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THERMAL BEHAVIOR AND IONIC CONDUCTIVITY OF POLY[LITHIUM-N(4-SULFO-PHENYL) MALEIMIDE -CO-METHOXY OLIGO(OXYETHYLENE) METHACRYLATE]

Wu Xu^a; Kok Siong Siow^a; Zhiqiang Gao^a; Swee Yong Lee^a

^a Department of Chemistry, National University of Singapore, Republic of Singapore

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THERMAL BEHAVIOR AND IONIC CONDUCTIVITY OF POLY[LITHIUM-*N*(4-SULFOPHENYL) MALEIMIDE -CO- METHOXY OLIGO(OXYETHYLENE) METHACRYLATE]

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

Key Words: Polyelectrolyte, Ionic Conductivity, *N*-Substituted Maleimide Copolymer

ABSTRACT

Poly[lithium-*N*(4-sulfophenyl) maleimide -co- methoxy oligo(oxyethylene) methacrylates] [P(LiSMOE_n)s] with three different oligoether side chains and different salt concentrations were synthesized. The copolyelectrolytes are essentially random in structure, with blocks of methoxy oligo(oxyethylene) methacrylate (MOE_nM) recurring sporadically in between the salt units of *N*(4-sulfophenyl) maleimide. They all show two glass transitions in the temperature range of –100 to 100°C. The first one below –30°C is assigned to the oligo(oxyethylene) side chain (T_{g1}), while the second one located between 20 and 50°C is attributed to the main chain of the polymer host (T_{g2}). The maximum ionic conductivity of the copolymer electrolytes, $1.6 \times 10^{-7} \text{ S cm}^{-1}$ at 25°C, occurs at lithium salt concentration $[\text{Li}^+]/[\text{EO}] = 2.2 \text{ mol}\%$. The ionic conductive behavior of the copolyelectrolytes follows the Vogel-Tammann-Fulcher (VTF) equation. Moreover, a spe-

* Author to whom correspondence should be addressed.

cial VTF behavior exists in the copolymers with shorter oligoether side chain and higher salt concentration. Sweep voltammetric results indicate that these copolyelectrolytes have a good electrochemical stability window.

INTRODUCTION

The last two decades have seen extensive research on polymer solid electrolytes, due to both its high theoretical significance and the promising application prospects of the materials [1]. Polymer lithium ionic conductors such as the complexes formed by poly(ethylene oxide) (PEO) or other polymer matrixes and lithium salts can be considered as bi-ionic conductors. They have ionic conductivity at ambient temperature as high as 10^{-6} S cm^{-1} . However, because of their high degree of crystallinity and poor direct current conducting stability, the applications of these polymer complexes in electrochemical devices have been limited. To overcome such drawback, single ionic conducting polymer electrolytes have been proposed [2–10] in which anions are covalently bonded to the polymer chains, and only cations can migrate in the electrolytes and contribute to the ionic conduction. Solid polymer electrolytes with single ionic conductivity have received much attention with the view of using them as electrolytic materials in solid state electrochemical devices, due to their good direct current conductivity and the unity of cationic transference number. However, the ionic conductivity of single ionic conductors is generally lower by one to two orders of magnitude than that of bi-ionic conductors, due to the lower ionic mobility and the lesser number of ionic carriers in the electrolytes. Therefore, it is important to improve the ionic conductivity of single ionic conductors for them to be of practically useful applications in lithium rechargeable batteries.

In our previous paper [11], a novel type of nearly alternating comb-like polymer electrolytes with single lithium ionic conduction, poly[lithium-*N*(4-sulfophenyl) maleimide -alt- methoxy oligo(oxyethylene) methacrylates], was reported. In this paper, a random type of copolymers of lithium-*N*(4-sulfo-phenyl) maleimide and methoxy oligo(oxyethylene) methacrylate has been synthesized. The thermal behavior, and the correlation between the structure and ionic conductivity of the copolyelectrolytes have been discussed.

