990; p 91.
(4) Buriez, O.; Han, Y. B.; Hou, J.; Kerr, J. B.; Qiao, J.; Sloop, S. E.; Tian, M.; Wang, S. *J. Power Sources* **2000**, *89*, 149.
(5) Zhang, Z.; Fang, S. *Electrochim. Acta* **2000**, *45*, 2131.
(6) Bruce, P. G.; Hardgrave, M. T.; Vincent, C. A. *Solid State Ionics* **1992**, *53−56*, 1087.
(7) Gorecki, W.; Jeannin, M.; Belorizky, E.; Roux, C.; Armand, M. *J. Phys.: Condens. Matter* **1995**, *7*, 6823.
(8) Angell, C. A.; Xu, K.; Zhang, S.-S.; Videa, M. *Solid State Ionics* **1996**, *86-88*, 17−28.
(9) (a) Angell, C. A.; Liu, C.; Sanchez, E. *Nature* **1993**, *362*, 137. (b) Angell, C. A.; Liu, C. U.S. Patent 5,506,073, April 9, 1996.
(10) Xu, K.; Angell, C. A. *Symp. Mat. Res. Soc.* **1995**, *369*, 505.
(11) Zhang, S.-S.; Chang, Z.; Xu, K.; Angell, C. A. *Electrochim. Acta* **2000**, *45*, 1229.

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impossible. This led, initially,[12,13] to rather poor ambient temperature conductivities, but recent developments by Ohno and co-workers by using more favorable anionic moieties[14−16] have given much improved performance. Such systems still need the addition of a long chain polymer component to impart solidity.

Most previous attempts to obtain single-ion-conducting polymers have yielded conductivities that have been very low, usually well below 10^{-6} S cm^{-1}. For instance, in the aluminosilicate/poly(ethylene glycol) copolymers described by Shriver and co-workers,[17] conductivities above 10^{-5} S cm^{-1} could only be obtained by using a cryptand to complex the alkali cation. Somewhat better results were obtained by Fujinami et al.[18] by using siloxyaluminate polymers with ethylene oxide side chains ($10^{-4.71}$ S cm^{-1} at 25 °C). Evidently, this electrolyte contained contaminants which reduced the transport number below 1.0. Furthermore, the temperature dependence of the conductivity in this case was peculiar and the conductivity never rose above $10^{-4.3}$ S cm^{-1} even at 100 °C.[18] However, it indicated a promising approach.

Recently, we briefly reported a novel kind of polyanionic electrolyte, poly[lithium mono-oxalato oligo(ethylene glycolato) borate], which was called the "polyMOB" electrolyte ("MOB" for mono-oxalato borate) and abbreviated as P(LiOEG$_n$B).[19] The polyMOB anions are built from a newly developed weakly coordinating anion, bis(oxalato)borate (BOB$^-$) anion.[20] In these polyanions, the tetrakis-coordinated boron has two ligands connected with an oxalyl group via two oxygens to form a mono-oxalato-capped ring structure, while the other two ligands are linked through the two other oxygens to the polymeric chain that contains repeating spacer units of oligo(ethylene glycols).

In this paper, we continue the studies on the characterization, thermal properties, ionic conductivities, and electrochemical stability of several examples of such kind of polyanionic electrolytes, in which different types of capped structures and different types and lengths of spacer chains are used. The effect of the structural parameters on the freedom of Li^+ to migrate in a manner that is independent of the polymer segmental relaxation will also be discussed by using a combination of T_g and conductivity data.

Experimental Section

Preparation. In this work, oxalic acid and malonic acid were chosen to form different types of capped orthoborate structures, i.e., mono-oxalato-capped and mono-malonato-capped orthoboric acids [$B(C_2O_4)(OH)_2^-$ (MOB$^-$) and $B(CH_2C_2O_4)(OH)_2^-$ (MMB$^-$), respectively]. They were then allowed to react with different oligo(alkylene glycols), chosen from poly(ethylene glycol), PEG, and poly(propylene glycol), PPG, with different molecular weights, i.e., different length of spacer repeating unit. The polyanionic electrolytes of whatever cation charge-compensated were obtained by eliminating water in a condensation polymerization process. In our case, the counter cation was always Li^+. The preparation procedures followed those of our abbreviated report.[19]

Measurements. The polymers obtained were characterized by ^{1}H, ^{13}C, ^{7}Li, and ^{11}B NMR spectra. A simple differential thermal analysis (DTA) method was used to determine the thermal behavior of the polymers, such as glass transition temperature (T_g), crystallization temperature (T_c), and liquidus temperature (T_l) (both T_c and T_l are for long polyether spacer cases). Ionic conductivities were obtained by ac impedance measurements as a function of temperature, and electrochemical properties were measured by cyclic voltammetry. The procedures have been described elsewhere.[19,21]

Results and Discussion

Characterization. Table 1 shows the physical appearances of these PEG- and PPG-spaced polymers at ambient temperatures, in which the data for PEG-spaced mono-oxalato-capped polymers, reported in ref 19, are also included for comparison. Similar to the PEG-spaced mono-oxalato-capped polymers, PEG-spaced mono-malonato-capped polymers are almost glassy for short spacer units, e.g., when tri(ethylene glycol) (n = 3) is used in the polymerization. They are almost rubbery (flowing very slowly at high temperatures but rubbery for short time stresses) when PEG200 ($n \approx 5$) is used in the polymerization and soft or sticky rubber when PEG400 ($n \approx 9$) and PEG600 ($n \approx 14$) are used in the polymerization. The polymer from PEG1000 ($n \approx 23$) is partly crystallized (the polyether segment) at room temperature. On the other hand, the three PPG-spaced MOB-capped polymers are all highly viscous liquids. These polymers are soluble in various polar solvents, like acetonitrile, acetone, and even chloroform. Slow hydrolysis or alcoholysis of the polymers takes place on prolonged exposure to water or alcohols. However, the reaction products are benign.

The polymer products were characterized by using ^{1}H, ^{13}C, ^{11}B, and ^{7}Li NMR spectra to determine their structures. The NMR data measured in DMSO-d_6 are also summarized in Table 1.

