Novel Alternating Comblike Copolymer Electrolytes with Single Lithium Ionic Conduction

Wu Xu, Kok Siong Siow,* Zhiqiang Gao, and Swee Yong Lee

Department of Chemistry, National University of Singapore, 10 Kent Ridge Crescent, Republic of Singapore 119260

Poly[lithium-*N*-(4-sulfophenyl)maleimide-*co*-methoxyoligo(oxyethylene)methacrylate], P(LiS-MOE$_n$), with three different oligo(oxyethylene) side chains (i.e., three different n values) have been synthesized. The copolymers are of a new type of comblike, nearly alternating copolymer electrolytes, showing single lithium ionic conductivity. All the three copolymers show a glass transition at about −50 °C (T_{g1}). In addition, copolymers with $n = 7$ and 12 also exhibit a second glass transition in the temperature range of 30−50 °C (T_{g2}), while the copolymer with $n = 16$ shows an endothermic peak near room temperature. T_{g1} is assigned to the oligo(oxyethylene) side chain, while T_{g2} is attributed to the main chain of the copolymer domain. The melting point (T_m) is attributed to the endothermic change of the partially crystalline phase formed by the long oligoether side chain. When the temperature is below 50 °C, P(LiSMOE$_n$)s with larger n values have a higher ionic conductivity. When the temperature is above 50 °C, however, P(LiSMOE$_n$)s with smaller n values show higher ionic conductivity because of their higher salt concentration. The maximum ionic conductivity at 30 °C is 1.5×10^{-7} S cm^{-1} for $n = 16$. The temperature dependence of ionic conductivity indicates that the Arrhenius behavior is not obeyed. The ionic conduction follows a special dual Vogel−Tamman−Fulcher (VTF) behavior.

Introduction

Since the discovery by Wright[1] of ionic conduction in polymers containing inorganic salts and the suggestion by Armand[2] in 1978 that polymer ionic conductors could be used as electrolytes in lithium batteries, much effort has been dedicated to exploring solid polymer electrolytes with high ionic conductivity at room temperature.[3,4] Initial work was mostly based on the complexes of poly(ethylene oxide) (PEO) with inorganic lithium salts such as LiClO$_4$ and CF$_3$SO$_3$Li, which are bi-ionic conductors. There are, however, two drawbacks for these complexes. One is the high degree of crystallinity of PEO which restricts these conventional polymer electrolytes to feasible conductivity values for battery applications only at temperatures above the melting points of the crystalline phases, normally 60 °C. The second drawback is the formation of a polarization potential across the electrolyte by the opposite migration of anions and cations in the electrolytes, which offsets the applied voltage and consequently decreases the ionic transportation.

Three different approaches have been tried to improve the ionic conductivity at room temperature. The first approach is to use polymers in modified forms, such as polymer blends, copolymers and cross-linked polymers,[5−7]

in place of PEO to reduce the degree of crystallinity in the inorganic lithium salt complexes which remains as bi-ionic conductors. The second is to use new salts of lithium imide or lithium methide with bulky, conformationally flexible and charge-delocalized anions, such as Li[(CF$_3$SO$_2$)$_2$N][8,9] and Li[(CF$_3$SO$_2$)$_3$C],[10,11] to improve the ionic conductivity of the complexes at all temperatures and slow the crystallization rate. The third approach is to design single cationic conductors with the opposite anions covalently fixed to the macromolecular chains.[12−17]

Compared with bi-ionic conductors, single ionic conductors show excellent polarization characteristics of constant dc conductivity during dc polarization.[14] How-

* Corresponding author. E-mail: chmsks@nus.edu.sg.
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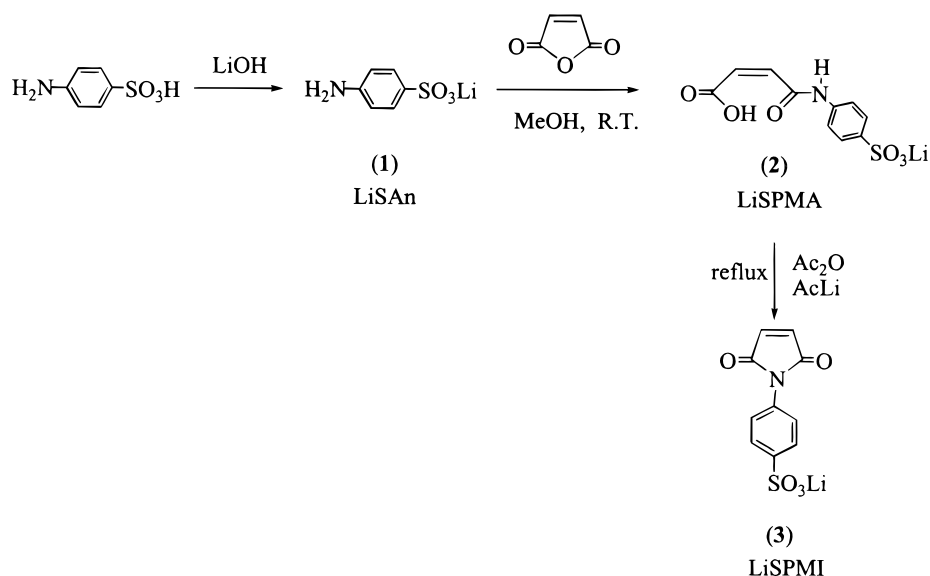(17) Itoh, K.; Tominaga, Y.; Ohno, H. *Electrochim. Acta* **1997**, *10*, 1561.