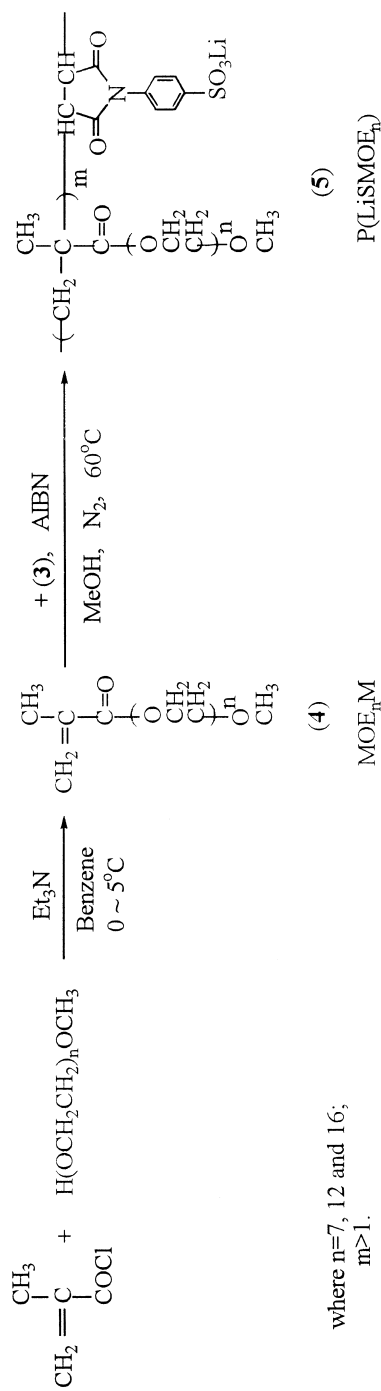
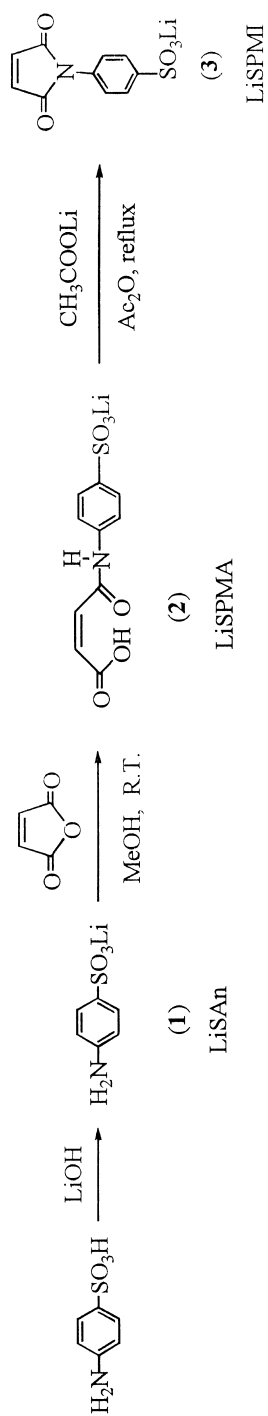
EXPERIMENTAL

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, respectively, (*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 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 nitrogen atmosphere. The synthesis routes of monomers, lithium-*N*-(4-sulfophenyl) maleimide (LiSPMI) and methoxy oligo(oxyethylene) methacrylate (MOE_nM) where $n=7$, 12 and 16, and copolyelectrolytes, poly[lithium-*N*(4-sulfophenyl) maleimide -co- methoxy oligo(oxyethylene) methacrylates] [P(LiSMOE_n)s], were shown in Scheme 1. All the experimental procedures have been described in detail previously [11], and an outline is given here.

Lithium sulfanilate monohydrate (LiSAn, **1**) was prepared by adding lithium hydroxide to a solution of sulfanilic acid in deionized water till pH = 9. Most of the water in the obtained yellow brown solution 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 hours, a white solid was obtained. Yield was 85.1%, m.p. 139.0~140.8°C. IR (cm⁻¹): 3452(ν_{N-H} , associated), 3403($\nu_{as,N-H}$), 3336($\nu_{s,N-H}$), 1627(δ_{N-H}), 1601, 1503 and 1434($\nu_{skeletal}$ of phenyl), 1237(ν_{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($\omega_{ring C=C}$). ¹H-NMR (in DMSO-d₆) δ (ppm): 7.30~6.40, m (doublet of doublets), 4H, AA'BB' system of phenyl group; 5.24, broad, weak, 2H, NH₂; 3.31, single, 2H, crystallized water. Elemental analysis: Calcd. for H₂NPhSO₃Li·H₂O: 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**) was synthesized by stirring the mixed solution of lithium sulfanilate monohydrate (**1**) (39.4g; 0.200 mol) and maleic anhydride (30.0g; 0.306 mol) in 500 ml absolute



where $n=7, 12$ and 16 ;
 $m \geq 1$.