The ^{11}B NMR data indicate that there are two kinds of boron structures in the PPG-spaced mono-oxalato-capped polymers, just like what have been found for PEG-spaced analogues. However, there is only one kind of boron structure in the mono-malonato-capped borate polymers. For mono-oxalato borate polymers, as we discussed in our previous report,[19] the larger value of chemical shift ($\delta \approx 12.0$ or 12.2 ppm) is attributed to the boron atom of the *b*is(*o*xalato) ortho*b*orate (BOB$^-$) anion impurity. The LiBOB impurity is formed by the reaction of oxalic acid, boric acid, and lithium hydroxide during evaporation of water in the first step (see reaction 1a below). The smaller chemical shift ($\delta \approx 9.4$ or 9.5 ppm) is assigned to the boron of the *m*ono-*o*xalato ortho*b*orate (MOB$^-$) anionic group in the polymer chain, which is the target of our synthesis. This boron atom connects with one oxalyl via two oxygen ligands to form

(12) Xu, K.; Angell, C. A. *Electrochim. Acta* **1995**, *40*, 2401.
(13) Angell, C. A.; Fan, J.; Liu, C.; Sanchez, E.; Xu, K. *Solid State Ionics* **1994**, *69*, 343.
(14) Ito, K.; Tominaga, Y.; Ohno, H. *Solid State Ionics* **1996**, *36−38*, 325.
(15) Tominaga, Y.; Ohno, H. *Electrochim. Acta* **1997**, *42*, 1561.
(16) Ohno, H.; Nakai, Y.; Ito, K. *Chem. Lett.* **1998**, 15.
(17) Rawsky, G. C.; Fujinami, T.; Shriver, D. F. *Chem. Mater.* **1994**, *6*, 2208.
(18) Fujinami, T.; Tokimune, A.; Mehta, M. A.; Shriver, D. F.; Rawsky, G. C. *Chem. Mater.* **1997**, *9*, 2236.
(19) (a) Xu, W.; Angell, C. A. European Conference Abstracts of Polymer electrolytes Symposium 2001, Volume 25E, L13, Noordwijkerhout, The Netherlands, May 14−16, 2001. (b) *Solid State Ionics*, in press.
(20) Xu, W.; Angell, C. A. *Electrochem. Solid-State Lett.* **2001**, *4*, E1.
(21) Xu, W.; Belieres, J-P.; Angell, C. A. *Chem. Mater.* **2001**, *13*, 575.

Table 1. Physical Appearances and NMR Data of the Mono-Oxalato-Capped and Mono-Malonato-Capped Polymers with PEG and PPG Spacer Groups after Chloroform Treatment

				chemical shift δ (ppm) in DMSO-d_6			
cap	spacer	*n* value	appearances	^{1}H	^{13}C	^{7}Li	^{11}B
MOB	PEG	3	stiff rubber	4.33 (weak)	157.90	0.99	12.02
				3.81 (weak)	72.98		9.37
				3.67 (weak)	70.45		
				3.49	60.87		
		5	rubber	4.33 (weak)	157.25	0.99	12.01
				3.81 (weak)	72.34		9.36
				3.67 (weak)	69.77		
				3.49	60.21		
		9	soft rubber	4.33 (weak)	157.29	0.99	12.02
				3.49	72.35		9.39
					69.81		
					60.23		
		14	sticky rubber	3.49	158.12	0.99	12.02
					72.33		9.38
					69.79		
					60.22		
		23	crystal solid	3.49	157.90	0.99	12.02
					72.32		9.37
					69.76		
					60.18		
	PPG	7	very viscous liquid	4.34 (weak)	158.69	0.98	12.20
				3.48, 3.40	75.09		9.57
				3.35	73.16, 72.69		
				1.01	16.93		
		13	very viscous liquid	4.33 (weak)	158.55	0.98	12.21
				3.44, 3.41	75.09		9.57
				3.32	73.04, 72.66		
				1.02	17.15		
		17	very viscous liquid	4.40 (weak)	158.58	0.98	12.20
				3.44, 3.41	75.10		9.52
				3.30	73.13, 72.70		
				1.02	17.20		
MMB	PEG	5	rubber	3.50	162.67	1.02	6.23
					72.34		
					69.79		
					60.20		
		9	rubber	3.50	162.20	0.97	6.36
				3.41, 3.40 (weak)	72.35		
					69.81		
					60.23		
		14	soft rubber	3.50	162.18	0.99	6.21
				3.41, 3.39 (weak)	72.28		
					69.74		
					60.16		
		23	crystal solid	3.50	162.16	0.98	6.35
				3.41, 3.40 (weak)	72.35		
					69.78		
					60.23		

a mono-oxalato borate ring and with two oligoether groups via other two oxygens to form a chain.

Similarly, the chemical shift for malonato-capped borate polymers, at $\delta \approx 6.3$ ppm, is assigned to the boron of the mono-malonato orthoborate (MMB^-) anionic group, when compared with that of the bis(malonato)-borate (BMB^-) group ($\delta \approx 8.3$ ppm for LiBMB as reported in ref 20). This boron atom connects with one malonyl via two oxygen ligands to form a mono-malonato borate ring and with two oligo(oxyethylene) via other two oxygens to form a chain.

The reactions taking place in our preparation of the mono-oxalato borate and mono-malonato borate polymers are proposed to be the following, using PEG as an example. Reactions 1 and 2 are the desired sequence

$$LiOH + HOOCCOOH + B(OH)_3 \rightarrow LiB(C_2O_4)(OH)_2 + 2H_2O \quad (1a)$$

$$LiOH + HOOCCH_2COOH + B(OH)_3 \rightarrow LiB(C_3H_2O_4)(OH)_2 + 2H_2O \quad (1b)$$

$$mLiB(C_2O_4)(OH)_2 + mHO(CH_2CH_2O)_nH \rightarrow H\{O[Li(C_2O_4)]B(OCH_2CH_2)_n\}_mOH + 2mH_2O \quad (2a)$$

$$mLiB(C_3H_2O_4)(OH)_2 + mHO(CH_2CH_2O)_nH \rightarrow H\{O[Li(C_3H_2O_4)]B(OCH_2CH_2)_n\}_mOH + 2mH_2O \quad (2b)$$

$$LiOH + 2HOOCCOOH + B(OH)_3 \rightarrow LiB(C_2O_4)_2 + 4H_2O \quad (3a)$$

$$LiOH + 2HOOCCH_2COOH + B(OH)_3 \rightarrow LiB(C_3H_2O_4)_2 + 4H_2O \quad (3b)$$