Scheme 1. Synthesis of Lithium *N*-(4-Sulfophenyl)maleimide (LiSPMI)

ever, single ionic conductors have much lower conductivity under the same conditions, generally in the range of 10^{-8}–10^{-6} S cm^{-1} at 25 °C for alkali metal ions,[12–17] because they have lower ion mobility and fewer ion carriers. It is therefore becoming necessary to improve the ionic conductivity of such single ionic conductors if they are to be used in practice in lithium rechargeable batteries.

We report here the synthesis of a new type of comblike, nearly alternating copolymer electrolyte, poly-[lithium-*N*-(4-sulfophenyl)maleimide-*co*-methoxyoligo-(oxyethylene)methacrylate]. For the sake of convenience, the copolymer electrolyte is abbreviated as P(LiSMOE$_n$), where *n* is the number of oxyethylene (CH$_2$CH$_2$O) repeating units in the side chain, i.e., the length of the oligo(oxyethylene) side chain. Their thermal behavior and the ionic conductivity have been studied and discussed.

Experimental Section

General Methods. IR spectra were taken with a Bio-Rad FT-IR spectrometer. Samples for IR spectroscopy were compressed with KBr into pellets. ^{1}H NMR spectra were obtained from a JEOL FX90Q Fourier transform NMR spectrometer. Elemental analyses were performed by using a Perkin-Elmer elemental analyzer 2400 series II for CHNS/O and a Thermal Jarrell Ash IRIS/AP for Li. The melting points of organic compounds were determined using a Thomas-Hoover 6406-K capillary melting point apparatus.

Materials. Sulfanilic acid and acetic anhydride were obtained from BDH and used as received. Lithium hydroxide, maleic anhydride, glacial acetic acid were obtained from Merck and used without further treatment. Poly(ethylene glycol) monomethyl ethers with average molecular weights of 350, 550, and 750 (i.e., *n* = 7, 12, and 16, respectively) were obtained from Fluka and azeotropically distilled with benzene to remove residual moisture before use. Methacryloyl chloride (from TCI) was redistilled under a nitrogen atmosphere to remove the inhibitor immediately before use. Triethylamine (from J. T. Baker) was purified by refluxing with anhydrous potassium hydroxide followed by distillation under a nitrogen atmosphere. Methanol (J. T. Baker) was dried by refluxing with magnesium powder and then distilled under dry conditions. Benzene (J. T. Baker) was rendered absolutely dry by refluxing with sodium wires and distillation under dry conditions. 2,2′-Azobisisobutyronitrile (AIBN) (TCI) was recrystal-

lized from methanol and dried in a vacuum oven at room temperature.

Polymer Preparation. Lithium *N*-(4-sulfophenyl)maleimide (LiSPMI) was prepared using a modified procedure described by Turner et al.[18] for sodium *N*-(4-sulfophenyl)-maleimide (Scheme 1). Methoxyoligo(oxyethylene)methacrylates (MOE$_n$M), where *n* = 7, 12, and 16, were synthesized following the method of Gramain et al.[19]

Lithium Sulfanilate Monohydrate (LiSAn, 1). To a solution of sulfanilic acid in deionized water was added lithium hydroxide till pH 9, giving a yellow brown solution. Most of the water was evaporated under reduced pressure, and the residual solution with some crystals was poured into a large amount of acetone to complete the precipitation. The solid was collected and recrystallized from water to give cream short needle crystals. After drying in a vacuum oven at 150 °C for 24 h, a white solid was obtained. Yield: 85.1%. Mp: 139.0–140.8 °C. IR (cm^{-1}): 3452 (ν_{N-H}, associated), 3403 ($\nu_{as,N-H}$), 3336 ($\nu_{s,N-H}$), 1908 and 1653 (overtone), 1627 (δ_{N-H}), 1601, 1503 and 1434 ($\nu_{skeletal\ of\ phenyl}$), 1237 ($\nu_{C-N}$), 1180 ($\nu_{as,S=O}$), 1050 ($\nu_{s,S=O}$), 1130 ($\nu_{as,C-S}$), 1010 ($\nu_{s,C-S}$), 843 and 831 (coupled, ω_{C-H}), 782 (ω_{N-H}), 696 ($\omega_{ring\ C=C}$). ^{1}H NMR (in DMSO-d_6) δ (ppm): 7.30–6.40 (m, doublet of doublets, 4H, AA′BB′ system of phenyl group), 5.24 (broad, weak, 2H, NH$_2$), 3.31 (single, 2H, crystallized water). Elemental analysis: calcd for H$_2$NPhSO$_3$Li·H$_2$O: C, 36.55%; H, 4.06%; N, 7.11%; S, 16.24%; Li, 3.55%. Found: C, 36.83%; H, 4.02%; N, 7.06%; S, 15.34%; Li, 3.41%.