Scheme 1. Synthesis route of poly[lithium-*N*-(4-sulphonyl) maleimide-co-methoxy oligo(oxyethylene) methacrylates] [P(LiSMOE_n)_s].

methanol at room temperature for half an hour. After the precipitates formed were removed by filtration from the solution, most of the solvent in the yellow 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 hours. Yield was 97.1%, m.p. 159.7~160.8°C. IR (cm⁻¹): 3462 (broad, mixture of $\nu_{\text{O-H}}$ and $\nu_{\text{N-H}}$), 1717($\nu_{\text{C=O}}$), 1630($\nu_{\text{C=C}}$), 1583 and 1496($\nu_{\text{skeletal of phenyl}}$), 1552($\nu_{\text{as,(O=C=O)-}}$), 1396($\nu_{\text{s,(O=C=O)-}}$), 1422($\delta_{\text{C-O-H}}$), 1268($\nu_{\text{C-O}}$), 1230($\nu_{\text{C-N}}$), 1178($\nu_{\text{as,S=O}}$), 1049($\nu_{\text{s,S=O}}$), 1122($\nu_{\text{as,C-S}}$), 1006($\nu_{\text{s,C-S}}$), 910($\omega_{\text{C-O-H}}$), 859 and 839(coupled, $\omega_{\text{C-H}}$), 717($\omega_{\text{N-H}}$). ¹H-NMR (in D₂O) 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 C₁₀H₈NO₆SLi: 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**) was prepared by reluxing a slurry of 0.1g lithium acetate (1.52 mmol) and compound (**2**) 39.2g (141 mmol) in 600 ml acetic anhydride overnight till a color change from yellow to tannish was noted. After being cooled to room temperature, the solid was filtered and washed with acetone twice, then slurried in ethanol-acetone (3:2 in volume), and followed by refiltration. The yellow-brown and highly hygroscopic solid, lithium-N(4-sulfophenyl) maleimide (LiSPMI, Compound **3**), was dried under high vacuum at 80°C for 48 hours. Yield was 72.4%, m.p. 226.7°C (decompose). IR (cm⁻¹): 1776 (weak, $\nu_{\text{C=O}}$ of anhydride), 1705($\nu_{\text{C=O}}$ of amide), 1659($\nu_{\text{C=C}}$), 1597, 1505 and 1410($\nu_{\text{skeletal of phenyl}}$), 1221 and 1202(coupled, $\nu_{\text{C-N}}$), 1152($\nu_{\text{as,S=O}}$), 1051($\nu_{\text{s,S=O}}$), 1129($\nu_{\text{as,C-S}}$), 1019($\nu_{\text{s,C-S}}$), 835 and 825(coupled, $\omega_{\text{C-H}}$), 694($\omega_{\text{ring C=C}}$). ¹H-NMR (in D₂O) 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 C₁₀H₆NO₅SLi: 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%.

Methoxy oligo(oxyethylene) methacrylate (MOE_nM, **4**) was prepared by dropwise adding 0.11 mole methacryloyl chloride into a mixture of 0.10 mole poly(ethylene glycol) monomethyl ether and 0.12 mole triethylamine in 200 ml dry benzene 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 for three times, dried over anhydrous magnesium sulphate 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 wax-like product, MOE_nM , was obtained. The yield was 76.8%. IR (cm^{-1}): 2873($\nu_{\text{C-H}}$), 1718($\nu_{\text{C=O}}$), 1637($\nu_{\text{C=C}}$), 1455($\delta_{\text{as,C-H}}$), 1351($\delta_{\text{a,C-H}}$), 1250($\nu_{\text{as,C-O-O}}$), 1110($\nu_{\text{as,C-O-C}}$), 1041($\nu_{\text{s,C-O-C}}$), 854 and 817($\omega_{\text{C-H}}$). $^1\text{H-NMR}$ (in CDCl_3) δ (ppm): 6.12 ~ 5.55, m, 2H, $\text{CH}_2=$; 4.35 ~ 4.25, m, 2H, $-\text{COOCH}_2-$; 3.79~3.50, m, 26H, $-(\text{OCH}_2\text{CH}_2)_6\text{OCH}_2-$; 3.38, s, 3H, $-\text{OCH}_3$; 1.96, s, 3H, $=\text{C}(\text{CH}_3)-$.