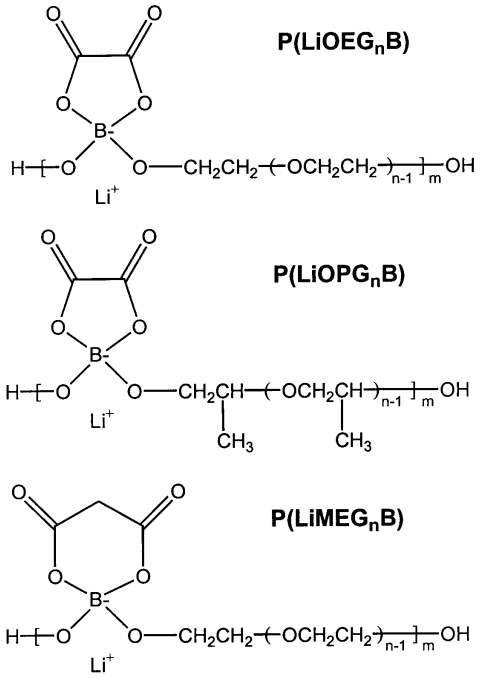
$$LiOH + B(OH)_3 \rightarrow LiBO_2 + 2H_2O \quad (4)$$

$$LiOH + HOOCCOOH \rightarrow LiOOCCOOH + H_2O \quad (5a)$$

$$LiOH + HOOCCH_2COOH \rightarrow LiOOCCH_2COOH + H_2O \quad (5b)$$

Reactions 3−5, that form LiBOB or LiBMB, lithium metaborate ($LiBO_2$), lithium hydrogen oxalate (LiOOC-COOH), or lithium hydrogen malonate ($LiOOCCH_2$-

Scheme 1. Chemical Structures of PEG- and PPG-Spaced, Mono-Oxalato-Capped and Mono-Malonato-Capped Orthoborate Polymers



COOH), are undesirable side reactions. From the ^{11}B NMR results, we did not find any evidence for the presence of the three-coordinated boron structure, i.e., poly[oligo(ethylene glycol) borate] from PEG and boric acid. There is no evidence either for the formation of poly[oligo(ethylene glycol) oxalate] or for poly[oligo-(ethylene glycol) malonate] from the chemical shift of ^{13}C of the carbonyl group (C=O). Thus, depending on which kind of cap structure was formed or which type of spacer (PEG or PPG) was used, the polymers that are formed are poly[lithium oxalato oligo(ethylene glycolato) orthoborate], poly[lithium oxalato oligo(propylene glycolato) orthoborate], or poly[lithium malonato oligo-(ethylene glycolato) orthoborate]. Their chemical structures are shown in Scheme 1. In general, we call these polyanionic polymers polyMOBs and polyMMBs, and specifically they are P(LiOEG$_n$B), P(LiOPG$_n$B), or P(LiMEG$_n$B), where n represents the number of the spacer repeat units.

Some unreacted PEG or PPG was still left during these reactions. However, they were removed by decanting and washing with benzene during the first post-treatment, as shown by the viscous liquids that remained when all benzene had been evaporated from the decanted supernatant. It is also known from ref 20 that LiBMB has very poor solubility in normal organic solvents such as tetrahydrofuran (THF) and acetonitrile while LiBOB is very soluble in these solvents. Thus, LiBMB can be removed from the polymer solutions by filtration along with $LiBO_2$ and $LiOOCCH_2COOH$ which were formed in the side reactions (Reactions 4 and 5b). Therefore, the polymers that are obtained are totally pure polyMMBs.

Unfortunately, the LiBOB formed in a side reaction of 3a cannot be removed completely in the above manner even though in pure form it does not dissolve in chloroform. The reason is that LiBOB, unlike the other impurities, dissociates easily into ions in the polar polymer medium, which is a consequence of the weakly coordinating character of the bis(oxalato)borate anion. The dissociated lithium ions then coordinate strongly with the ether oxygen atoms on the polymer chains to form transient complexes. Thus, LiBOB segregates microscopically with the polymer even in chloroform solution and remains there when the chloroform is removed. The greater the length of the ethyleneoxy chain in the spacer, the greater is the number of lithium ions that are coordinated. The residual LiBOB content is therefore higher in the high n polymers. This is shown in Table 2, where the integral value for ^{11}B at $\delta \approx 12.0$ ppm (the signal for BOB^-) increases with increase of the length of spacer PEG or PPG, i.e. the n value. The LiBOB side-product is particularly important in the case of the PPG-spaced polymer, where it is actually the major product of reaction. To obtain a pure polyMOB, all LiBOB must be removed. Work on this problem is in progress, but so far the lowest LiBOB contents obtained have been ca. 5 mol %. For long spacer cases, like $n \approx 23$, the LiBOB content can be as high as 30 mol %. Fortunately, the effect of LiBOB content on conductivity is small, and the conductivity of the pure polyMOB can be obtained by short extrapolation as discussed below.

Thermal Behavior. The DTA results for the polymers, before and after treatment with chloroform, are listed in Table 3. It is seen that most of the polymers exhibit only glass transitions in the studied temperature range between −150 and 100 °C. The glass transition temperature (T_g) decreases with increase in the spacer length for both types of spacers. This is because the shorter spacer polymer has higher lithium ion concentration, raising the cohesive energy via transient cross-linking. Thus, at ambient temperature, the segmental mobility and hence the Li^+ mobility increase with increase in the spacer length.

The phase changes at 23.1 °C for P(LiOEG$_{14}$B), 39.7 °C for P(LiOEG$_{23}$B), 27.0 °C for P(LiMEG$_{14}$B), and 42.9 °C for P(LiMEG$_{23}$B) in Table 3 are due to the melting (at the analogue of the usual salt-in-polymer liquidus) of the polyether nanocrystals that form by local packing of the long oligoether chains during cooling. On supercooling, the crystallization occurs at −15.4, −47.2, −30.3, and −50.0 °C for the four polymers, respectively. There are no such crystallization transitions or melting (liquidus) transitions for the short length PEG-spaced polymers or for any of the three PPG-spaced polymers. When comparison is made between the DTA data of PEG-spaced polyMOBs and polyMMBs, it is seen that the effect of the cap structure on the thermal behavior is large, when the spacer group is short, but little, when the spacer is long.