***N*-(Lithium-4-sulfophenyl)maleamic Acid (LiSPMA, 2).** To a solution of lithium sulfanilate monohydrate (**1**) (39.4 g; 0.200 mole) in 400 mL of absolute methanol was added a solution of maleic anhydride (30.0 g, 0.306 mol) in 100 mL of absolute methanol. After the mixture was stirred at room temperature for a few minutes, some precipitates were formed from the solution, which turned yellow. The reaction was allowed to continue for half an hour. The solid was then removed by filtration. Most of the solvent in the filtrate was evaporated and the residue was added with an excess of diethyl ether to yield a yellow solid, which was recrystallized from methanol and dried in a vacuum oven at 70 °C for 24 h. Yield: 97.1%. Mp: 159.7–160.8 °C. IR (cm^{-1}): 3462 (broad, mixture of ν_{O-H} and ν_{N-H}), 1717 ($\nu_{C=O}$), 1630 ($\nu_{C=C}$), 1583 and 1496 ($\nu_{skeletal\ of\ phenyl}$), 1552 ($\nu_{as,(O=C=O)-}$), 1396 ($\nu_{s,(O=C=O)-}$), 1422 ($\delta_{C-O-H}$), 1268 ($\nu_{C-O}$), 1230 ($\nu_{C-N}$), 1178 ($\nu_{as,S=O}$), 1049 ($\nu_{s,S=O}$), 1122 ($\nu_{as,C-S}$), 1006 ($\nu_{s,C-S}$), 910 ($\omega_{C-O-H}$), 859 and 839

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(coupled, ω_{C-H}), 717 (ω_{N-H}). ^{1}H NMR (in D$_2$O) δ (ppm): 7.77–7.48 (m, doublet of doublets, 4H, AA′BB′ system of phenyl group), 7.26 (broad, weak, 1H, NH), 6.39 (m, doublet of doublets, 2H, −CH=CH−). Elemental analysis: calcd for C$_{10}$H$_8$NO$_6$SLi: C, 43.32%; H, 2.89%; N, 5.05%; S, 11.55%; Li, 2.52%. Found: C, 42.59%; H, 3.37%; N, 5.05%; S, 10.81%; Li, 2.51%.

Lithium *N*-(4-sulfophenyl)maleimide (LiSPMI, 3). A slurry of 0.1 g of lithium acetate (1.52 mmol) and compound (**2**) (39.2 g, 141 mmol) in 600 mL of acetic anhydride was refluxed overnight, and a color change from yellow to tannish was noted. After being cooled to room temperature, the solid was filtered and washed with acetone twice and then slurried in ethanol−acetone (3:2 in volume), followed by refiltration. The yellow-brown and highly hygroscopic solid, lithium *N*-(4-sulfophenyl)maleimide (LiSPMI, **3**), was dried under high vacuum at 80 °C for 48 h. Yield: 72.4%. Mp: 226.7 °C (decomp). IR (cm^{-1}): 1776 (weak, $\nu_{C=O \text{ of anhydride}}$), 1705 ($\nu_{C=O \text{ of amide}}$), 1659 ($\nu_{C=C}$), 1597, 1505 and 1410 ($\nu_{\text{skeletal of phenyl}}$), 1221 and 1202 (coupled, ν_{C-N}), 1152 ($\nu_{as,S=O}$), 1051 ($\nu_{s,S=O}$), 1129 ($\nu_{as,C-S}$), 1019 ($\nu_{s,C-S}$), 835 and 825 (coupled, ω_{C-H}), 694 ($\omega_{\text{ring }C=C}$). ^{1}H NMR (in D$_2$O) δ (ppm): 8.01–7.47 (m, doublet of doublets, 4H, AA′BB′ system of phenyl group), 7.05 (s, 2H, −CH=CH−). Elemental analysis: calcd for C$_{10}$H$_6$NO$_5$SLi: C, 46.33%; H, 2.32%; N, 5.41%; S, 12.36%; Li, 2.70%. Found: C, 44.95%; H, 3.22%; N, 4.66%; S, 10.31%; Li, 2.63%.

Methoxyoligo(oxyethylene)methacrylate (MOE$_n$M). A mixture of 0.10 mol poly(ethylene glycol) monomethyl ether and 0.12 mol triethylamine in 200 mL of dry benzene was cooled to a temperature below 5 °C in an ice−water bath. Methacryloyl chloride (0.11 mol) was added dropwise into the stirred mixture with the temperature maintained below 5 °C. When the addition was complete, the reaction mixture was stirred at room temperature overnight. The precipitate was filtered off, and the filtrate was washed with warm saturated lithium carbonate solution three times and dried over anhydrous magnesium sulfate overnight in a refrigerator. After the solid was removed, the solvent in the solution was evaporated under reduced pressure at a temperature below 40 °C. The residue was allowed to flow through a silica gel column with chloroform as eluent. When the chloroform was carefully evaporated off under reduced pressure, a pale yellow waxlike product, MOE$_n$M, was obtained. Yield: 76.8%. IR (cm^{-1}): 2873 (ν_{C-H}), 1718 ($\nu_{C=O}$), 1637 ($\nu_{C=C}$), 1455 ($\delta_{as,C-H}$), 1351 ($\delta_{a,C-H}$), 1250 ($\nu_{as,C-O-O}$), 1110 ($\nu_{as,C-O-C}$), 1041 ($\nu_{s,C-O-C}$), 854 and 817 (ω_{C-H}). ^{1}H NMR (in CDCl$_3$) δ (ppm): 6.12−5.55 (m, 2H, CH$_2$=) 4.35−4.25 (m, 2H, −COOCH$_2$−), 3.79−3.50 (m, 26H, −(OCH$_2$CH$_2$)$_6$OCH$_2$−), 3.38 (s, 3H, −OCH$_3$), 1.96 (s, 3H, =C(CH$_3$)−).