Copolymerization of LiSPMI (**3**) and MOE_nM (**4**) in different molar ratios was carried out in methanol under nitrogen atmosphere at 60°C for 24 hours. AIBN was added as an initiator at 0.5 mol% of the total amount of monomers. The solvent was then evaporated and the residue was further thermally copolymerized for 1 day at 100°C until no peak at about 1640 cm^{-1} was observed in the infrared spectra. The final products were dried under high vacuum at 80°C for at least 2 days to thoroughly remove the residual moisture, which yields the copolyelectrolytes, poly[lithium-*N*(4-sulfophenyl) maleimide -co-methoxy oligo(oxyethylene) methacrylates] [$\text{P}(\text{LiSMOE}_n)_s$, **5**]. A typical IR spectrum of $\text{P}(\text{LiSMOE}_{16})$ with the feed molar ratio of LiSPMI to MOE_{16}M of 0.4:0.6 is shown in Figure 1. The characteristic peaks are located at 1716 cm^{-1}

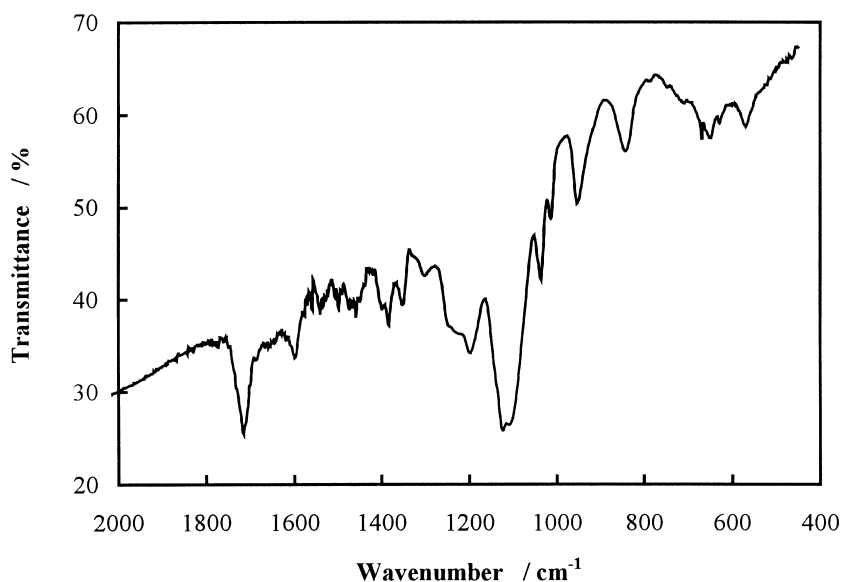


Figure 1. Infrared spectrum of a typical copolyelectrolyte, $\text{P}(\text{LiSMOE}_{16})$ with feed molar ratio of LiSPMI to MOE_{16}M of 0.4:0.6.

for $\nu_{\text{C=O}}$, 1598, 1540 and 1498 cm^{-1} for $\nu_{\text{skeletal of phenyl}}$, 1220 cm^{-1} (shoulder) for $\nu_{\text{as, C-N}}$, 1198 cm^{-1} for $\nu_{\text{S=O}}$, 1123 cm^{-1} for $\nu_{\text{as, C-S}}$ and 1110 cm^{-1} for $\nu_{\text{as, C-O-C}}$.

Measurements

IR spectra were taken with a BIO-RAD FT-IR Spectrometer. Samples for IR spectroscopy were compressed with KBr into pellets. ¹H-NMR spectra were obtained from a JEOL FX90Q Fourier transform NMR Spectrometer. Elemental analyses were performed using Perkin Elmer Elemental Analyzer 2400 Series II for CHNS/O and using Thermal Jarrell Ash IRIS/AP for Li. The melting points of organic compounds were determined using a 6406-K Thomas-Hoover Capillary Melting Point Apparatus.