It is also seen from Table 3 that the glass transition temperature for polyMOBs has decreased after chloroform treatment in nearly every case. This is because the LiBOB content has been reduced and the number of transient cross-linking sites has decreased. However, the liquidus temperature for $n \approx 14$ and 23 PEG-spaced polymers increases relative to that before chloroform treatment. Clearly, therefore, the LiBOB is dissolved preferentially in the polyether chains domains and this has the usual mp lowering effect. When the salt is removed, the mp goes up again.

Table 2. Comparison of Boron Content in PEG- and PPG-Spaced PolyMOBs before and after Chloroform Treatment (from ^{11}B NMR Spectra Integration)[a]

			boron peak integration					
			before $CHCl_3$ treatment			after $CHCl_3$ treatment		
cap	spacer	*n* value	peak for BOB^-	peak for MOB^-	BOB/MOB	peak for BOB^-	peak for MOB^-	BOB/MOB
MOB	PEG	3	24.75	75.25	0.33	4.89	95.11	0.05
		5	42.17	57.83	0.73	4.05	95.95	0.04
		9	55.51	44.49	1.25	12.50	87.50	0.14
		14	68.84	31.16	2.21	29.17	70.83	0.41
		23	43.29	56.71	0.76	30.21	69.79	0.43
	PPG	7	71.28	28.72	2.48	24.73	63.76	0.39
		13	78.45	21.55	3.64	63.72	36.28	1.76
		17	74.90	25.10	2.98	65.47	34.53	1.90

[a] Peak for BOB^- in $P(LiOEG_nB)$ is 12.0 ppm and in $P(LiOPG_nB)$ is 12.2 ppm. Peak for MOB^- in $P(LiOEG_nB)$ is 9.4 ppm and in $P(LiOPG_nB)$ is 9.5 ppm. BOB/MOB represents the molar ratio of monomeric anion to polymeric anion content.

Table 3. DTA Data for the Polymers before and after Chloroform Treatment

			before $CHCl_3$ treatment			after $CHCl_3$ treatment		
cap	spacer	*n* value	T_g (°C)	T_c (°C)	T_l (°C)	T_g (°C)	T_c (°C)	T_l (°C)
MOB	PEG	3	*a*	*a*	*a*	−0.9		
		5	−22.9			−20.1		
		9	−41.8			−44.3		
		14	−51.5	−15.4	6.6	−53.3	−15.4	23.1
		23	−54.5	−2.3	20.6	−63.1	−47.2	39.7
	PPG	7	−43.3			−47.0		
		13	−56.9			−56.0		
		17	−63.4			−61.0		
MMB	PEG	5	*a*	*a*	*a*	−36.7		
		9	*a*	*a*	*a*	−57.6		
		14	*a*	*a*	*a*	−58.2	−30.3	27.0
		23	*a*	*a*	*a*	−63.1	−50.0	42.9

[a] Not measured.

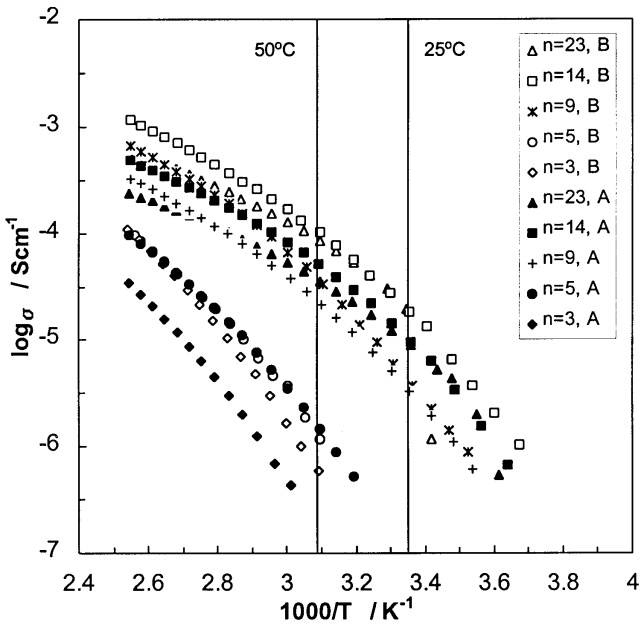


Figure 1. Temperature dependence of ionic conductivity of PEG-spaced polyMOB electrolyte $P(LiOEG_nB)$s, before (B) and after (A) treatment with chloroform to reduce LiBOB content.

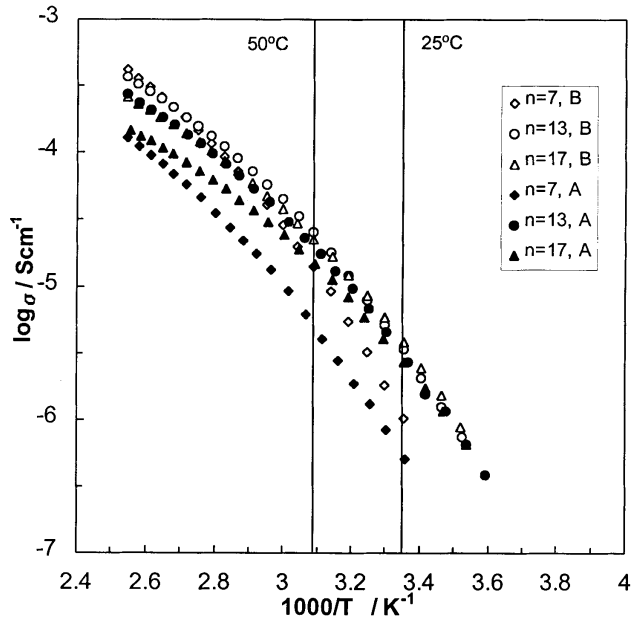


Figure 2. Temperature dependence of ionic conductivity of PPG-spaced polyMOB electrolyte $P(LiOPG_nB)$s, before (B) and after (A) treatment with chloroform to reduce LiBOB content.