Poly[lithium-*N*-(4-sulfophenyl)maleimide-*co*-methoxyoligo(oxyethylene)methacrylate] [P(LiSMOE$_n$)]. LiSPMI and MOE$_n$M were dissolved in dry methanol, and AIBN was added at 0.5 mol % of the total double bonds. After being degassed with nitrogen several times, the solution was stirred in a water bath at about 60 °C under a nitrogen atmosphere for 24 h. When the copolymerization was over, most of the solvent was evaporated on a rotary evaporator under reduced pressure, and the residue was precipitated in a large amount of diethyl ether and washed with diethyl ether several times. The polymers, which were very hygroscopic, were dried in a high-vacuum oven at about 80 °C. Yield: ~40.3%.

Film Preparation. Solutions of the copolymers in methanol were cast on Teflon dishes, and the solvent was allowed to evaporate at room temperature. The films obtained were dried in a high-vacuum oven at 80 °C for at least 72 h and then stored in a drybox filled with purified argon.

Measurements. Differential scanning calorimetry (DSC) measurements were carried out under a nitrogen atmosphere using a DuPont Instrument 2200 thermal analyzer at a heating rate of 20 °C min^{-1}. Polymer samples were hermetically sealed in aluminum pans. The samples were subjected to a heating−cooling−heating cycle in the temperature range from −130 to 140 °C. The glass transition temperature (T_g) was taken as the midpoint of the baseline shift observed during the transition from glassy to rubbery state, and the melting point (T_m) was taken as the peak temperature. The crystallinity (χ_c) was estimated from the ratio of the experimentally determined ΔH_m to the value of 203 J g^{-1} reported for the enthalpy of melting of 100% crystalline PEO.[20]

The average molecular weight of the copolymer was measured by gel permeation chromatography (GPC) using a Waters 600E system controller and a Waters 410 differential refractometer equipped with PL Aquagel-OH columns. The measurements were carried out under a helium atmosphere at 35 °C. The molecular weight was calibrated with several standard PEOs with different molecular weights.

Ionic conductivity measurements were made using an EG&G PAR 273A potentiostat/galvanostat equipped with an EG&G 5210 lock-in amplifier over the frequency range from 100 kHz to 5 Hz from 10 to 80 °C. The cylindrical disk sample was sandwiched between two polished stainless steel electrodes and sealed in a test cell. This process was carried out in a drybox filled with purified argon. To ensure a close contact for the copolymer electrolyte with the electrodes, the test cell was heated to 90 °C for half an hour, followed by natural cooling to the measurement temperature. The sample was kept at the testing temperature for at least 30 min before each measurement was made.

Results and Discussion

Characterization of P(LiSMOE$_n$)s. N-Substituted maleimides are monomers with electron-poor double bonds and rigid, bulky frame structures. They are believed to be impossible to homopolymerize into high molecular weight polymers under usual conditions, such as for maleic anhydride.[21] However, it is possible for them to participate in an alternating copolymerization with electron-rich comonomers to form alternating copolymers. This alternating copolymerization takes place probably as a result of the formation of a precomplex of the comonomer pair or a preference of a terminal radical for a monomer with opposite polarizability.

A qualitative measurement of the electron density of the polymerizable double bond in LiSPMI and MOE$_n$M can be obtained from their *e* values. Since lithium *N*-(4-sulfophenyl)maleimide (LiSPMI) has a structure similar to that for *N*-phenylmaleimide (NPMI), it may be reasonable to assume that LiSPMI has an *e* value near that for NPMI, i.e., 1.69.[22] Similarly, the *e* value for methoxyoligo(oxyethylene)methacrylate (MOE$_n$M) may be assumed to be close to that for MMA (0.40).[23] In the case of copolymerization of MMA and NPMI, Barrales-Rienda et al.[22] reported that since MMA is more reactive than NPMI, the copolymer would be richer in the more reactive monomer, i.e., MMA, in random placement. Therefore, in the present case, when LiSPMI and MOE$_n$M, which is an electron-rich comonomer, are mixed in equal molar ratio and in the presence of free radical initiator, their copolymerization may be expected to proceed in a "nearly alternating" fashion. The copolymers formed would tend to contain more MOE$_n$M than LiSPMI. The schematic structure of the copolymers is shown in Figure 1.

Figure 2 shows that the peak at about 1640 cm^{-1} for carbon−carbon double bonds in the two monomers does
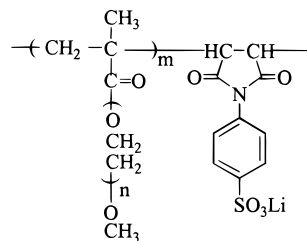
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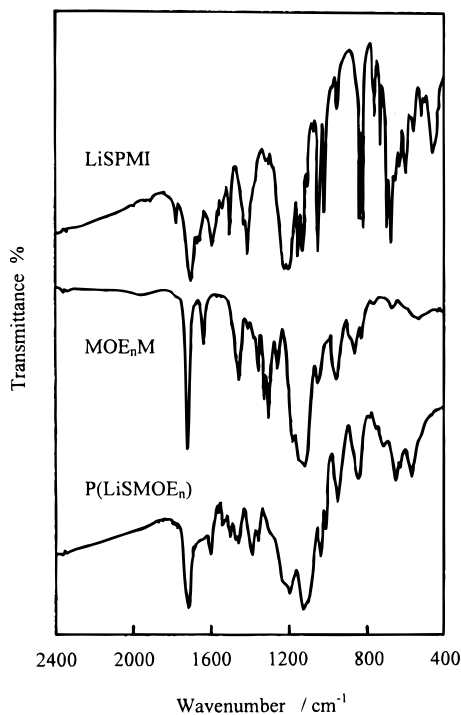
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Where $m \geq 1$; n=7, 12 and 16, respectively.