Thermal Behavior Measurements

Differential scanning calorimetry (DSC) measurements were carried out under nitrogen atmosphere using a DuPont Instrument 2200 Thermal Analyzer at a heating rate of 10°C min⁻¹ in the temperature range from -130 to 150°C. The polymer samples were hermetically sealed in aluminum pans. The glass transition temperature (T_g) was taken as the midpoint temperature of the baseline shift from the second scans, and the melting point (T_m) as the peak temperature. The crystallinity (χ_c) was obtained from the ratio of the experimentally determined ΔH_m to the value of 203 J g⁻¹ which was reported for the enthalpy of melting of 100% crystalline PEO [12].

Conductivity Measurements

Ionic conductivity was obtained from impedance spectra using an EG&G 5210 Lock-In Amplifier coupled to an EG&G PAR 273A potentio-stat/galvano-stat over the frequency range of 100 kHz to 5 Hz, from 10 to 80°C. The cylindrical disk samples were sandwiched between two polished stainless steel electrodes and sealed in a test cell. To ensure a close contact between the samples and the electrodes, the test cell was heated to 90°C and allowed to cool naturally to the measured temperature. The sample was kept at the testing temperature for 30 minutes before each measurement was made.

Voltammetry Measurements

The electrochemical stability window of the composite polymeric electrolytes was determined by voltammetry in a three-electrode cell with a stainless steel (SS) plate as the working electrode, a lithium disk as the counter electrode and a lithium strip placed between two adjacent layers of copolyelectrolyte films

as the reference electrode, with a scan rate of 10 mV s^{-1} and under room temperature. The decomposition voltage was assumed to be that at which a sharp anodic current from the baseline (*i.e.*, $> 20 \mu\text{A cm}^{-2}$) began to flow through the cell. This measurement was driven by an EG&G PAR 273A potentiostat/galvanostat coupled with a PC computer. All cells used in this experiment were assembled in an AVC dry box filled with purified argon.

RESULTS AND DISCUSSION

Polymer Structure

N-Substituted maleimides are monomers with electron-deficient double bonds and rigid bulky frame structures. They are known to be unable to homopolymerize to high molecular weight under usual conditions, like maleic anhydride [13, 14]. However, when they are mixed with electron-rich comonomers, such as vinyl ethers or styrene, they are able to participate in alternating copolymerization processes [15]. This alternating copolymerization takes place as a result of the existence of a pre-complex of the comonomer pair or the preference of a terminal radical for a monomer with opposite polarizability. Although the acrylate and methacrylate moieties are considered in most cases as electron deficient, they are much weaker electron attractors than the *N*-substituted maleimides. A qualitative measurement of the electron density of the polymerizable double bond in LiSPMI and MOE_nM can be obtained from their e (the polarity of the comonomer and its radical) values. Since LiSPMI has a structure similar to *N*-phenyl maleimide (NPMI), it may be reasonable to assume that LiSPMI has an e value close to that for NPMI, *i.e.*, 1.69 [15]. Similarly, the e value for MOE_nM may be assumed to be near that for MMA (0.40) [16]. The difference in electron deficiency between LiSPMI and MOE_nM is sufficient to induce the formation of charge transfer complexes between the two kinds of monomers, a necessary step prior to alternating copolymerization.

On the other hand, as stated by Turner *et al.* [17] and Xu *et al.* [18], the copolymerization conversion is strongly composition-dependent. If the *N*-substituted maleimide is the dominant component, its inert double bond will make it difficult for the excess maleimide monomers to participate in the polymerization. Most of them will remain intact through the reaction and the conversion yield will be low. However, when MOE_nM is overwhelming in molar fraction, polymerization will occur not only between the two kinds of monomers, but also

among the excess MOE_nM monomers themselves. The yield in this case can be above 80%. In the present work, therefore, when LiSPMI was mixed with MOE_nM in the presence of free radical initiators, they copolymerize alternatively. Since MOE_nM is more reactive than *N*-substituted maleimide [11], the copolymers will tend to contain more MOE_nM in a random placement. At the same time, due to the excess portion of MOE_nM, this procedure may result in highly inhomogeneous materials. The resultant copolymers are likely to have a random structure with blocks of MOE_nM recurring sporadically in between the salt units of *N*(4-sulfophenyl) maleimide.