Ionic Conductivity. Figure 1 and Figure 2 show the temperature dependence of the ionic conductivities of PEG- and PPG-spaced polyMOBs measured during steady cooling, before (B) and after (A) chloroform treatment to remove LiBOB. Figure 3 shows the temperature dependence of the ionic conductivities of PEG-spaced polyMMBs measured during steady cooling. The conductivities of these polymeric forms are strongly dependent on the length of the PEG or PPG spacer between the anionic groups, which can be characterized by the number of ethyleneoxy or propyleneoxy units (*n* value). The actual separation of anions depends on chain conformations, and is not known. For equal *n* value, PPG-spaced polymers are distinctly less conducting than PEG-spaced polymers. For the same PEG spacer, polyMOBs with some LiBOB show much higher conductivity than polyMMBs. From the following discussion, we can

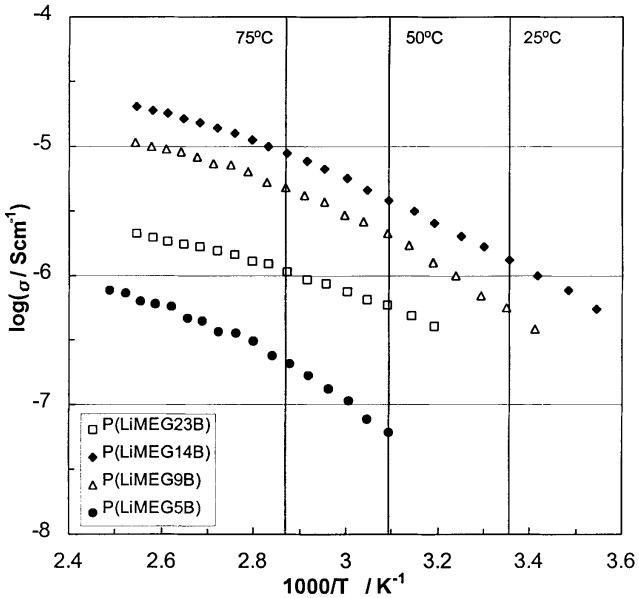


Figure 3. Temperature dependence of ionic conductivity of PEG-spaced polyMMB electrolyte P(LiMEG$_n$B)s.

see that LiBOB-free polyMOBs are more conducting than polyMMBs.

For polyMOBs, the conductivity is not strongly dependent on LiBOB content as shown in Figures 1 and 2, and in the case of the $n \approx 5$ PEG spacer, there is little change in conductivity despite the major reduction (from 42 to 4%) in BOB^- content (accordingly to the NMR data in Table 2). We note that the glass transition temperature also was scarcely affected by the decrease in LiBOB content. Whether this is due to experimental error or a favorable combination of Li^+ decoupling vs free anion effects is not clear at this time.

The maximum conductivity of PEG-spaced polyMOBs after chloroform treatment (10^{-5} S cm^{-1} at ambient temperature) is obtained with $n \approx 14$. The maximum ambient conductivity for PPG-spaced polyMOBs is $10^{-5.60}$ S cm^{-1} at $n \approx 13$ and that for PEG-spaced polyMMBs is $10^{-5.89}$ S cm^{-1} at $n \approx 14$. The ionic conductivities of $n \approx 14$ and 23 PEG-spaced polyMOBs and polyMMBs below 20 °C do not show sudden decrease even when the temperature is below their liquidus temperature, due to supercooling (T_l in Table 3).

The effect of LiBOB content on the isothermal conductivities of polyMOBs is small. For example, in the case of the $n \approx 9$ polyMOB, raising the LiBOB content from 12.5 to 55.5 mol % raises the conductivity only by a factor of 1.3. With such small dependences and no physical reasons to expect new behavior at lower concentrations, the LiBOB-free behavior can be estimated, by short extrapolation, within an uncertainty of ±6% (depending on whether a linear or exponential dependence on composition is assumed). The case of $n \approx 23$, in which spacer crystallization adds uncertainty, is an exception.

Based on the log σ vs mol % LiBOB extrapolation, we obtain the temperature dependences of ionic conductivities of both the PEG- and PPG-spaced pure polyMOBs, shown in parts a and b of Figure 4, respectively. It is seen from Figures 3 and 4a that the conductivity of pure PEG-spaced polyMOBs is nearly 1 order of magnitude higher than that of the polyMMBs with the same PEG spacer.

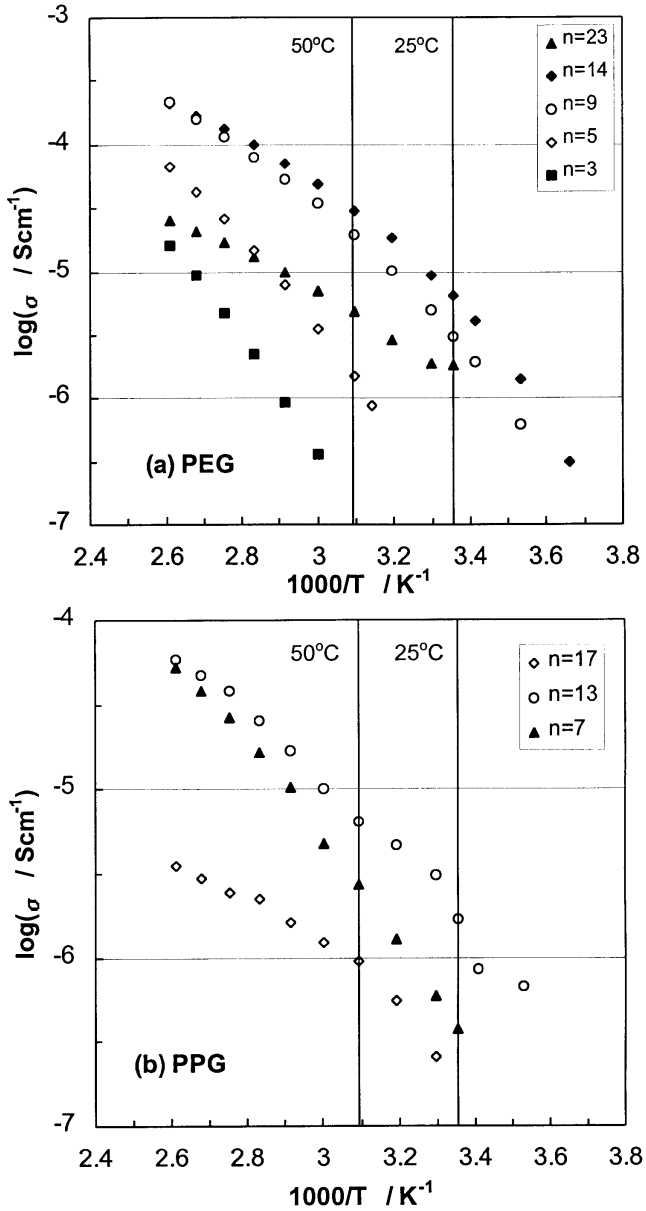


Figure 4. Temperature dependence of ionic conductivities of LiBOB-free polyMOB electrolytes (by extrapolations), with PEG (a) and PPG (b) spacers, respectively.