Figure 1. Schematic diagram of the structure of poly[lithium-*N*-(4-sulfophenyl)maleimide-*co*-methoxyoligo(oxyethylene)-methacrylate] [P(LiSMOE$_n$)].

Figure 2. Infrared spectra of a typical P(LiSMOE$_n$) along with those of LiSPMI and MOE$_n$M.

not appear in the infrared spectrum for the copolymer. In the ^{1}H NMR spectra shown in Figure 3, the signals at δ 7.05 ppm for the protons on the double bond of LiSPMI and δ 6.12−5.55 ppm for CH$_2$= and 1.96 ppm for =C(CH$_3$)− of MOE$_n$M disappear in the spectrum for the copolymer. Instead, new peaks at δ 2.91, 1.14, and 0.96 ppm appear in the spectrum for protons of methine, methylene and methyl, respectively. The integral results suggest that the ratio of the number of protons on the oligo(oxyethylene) unit to that on the phenyl group is slightly larger than that in the alternating copolymer (see Table 1). Elemental analysis results for the copolymers, along with the composition of each copolymer taken as the average value calculated from the measured contents of individual elements and the ^{1}H NMR results, are also listed in Table 1. The values in the parentheses are the expected values for the elemental composition for the perfectly alternating copolymers, while those in the brackets are calculated according to the average composition defined by the ^{1}H NMR results. It is seen that the calculated percentage content of each element, based on the NMR data and shown in brackets,
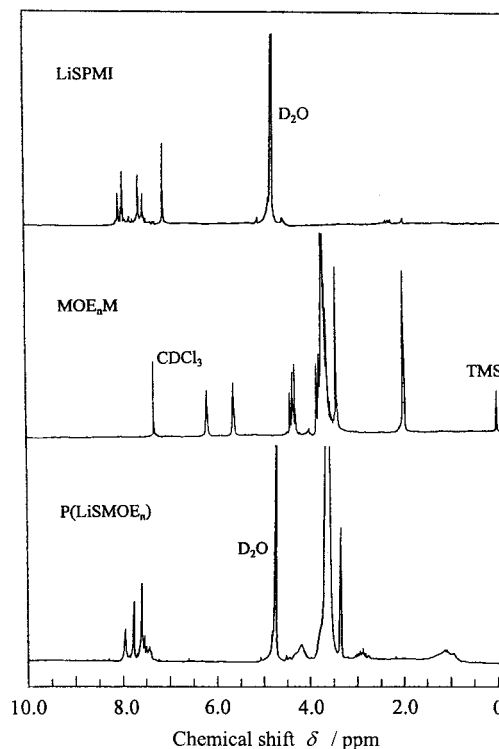
Figure 3. ^{1}H NMR spectra of a typical P(LiSMOE$_n$) as well as those of LiSPMI and MOE$_n$M.

Table 1. Elemental Analyses Results and the Composition of P(LiSMOE$_n$)s[a]

|	elemental analyses (%)					composition/mole	
n	C	H	N	S	Li	LiSPMI	MOE$_n$M
7	50.29	6.09	1.64	3.29	0.94	1	1.19,[b] 1.49[c]
	(52.22)	(6.34)	(2.07)	(4.73)	(1.03)		
	[52.87]	[6.89]	[1.58]	[3.62]	[0.79]		
12	51.64	7.36	1.31	3.17	0.75	1	1.12,[b] 1.44[c]
	(52.62)	(6.95)	(1.60)	(3.65)	(0.80)		
	[53.24]	[7.40]	[1.22]	[2.78]	[0.61]		
16	51.62	7.86	0.88	2.25	0.64	1	1.24,[b] 1.60[c]
	(52.97)	(7.34)	(1.30)	(2.97)	(0.65)		
	[53.63]	[7.84]	[0.89]	[2.04]	[0.45]		

[a] The values in parentheses are the expected elemental composition values for the perfectly alternating copolymers, while those in brackets are calculated on the basis of the average composition defined by the NMR results. [b] The average value calculated from elemental analyses results. [c] The ratio of the number of protons on oligo(oxyethylene) to that on phenylene, obtained from ^{1}H NMR results.

Table 2. Average Molecular Weights of P(LiSMOE$_n$)s

n	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
7	8.50×10^4	2.06×10^4	4.13
12	2.19×10^5	8.36×10^4	2.61
16	3.51×10^5	1.85×10^5	1.89

is very close to the measured result. It is therefore reasonable to accept the composition defined by the NMR results as the true composition of the copolymers since methacrylate monomer (MOE$_n$M) addition to methacrylate chain ends competes with the alternating copolymerization.