The subsequent thermal polymerization ensures that the unreacted monomers, chiefly MOE_nM, would completely polymerize. In the meantime, the thermal polymerization at high temperatures will cause the gelation of macromolecules. As a result, the copolymers formed will have a wide distribution of molecular weight. In the case of gelation, the average molecular weights of these copolyelectrolytes cannot be measured by gel permeation chromatography (GPC).

Due to the symmetric character of the oligo(oxyethylene) units, poly[methoxy oligo(oxyethylene) methacrylate]s in the MOE_nM-rich microscopic regions of the copolyelectrolytes will exhibit a highly crystalline morphology, especially when the oligo(oxyethylene) side chain (*n* value) is long enough. However, in the region where lithium-*N*(4-sulfophenyl) maleimide occurs, the local uniformity due to the symmetry character of the oligo(oxyethylene) side chains is destroyed by the co-ordination of lithium cations to oligoether oxygen atoms. This coordination leads to the formation of transient cross-linking among the macromolecules. As a result, the ordered arrangements of the polymer segments are replaced by a random aggregation. Therefore, the crystallinity of the crystalline phase will be reduced. This situation is demonstrated by the DSC results of the copolyelectrolytes shown in Figure 2 which will be discussed below.

Thermal Behavior

Figure 2 shows that all the copolyelectrolytes, except for P(LiSMOE₁₆) with the feeding molar ratio of [LiSPMI]/[MOE_nM] = 0.4:0.6, have two glass transitions in the studied temperature range. One of them is located at temperatures below -30°C (T_{g1}), and another in the temperature range of 20 to 50°C (T_{g2}). Lin *et al.* [19] have reported a similar behavior about the comb-like polymer electrolytes based on methyl vinyl ether/maleic anhydride alternating

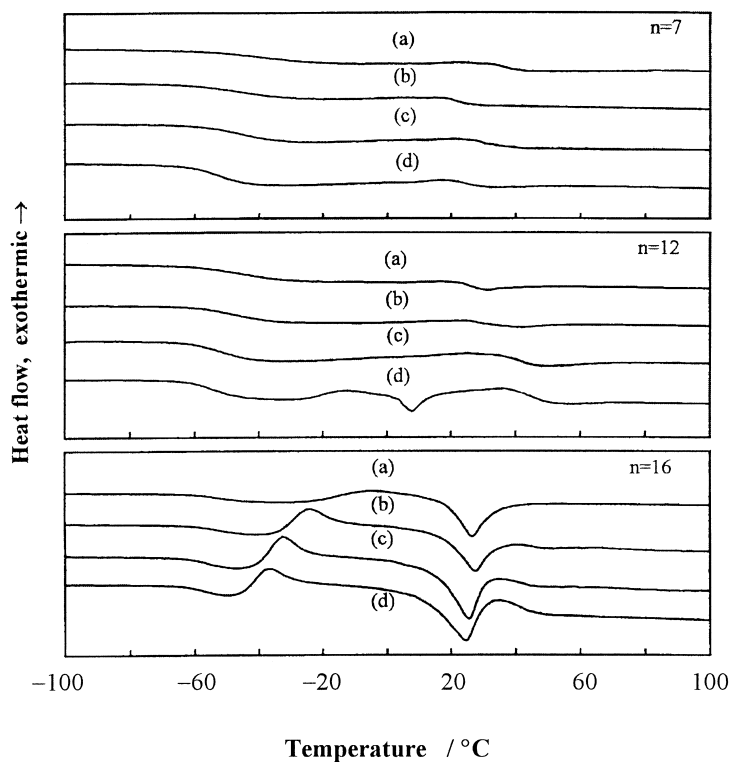


Figure 2. DSC curves of P(LiSMOEn)s with different n value and salt concentration ($[\text{Li}^+]/[\text{EO}]$). Feeding molar ratio of $[\text{LiSPMI}]/[\text{MOEnM}]$: (a) 0.4:0.6, (b) 0.3:0.7, (c) 0.2:0.8 and (d) 0.1:0.9.