We could also obtain the variation of the isothermal conductivities of the pure polymers with the length of spacer, i.e., n value, as shown in parts a, b, and c of Figure 5 for PEG- and PPG-spaced polyMOBs and PEG-spaced polyMMBs, respectively. The presence of maximum is reminiscent of the behaviors of the salt-in-polymer solution[22] and the salt-in-molecular solvent.[23,24] It no doubt has the same explanation in terms of the balancing of charge concentration and ion mobility effects, the latter dominating at high charge concentration. The maximum conductivity appears at a lower n value or with a shorter oligoether spacer with increase

(22) Angell, C. A.; Fan, J.; Liu, C.; Sanchez, E.; Xu, K. *Solid State Ionics* **1994**, *69*, 343.
(23) Angell, C. A. *J. Chem. Phys.* **1967**, *46*, 4673.
(24) Barthel, J.; Buestrich, R.; Carl, E.; Gores, H. J. *J. Electrochem. Soc.* **1996**, *143*, 3565.

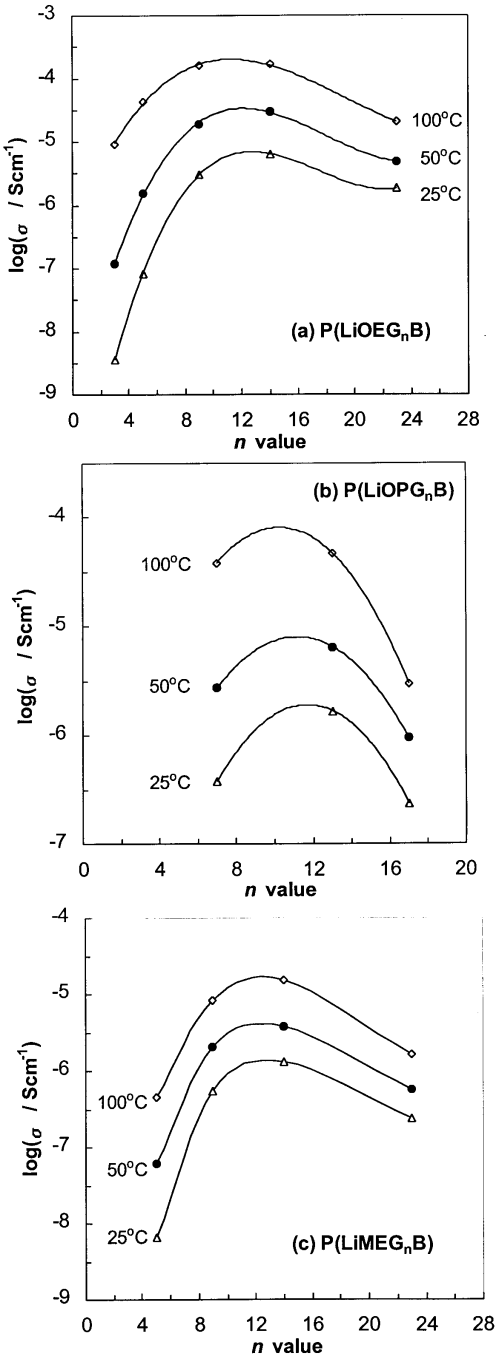


Figure 5. Variation of isothermal conductivities for pure polymers with the length of spacer, i.e., *n* value, for polyMOBs with PEG (a) and PPG (b) spacers (by extrapolations) and polyMMBs with a PEG spacer (c), respectively.

of temperature, as in normal solutions. It is seen that the maximum conductivity at room temperature is ca. $10^{-5.16}$ S cm^{-1} at $n = 12-14$ for the PEG-spaced polyMOB, ca. $10^{-5.72}$ S cm^{-1} at $n = 11-13$ for the PPG-spaced polyMOB, and ca. $10^{-5.85}$ S cm^{-1} at $n = 11-14$ for the PEG-spaced polyMMB.

The combination of conductivity and T_g data permits us to learn the effect of the structural parameters on the freedom of Li^+ cations to migrate in a manner that is independent of the polymer segmental relaxation. We obtain this information from the "decoupling index" $R_\tau = \tau_s/\tau_\sigma$,[25] where τ_s is the structural relaxation time and τ_σ is the conductivity relaxation time. At T_g, where the structural relaxation time is 200 s,[26] the decoupling index is given by the approximate relation: $\log R_\tau = 14.3 + \log \sigma_{T_g}$.[27] To estimate the conductivity at T_g, we extrapolate the data of Figures 1 and 2 by using the well-known Vogel–Fulcher–Tamman (VFT) equation

$$\sigma = A_\sigma T^{-1/2} \exp[-B_\sigma/(T - T_o)] \qquad (6)$$

where A_σ and B_σ are constants, characteristic of the conduction process, and T_o is the vanishing mobility temperature. Since the pre-exponential $T^{-1/2}$ has little effect on the fitting where a good range of low-temperature data are available, it is often omitted so that the pre-exponent can be compared more simply with theoretical expectations for unassociated ionic conductors. Thus, it is common to use the equation

$$\sigma = \sigma_o \exp[-D_\sigma T_o/(T - T_o)] \qquad (7)$$

where $D_\sigma = B_\sigma/T_o$. D_σ is inversely proportional to the "fragility" of the liquid,[28] provided conductivity is coupled to viscosity (see below). Values of A_σ, B_σ, and T_o from eq 6 fittings and σ_o, D_σ, and T_o from eq 7 fittings are collected in Tables 4 and 5, respectively. It is seen that the T_o parameters are little affected by the choice of equation.