The average molecular weights ($\bar{M}_w$ and $\bar{M}_n$) of the copolymers are listed in Table 2. The value of $\bar{M}_w/\bar{M}_n$ for each copolymer is much greater than 1, indicating that these copolymers are polydispersed. The copolymer with the shorter oligo(oxyethylene) side chain (i.e., the smaller n value) shows the higher polydispersity. It is
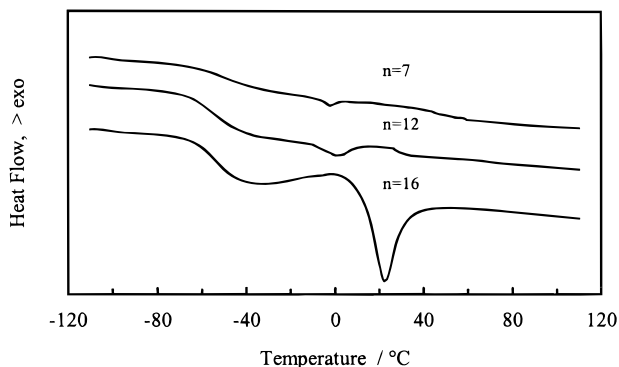
Figure 4. DSC curves of P(LiSMOE$_n$)s with different lengths of oligo(oxyethylene) side chain.

Table 3. DSC Data for P(LiSMOE$_n$)s

n	[EO]/[Li$^+$] molar ratio	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	ΔH_m (J g^{-1})	χ_c
7	10.8	−49.5	47.5	−0.5	0.3	0.1%
12	16.9	−57.0	32.3	0.6	1.6	0.8%
16	26.0	−54.5		22.4	14.6	7.2%

probable that the monomer MOE$_n$M, with a smaller n value, is more reactive and of relatively higher molar concentration, both of which would result in a polymer of broader polydispersity.

From the above analytical results, it appears reasonable that the copolymers are broadly considered as a kind of "nearly alternating" copolymers.

Thermal Behavior of P(LiSMOE$_n$)s. The DSC curves of P(LiSMOE$_n$)s with three different n values are illustrated in Figure 4. These curves reflect the effect of the length of the oligo(oxyethylene) side chain on the morphological structure of the copolymer. For all three n values, the DSC curves show a glass transition near −50 °C and an endothermic peak in the temperature range between −5 and 25 °C, indicating that there is a partially crystalline phase in the copolymers. The formation of the partially crystalline phase is attributed to the long oligo(oxyethylene) side chains.

The DSC data of the three copolymers are summarized in Table 3 along with the crystallinity values (χ_c). With the increase of the length of the oligo-(oxyethylene) side chain (i.e., the n value), the melting point (T_m) increases from −0.5 (for $n = 7$) to 22.4 °C (for $n = 16$), and the crystallinity increases from 0.1% (for $n = 7$) to 7.2% (for $n = 16$). However, T_{g1} shows a minimum at $n = 12$ with increasing n value. This phenomenon is similar to what Zhang et al. have reported[15] for the homopolymer electrolytes of sodium 2-methacryloyl-3-[ω-methoxyoligo(oxyethylene)]propyl-sulfonate [P(NEO$_n$Na)]. It is probably due to the interactions of the coordination of lithium cations with ether oxygen atoms and the dipole−dipole interaction between the side chains. P(LiSMOE$_n$), with a smaller n value, will have a higher salt content, which offers a greater chance for the coordination of lithium cations with ether oxygen atoms, resulting in a higher T_{g1}. On the other hand, the long oligo(oxyethylene) side chain will strengthen the dipole−dipole interactions between the oligoether side chains, which also results in increasing T_{g1}. The counter effects of these two factors give rise to a minimum T_{g1} of −57.0 °C for the copolymers at $n = 12$.

The value of T_{g1} for P(LiSMOE$_n$)s is about −50 °C, which is close to the glass transition temperature of oligo-PEO. Therefore, the phase change below −30 °C can be assigned to the glass transition of the oligo-(oxyethylene) side chain. On the other hand, the copolymers with n values of 7 and 12 show a second glass transition (T_{g2}) in the temperature range of 30−50 °C. This glass transition can be attributed to the main chain of the copolymer domain. Lin et al.[24] reported a similar phenomenon for the comblike poly-mer electrolytes based on a methyl vinyl ether/maleic anhydride alternating copolymer backbone and an oligo-(oxyethylene) side chain. These polymers also showed two glass transitions (α and β transitions) in the temperature range of −100 to 100 °C. The β transition below 0 °C was assigned to the oligo-PEO side chain, while the α transition near room temperature was assigned to the main chain of the comblike polymers.

In the present comblike copolymers, when the n value is small, the high salt concentration would produce a large quantity of lithium cations for coordinating with the oxygen atoms in the oligoether side chains to form many transient cross-linkages in the macromolecules. The transient cross-linkages increase the microscopic viscosity of the copolymer. In addition, the influence of the rigid *N*-(4-sulfophenyl)maleimide on the morphol-ogy of P(LiSMOE$_n$) is much greater than that of the flexible oligo(oxyethylene) side chain. Hence the co-polymer behaves as a stiff solid and has a high T_{g2}. With increasing n values, the salt concentration in the copolymer decreases, resulting in the formation of fewer transient cross-linkages among the lithium cations and the oligoether oxygen atoms. At the same time, the effect of the flexible oligo(oxyethylene) side chain in-creases gradually. As a result, the second glass transi-tion of the copolymer becomes less and less obvious. When $n = 16$, the copolymer shows no glass transition near room temperature in the DSC curve. It may be that this glass transition is overshadowed by the melt-ing process of the oligo(oxyethylene) side chains. At this moment, the effect of the rigid *N*-(4-sulfophenyl)male-imide on the morphology of P(LiSMOE$_n$) is overwhelmed by that of the flexible oligo(oxyethylene) side chain. The copolymer then becomes more flexible. Therefore, one may say that the second glass transition temperature for the nearly alternating copolymer is dependent on the salt concentration or the length of the oligoether side chain.