copolymer backbone and oligo(oxyethylene) side chain, which showed two glass transitions (α - and β -transitions) in the temperature range of -100 to 100°C . They examined the dynamic mechanical properties (the variation of moduli with temperature) of the copolymers by means of viscoelastic spectrometry and found that the β -transition below 0°C was assigned to the oligo-PEO side chain while the α -transition near room temperatures was assigned to the main chain of the comb-like copolymers. In the case of our present copolyelectrolytes, therefore, the transition at lower temperatures (below -30°C) can be assigned to the glass transition of oligo(oxyethylene) side chains. The transition in the temperature range of 20 to 50°C can be attributed to the glass transition of the main chain of the copolyelectrolyte domain, which is associated with the rigid $N(4\text{-sulphophenyl})$ maleimide groups.

For all P(LiSMOE₁₆)s with feeding molar ratios of LiSPMI to MOE_nM ([LiSPMI]/[MOE_nM]) ranging from 0.1:0.9 to 0.4:0.6, there is an endothermic peak at about 25°C; and for P(LiSMOE₁₂) with [LiSPMI]/[MOE_nM] of 0.1:0.9 the endothermic peak is near 10°C. This endothermic peak can be assigned to the melting of crystals formed by blocks of excess long oligo(oxyethylene) side chains. Interestingly, this melting (endothermic) peak is nearly always accompanied by an exothermic peak at a lower temperature, which may be ascribed to the cooling crystallization of the oligo(oxyethylene) side chains. This phenomenon has also been observed by Zhang *et al.* [8] for the homopolymer-based electrolytes.

It is seen from Figure 2 that for the same feeding molar ratio, the first glass transition temperature (T_{g1}) decreases gradually with increasing n value. On the other hand, for polymers with the same n value, T_{g1} decreases with the increase of feeding molar ratio of LiSPMI to MOE_nM, *i.e.*, the increase of salt content. It is also seen from Figure 2 that the second glass transition for P(LiSMOE₁₆)s becomes less and less obvious with increasing feeding molar ratio of LiSPMI to MOE_nM. When [LiSPMI]/[MOE_nM] reaches 0.4:0.6, the second glass transition disappears, similar to what was observed in the case of the nearly alternating copolyelectrolyte reported in our previous work [11]. It is probably that this glass transition process is overshadowed by the melting process of the oligo(oxyethylene) side chains.

For the partially crystalline copolyelectrolytes P(LiSMOE₁₆)s, the melting point (T_m) and the cooling crystallization temperature (T_c) decrease with decreasing salt concentration. The crystallinity (χ_c), however, increases with decreasing salt concentration, from $\chi_c = 17.5\%$ for [Li⁺]/[EO] = 4.1 mol% to $\chi_c = 20.1\%$ for [Li⁺]/[EO] = 0.68 mol%. It seems that P(LiSMOE₁₆)s with more MOE₁₆M content, or lower salt content, can form more crystals of MOE₁₆M.

Under the present experimental conditions, the composition of the copolyelectrolytes P(LiSMOE_n)s can be taken as the feeding molar ratio of LiSPMI to MOE_nM. Therefore, the salt concentration ([Li⁺]/[EO]) in each copolyelectrolyte can be calculated according to the feeding molar ratio and the length of the oligo(oxyethylene) side chain. The influence of salt concentration on the two glass transitions temperatures (T_{g1} and T_{g2}) of all the copolyelectrolytes is shown in Figure 3. T_{g1} increases with increasing salt concentration. It is probably because that the increase of salt concentration results in the increase of the co-ordination of lithium cations to oligoether oxygen atoms, leading to the formation of transient crosslinking among the macromolecules and an increase in the microscopic viscosity of the polymer domain. As a result, the segmental