Also included in Tables 4 and 5 are the differences between T_g and T_o, the conductivity of the polymers at T_g (σ_{T_g}) and the corresponding decoupling indexes R_τ. For polyMOBs, the values of σ_o are consistent with expectations for dissociated electrolytes and decrease as expected with decreasing [Li^+] as *n* increases. There is some indication of increasing ionic association with increasing *n* value. Although the extrapolations to T_g are long (hence must be regarded with much caution), the values of σ_{T_g} show some significant trends. They indicate that as the Li^+ ion concentration increases, the logarithmic decoupling index $\log R_\tau$ increases from negative to positive values, just as seen in salt-in-polymer electrolytes.[29] In the latter case, it was possible to increase the Li:[O] concentration above 1:1 and observe large decoupling ratios which produced high uni-ionic conductivities. This pointed the way to the idea of polymer-in-salt electrolytes.[22,30,31] It is possible that larger decoupling in the present systems could be induced by adding a salt such as $LiClO_4$ to the present polymers. Since $LiClO_4$ has a lower T_g than the $n = 3$ polyMOB, the addition of $LiClO_4$ would amount to plasticization by a liquid salt with decoupled cation mobility— the polymer-in-salt concept.[9] When conductivity is decoupled from viscosity, single-ion conductivity is maintained even in the absence of polyanions.

Unfortunately, the extent of decoupling predicted by the equations is unreliable in the cases of longer spacer units. Note that the T_o parameters for polyMOBs with long spacers are approaching the T_g value, unrealisti-

(25) (a) Moynihan, C. T.; Balitactac, N.; Boone, L.; Litovitz, T. A. *J. Chem. Phys.* **1971**, *55*, 3013. (b) Angell, C. A. *Solid State Ionics* **1983**, *9–10*, 3; **1986**, *18-19*, 72.
(26) Moynihan, C. T.; Macedo, P. B.; Montrose, C. J.; Gupta, P. K.; DeBolt, M. A. *Ann. N. Y. Acad. Sci.* **1976**, *279*, 15.
(27) Angell, C. A. *Annu. Rev. Phys. Chem.* **1992**, *43*, 693.
(28) Videa, M.; Angell, C. A. *J. Phys. Chem.* **1999**, *103*, 4185.
(29) McLin, M. G.; Angell, C. A. *Solid State Ionics* **1992**, *53–56*, 1027.
(30) Wei, X.; Shriver, D. F. *Chem. Mater.* **1998**, *10*, 2307.
(31) Ferry, A.; Edman, L.; Forsyth, M.; MacFarlane, D. R.; Sun, J. *J. Appl. Phys.* **1999**, *86*, 2346.

Table 4. VFT Best Fitting Parameters from Equation 6 for PolyMOBs and PolyMMBs after Chloroform Treatment

cap	spacer	*n* value	T_g (K)	A_σ ($K^{1/2}$ S cm^{-1})	T_o (K)	B_σ (K)	$T_g - T_o$ (K)	log σ_{T_g}	log R_τ[a]
MOB	PEG	3	272.3	4.7	212.7	1590	59.6	−12.1	2.2
		5	253.1	2.3	207.6	1316	45.5	−13.4	0.9
		9	228.9	1.3	193.2	1047	35.6	−13.8	0.5
		14	219.9	0.5	206.1	727	13.8	−24.4	−10.1
		23	210.1	0.2	196.5	716	13.6	−24.9	−10.6
	PPG	7	226.2	1.4	194.7	1237	31.5	−18.1	−3.8
		13	217.2	1.5	184.4	1165	32.8	−16.4	−2.1
		17	212.2	0.3	193.7	914	18.5	−23.1	−8.8
MMB	PEG	5	236.5	1.8×10^{-4}	251.1	371	−14.6	6.1	20.4
		9	215.6	3.6×10^{-3}	215.2	496	0.4	−636.5	−622.2
		14	215.0	2.7×10^{-2}	164.3	944	50.7	−10.8	3.5
		23	210.1	4.0×10^{-3}	212.3	405	−2.2	72.3	86.6

[a] $\log R_\tau = 14.3 + \log \sigma_{T_g}$.[25]

Table 5. VFT Best Fitting Parameters from Equation 7 for PolyMOBs and PolyMMBs after Chloroform Treatment

cap	spacer	*n* value	T_g (K)	σ_o (S cm^{-1})	T_o (K)	D_σ	$T_g - T_o$ (K)	log σ_{T_g}	log R_τ[a]
MOB	PEG	3	272.3	0.17	214.8	7.1	57.5	−13.4	0.9
		5	253.1	0.09	209.9	5.9	43.2	−14.8	−0.5
		9	228.9	0.05	195.8	5.0	33.1	−15.4	−1.1
		14	219.9	0.02	208.5	3.2	11.4	−28.7	−14.4
		23	210.1	0.01	200.3	3.2	9.8	−32.3	−18.0
	PPG	7	226.2	0.05	197.3	5. 9	28.9	−19.9	−5.6
		13	217.2	0.06	187.0	5.8	30.2	−18.1	−3.8
		17	212.2	0.01	196.6	4.3	15.6	−26.7	−12.4
MMB	PEG	5	236.5	7.4×10^{-6}	254.5	1.3	−18.0	2.9	17.2
		9	215.6	1.4×10^{-4}	218.9	2.0	−3.3	54.3	68.6
		14	215.0	9.6×10^{-4}	169.2	5.0	45.8	−11.1	3.2
		23	210.1	1.5×10^{-5}	219.0	1. 6	−8.9	11.8	26.1

[a] $\log R_\tau = 14.3 + \log \sigma_{T_g}$.[25]

cally, which induces values of σ_{T_g} and R_τ that are also unrealistic. This is because, with longer spacer units, Li ions can become chelated and then are not free to move on the segmental relaxation time scale. Consequently, they behave like paired ions giving rise to a temperature dependence of conductivity, which is not included in the equations. Hence, the equation parameters are distorted and the predictions outside the range of data are unreliable. In the case of polyMMB electrolytes, on the other hand, some values of $T_g - T_o$ are negative, which is quite unphysical. This is a result of the very small range of conductivity data (<1 order of magnitude) being fitted in these cases. No extrapolations can be made in such cases.