Single Ionic Conductivity in P(LiSMOE$_n$)s. From the structure of P(LiSMOE$_n$)s, it is seen that the sul-fonate anions, −SO$_3^-$, are covalently bonded to the mac-romolecules. Thus the anions can hardly migrate in the copolymers under a direct current electric field, and only the lithium cations transport. Therefore, P(LiSMOE$_n$)s should exhibit a single cationic conduction. Since the length of the oligo(oxyethylene) side chain influences the salt concentration and the T_g (both T_{g1} and T_{g2}) of the copolymer electrolyte, it will in turn influence the ionic conductivity.

To evaluate the effect of the oligo(oxyethylene) side chain on ionic conductivity, the isothermal conductivi-ties of P(LiSMOE$_n$)s at a number of different temper-

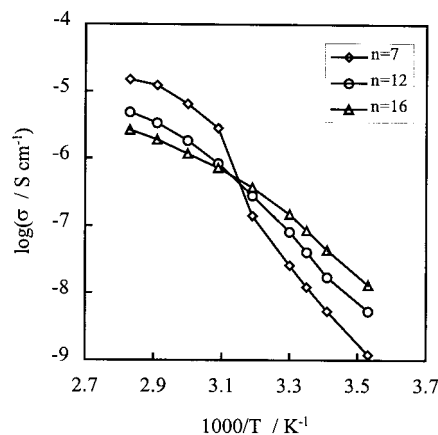(24) Lin, Y.; Qi, L.; Chen, D.; Wang, F. *Solid State Ionics* **1996**, *90*, 307.
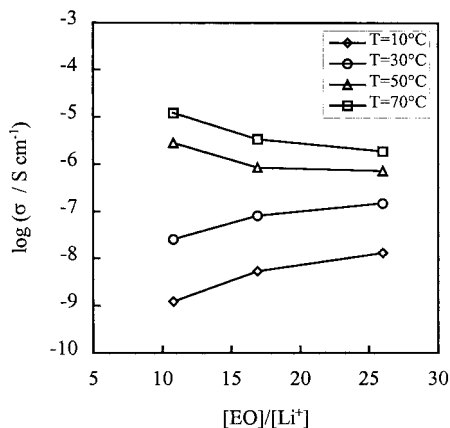
Figure 5. Influence of salt concentration on isothermal ionic conductivity of P(LiSMOE$_n$)s.

atures were determined as a function of salt concentration (Figure 5). P(LiSMOE$_n$)s with smaller n values show poor conductivity at temperatures below 50 °C. This is due mainly to the higher T_{g1} resulting from the higher salt concentrations and the higher T_{g2} arising from the greater effects of the rigid structure of N-(4-sulfophenyl)maleimide which make the movements of polymer main chains more difficult. However, at temperatures above 50 °C, P(LiSMOE$_n$)s with smaller n values show a better conductivity. This phenomenon can be explained as follows: the copolymer electrolyte becomes a completely amorphous material in this high-temperature range. The higher salt concentration would then provide more mobile ions, i.e., charge carriers, so that a higher ionic conductivity can be achieved. The maximum ionic conductivity for these three copolymer electrolytes can be as high as 1.5×10^{-7} S cm^{-1} at 30 °C when $n = 16$, and 2.8×10^{-6} S cm^{-1} at 50 °C when $n = 7$.

Ionic Conductive Behavior in P(LiSMOE$_n$)s. The temperature dependence of the ionic conductivity of P(LiSMOE$_n$)s with different n values is plotted in Figure 6. The curves reveal a non-Arrhenius behavior of ionic conduction in these copolymer electrolytes. A linear relationship in the empirical Vogel−Tamman−Fulcher (VTF) equation is also suggested from the curves at temperatures above the melting point (T_m) or the second glass transition temperature (T_{g2}). This equation is usually used to describe the ionic conduction in elastic materials,[25] namely,

$$\sigma = AT^{-1/2} \exp[-E_a/R(T - T_0)] \qquad (1)$$

where A is a constant, E_a is the apparent activation energy of ionic conduction, and T_0 is the ideal glass transition temperature at which the configurational entropy vanishes. According to the Adam−Gibbs analysis, T_0 is usually taken as 50K below the measured T_g.[26] As mentioned above, there are two glass transition temperatures in the copolymer electrolytes, T_{g1} and T_{g2}. It would be unreasonable to take T_{g2} as the T_g value used in the VTF equation, because in the temperature range below T_{g2} and above T_{g1}, the comblike side chains

(25) (a) Vogel, H. *Phys. Z.* **1921**, *22*, 645. (b) Tammann, G.; Hesse, W. *Z. Anorg. Allg. Chem.* **1926**, *156*, 245. (c) Fulcher, G. S. *J. Am. Ceram. Soc.* **1925**, *8*, 339.
(26) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.

Figure 6. Temperature dependence of ionic conductivity for P(LiSMOE$_n$)s with different n values.
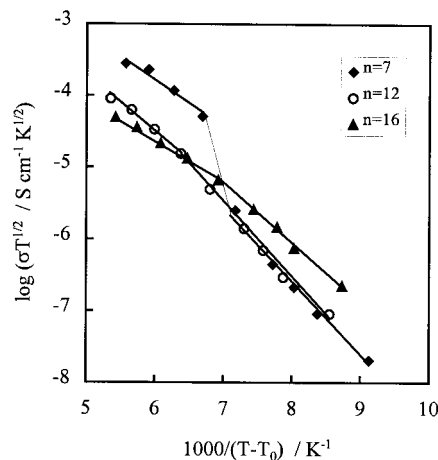
Figure 7. VTF plots of $\log(\sigma T^{1/2})$ vs reciprocal $(T - T_0)$ for P(LiSMOE$_n$)s.

of the host copolymers are still mobile. Therefore, T_{g1} has been adopted to fit the ionic conductivity data in the VTF equation.

The VTF plots of $\log(\sigma T^{1/2})$ vs reciprocal $(T - T_0)$ (Figure 7) for P(LiSMOE$_{12}$) and P(LiSMOE$_{16}$) show two reflected straight lines with regression factors above 0.99, while the plot for the $n = 7$ copolymer gives two unconnected straight lines. The results indicate that the temperature dependence of ionic conductivity for the three comblike copolymer electrolytes obeys the VTF relationship, and moreover, that it is a special dual VTF behavior. This phenomenon of a broken or a reflected VTF line has also been observed in a partially crystalline PEO−LiI system by Armand et al.[27] and in a methyl vinyl ether/maleic anhydride copolymer by Lin et al.[24]

It is found that the VTF intersections or the turning points (regarded as T_t) for P(LiSMOE$_7$) and P(LiSMOE$_{12}$) are around 50 °C, while that for P(LiSMOE$_{16}$) is close to 40 °C. As mentioned above, the second glass transition temperature of the main chain and the endothermic change near room temperature for these copolymers are dependent on the length of the oligoether side chain. Meanwhile, as seen from the DSC curves, the change near room temperature (including the second

(27) Armand, M. B.; Chabagno, J. M.; Dulcot, M. In *Fast Ion Transport in Solids*; Vashisita, P., Munday, J. N., Shenoy, G. K., Eds.; North-Holland: New York, 1979; p 131.

Table 4. VTF Parameters for P(LiSMOE$_n$)s

n	A (S cm^{-1} K$^{1/2}$)	E_a (KJ mol^{-1})	γ^a
7	73.7,[b] 2.0[c]	20.2,[b] 13.0[c]	0.988,[b] 0.965[c]
12	61.2,[b] 1.2[c]	20.2,[b] 14.6[c]	0.993,[b] 0.989[c]
16	3.3,[d] 0.1[e]	15.7,[d] 11.1[e]	0.996,[d] 0.997[e]

[a] γ represents the linear regression factor of the log($\sigma T^{1/2}$) vs $1/(T - T_0)$ relation. [b] $T < T_t$ (50 °C). [c] $T \geq T_t$ (50 °C). [d] $T < T_t$ (40 °C). [e] $T \geq T_t$ (40 °C).

glass transition and the endothermic change) involves a broad temperature range from beginning to end. The higher end of this temperature range for each copolymer is very close to the corresponding VTF turning point. Therefore, the dual VTF behavior should be due to the influence of the second glass transition temperature near room temperature for copolymers with $n = 7$ and 12, and the melting point for $n = 16$. The ionic conduction in these copolymer electrolytes follows the VTF behavior, meaning that the migration of lithium cations depends mainly on the segmental movements of the polymer macromolecules in the amorphous region.

The VTF parameters were obtained from the slope and the intersection of each straight line in Figure 7 and are listed in Table 4. The activation energy (E_a) of ionic conduction for each copolymer electrolyte in the temperature range above the VTF turning point ($T \geq T_t$) is lower than that in the range $T < T_t$. This implies that the effect of temperature on the ionic conduction in the copolymer electrolyte at $T < T_t$ is greater than that at $T \geq T_t$. However, these E_a values for different n value at $T < T_t$ or $T \geq T_t$ do not differ significantly. A similar behavior has also been observed in polyester network electrolytes containing LiClO$_4$.[7] It may be suggested that the length of the oligoether side chain do not have an obvious influence on the energy required to create adequate space for ion migration, although the E_a value shows a tendency to decrease with increasing n value or decreasing salt concentration.

Conclusions

Poly[lithium-*N*-(4-sulfophenyl)maleimide-*co*-methoxyoligo(oxyethylene)methacrylate] [P(LiSMOE$_n$)] copolymers with three different oligoether side chains were synthesized as a new type of comblike, nearly alternating copolymer electrolytes. All three copolymers exhibit single lithium cationic conductivity. The length of the oligo(oxyethylene) side chain (i.e., the n value) affects both the thermal properties, such as the glass transition temperature (T_g) and the melting point (T_m), and the salt concentration ([EO]/[Li$^+$]) of the copolymer electrolytes, which consequently influences the ionic conductivity.

All three copolymers show a glass transition at about -50 °C for the oligo(oxyethylene) side chain (T_{g1}). The copolymer with the smaller n value also exhibits a second glass transition in the temperature range of 30–50 °C, which is attributed to the main chain of the copolymer, while the copolymer with the larger n value shows an endothermic peak near room temperature which is a result of the formation of partial crystals by the long oligoether side chain. When the temperature is below 50 °C, P(LiSMOE$_n$) with a larger n value has a higher ionic conductivity. When the temperature is above 50 °C, however, P(LiSMOE$_n$) with a smaller n value shows a higher ionic conductivity because of its higher salt concentration. The maximum ionic conductivity at 30 °C is 1.5×10^{-7} S cm^{-1} for $n = 16$. The temperature dependence of ionic conductivity indicates that the Arrhenius behavior is not obeyed. The ionic conduction follows a special dual VTF behavior.

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