Plasticization by salts such as $LiClO_4$ and $LiAlCl_4$, in which Li conductivity dominates, is only one means of increasing the conductivity while maintaining quasi-single-ion conductivity. An alternative means of increasing the conductivity, while maintaining the single-ion character, is plasticization with molecular liquid solvents (since the polyanions cannot move significantly in the resulting gel). The results of each of these types of plasticization will be reported in future articles on these materials.

Finally, it is interesting to make comparisons of the ionic conductivities of some of the newly prepared pure polymers with those of previous highly conducting polymeric systems. This comparison is made in Figure 6, which displays our data along with those for the siloxyaluminate polymer II ($n = 3$) reported by Fujinami et al.[18] and those for the $(PEO)_{10}$−LiTFSI complex reported by Armand et al.[3] The former is, like our systems, dominated by Li^+ conduction, while the latter is primarily anionic. It is seen that the oligoether spaced polyMOBs in this work have lower ambient conductivity than the siloxyaluminate polymer II but have higher

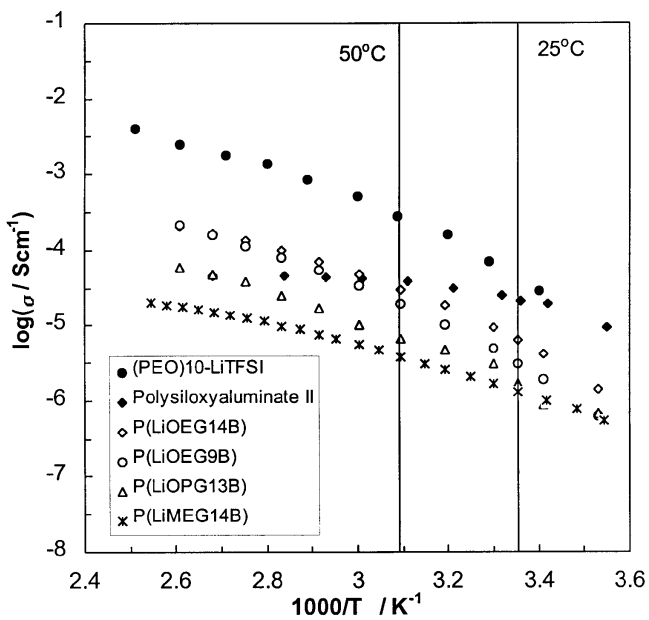


Figure 6. Comparison of temperature dependence of ionic conductivities of two PEG- and one PPG-spaced lithium polyMOB electrolytes (extrapolated LiBOB-free values) and one PEG-spaced polyMMB electrolyte, with (1) that of the siloxyaluminate polymer II ($n = 3$) having very high single-lithium conductivity reported by Fujinami et al.[16] and (2) that of the $(PEO)_{10}$−LiTFSI complex reported by Armand et al.[3] Note that the higher conductivity of the latter case is mostly due to anion contributions.

conductivity when the temperature is above 60 °C. The salt-in-polymer system[3] remains the most highly conducting system of the group due to its dual-ion conduction.

Electrochemical Stability. The electrochemical stability of the mono-capped orthoborate polyanionic

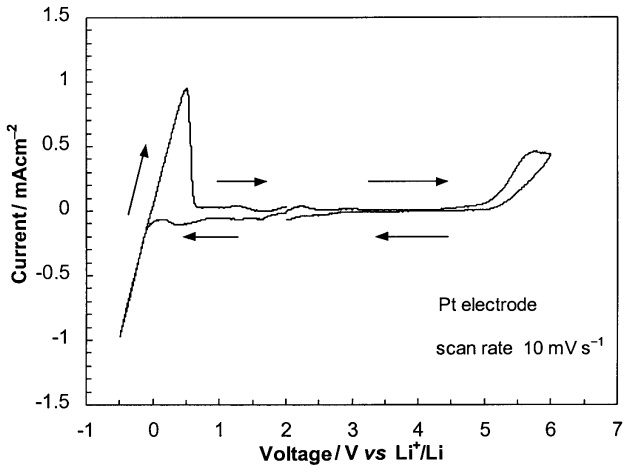


Figure 7. Electrochemical stability of P(LiOEG$_{14}$B) on platinum working electrode at a scan rate of 10 mV s^{-1} at room temperature. Platinum area is 4.91×10^{-4} cm^2. Note that the polymer contains some LiBOB.

electrolytes was studied by cyclic voltammetry, and the result of the first cycle for a typical polymer, P(LiOEG$_{14}$B), is shown in Figure 7. The polyMOBs have good electrochemical stability up to 4.5 V vs Li$^+$/Li. The preliminary scan of cyclic voltammograms also indicates that the coulomb efficiency of the lithium deposition/stripping process is about 75% for the 1st cycle. The low efficiency is caused probably due to the moisture in the polymers and the drybox.

In our recent work[32] on the cell performances of lithium ion batteries containing LiBOB electrolytes, it is found that the salt with the bis(oxalato)borate anion has much better charge−discharge cycling performance than does $LiPF_6$, especially at high temperatures. There is therefore no doubt that the polyMOB and polyMMB electrolytes would show good electrochemical stability as opposed to conventional anode (e.g., graphite) and cathode (e.g., $LiCoO_2$) materials.

Conclusions

The new oligoether spaced mono-oxalato orthoborate and mono-malonato orthoborate polyanionic electrolyte materials that we have described are easily prepared from cheap starting materials and are benign to the environment. Different polymer electrolytes can be prepared by using different types of cap structures and different types and lengths of spacers. The highest ionic conductivity that has been obtained is 10^{-5} S cm^{-1} at 25 °C for the polymer with a mono-oxalato cap structure and a spacer PEG with 14 ethyleneoxy repeating units. These new polymer electrolytes should be very suitable as solid-state electrolyte materials for electrochemical devices requiring single-ion conductivity.

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(32) Xu, K.; Zhang, S.-S.; Jow, R.; Xu, W.; Angell, C. A. *Electrochem. Solid-State Lett.* **2002**, *5* (1).