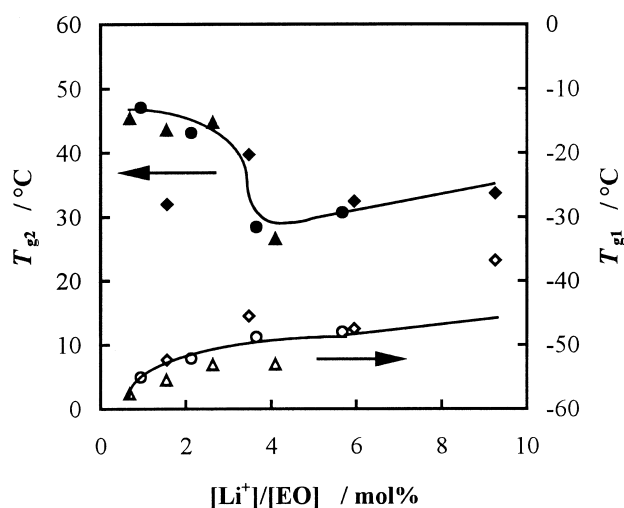


Figure 3. The influence of salt concentration on the two glass transitions temperatures for P(LiSMOEn)s. $\triangle, \blacktriangle$ $n=7$; \circ, \bullet $n=12$ and \diamond, \blacklozenge $n=16$.

movements of the flexible oligo(oxyethylene) side chains in the macromolecules are retarded and T_{g1} increased.

However, the variation of the second glass transition temperature (T_{g2}) with salt concentration differs considerably from that of T_{g1} (Figure 3). It decreases initially with increasing lithium salt concentration, then increases slightly after a minimum value appears at $[\text{Li}^+]/[\text{EO}]$ of about 4.0 mol%. This phenomenon is similar to the observations in the complexes of poly[methoxy oligo(oxyethylene) methacrylate-co-acrylonitrile] and LiClO_4 by Xu *et al* [20], homopolyelectrolytes poly{sodium 2-methacryloyl 3- $[\omega$ -methoxy oligo(oxyethylene) propylsulfonates} by Zhang *et al*. [8] and the complexes by Lin *et al* [19]. It can be explained as follows: P(LiSMOEn)s with higher salt concentration contain more salt species which supply more chance for the co-ordination of cations with oligoether oxygen atoms, leading to a higher T_{g1} and in turn increasing T_{g2} . However, this coordination of cations with oligoether side chains should not have apparent effect on the main chain of the polymer host. Thus, the glass transition of the main chain (T_{g2}) just increases a little with the increase of the salt concentration. On the other hand, P(LiSMOEn)s with lower salt concentration mean that they have a higher content of oligoether and higher content of methacrylate moiety. Due to the rigid structure of the methacrylate chain, the glass transition describing the main chain of the copolyelectrolytes (T_{g2}) will increase with increasing the content of the methacrylate group. These two oppo-

site factors lead to a minimum of T_{g2} (at about 28°C) appearing at the salt concentration $[\text{Li}^+]/[\text{EO}]$ of about 4.0 mol%.

Effect of Salt Concentration on Ionic Conductivity

Ionic conductivity is influenced by the mobility and number of ionic carriers. However, both the mobility and the number of ionic carriers vary with the salt species, salt concentration, temperature and polymer structure. The salt content has a significant effect on polymer morphology, as described above, and influences consequently the ionic conduction of the polymer electrolytes.

Figure 4 shows the effect of salt concentration on the isothermal conductivity of P(LiSMOE_n)s. It is seen that P(LiSMOE_n)s with similar salt concentration have nearly the same ionic conductivity, even though the length of oligo(oxyethylene) side chains is different. With increasing salt concentration, the ionic conductivity at temperatures below 50°C shows a maximum at the salt concentration $[\text{Li}^+]/[\text{EO}]$ of about 2.2 mol%. The highest ionic conductivity at 25°C is $1.6 \times 10^{-7} \text{ S cm}^{-1}$ at $[\text{Li}^+]/[\text{EO}] = 2.2 \text{ mol}\%$. The variation of ionic conductivity with salt concentration can be explained as follows. At very low salt concentration ($[\text{Li}^+]/[\text{EO}]$ lower than 2.2 mol%), the number of free ion carriers increases with the increase of salt concentration, while T_{g1} changes only slightly. The ionic conductivity of the copolyelectrolyte thus increases. In the next salt concentration range ($[\text{Li}^+]/[\text{EO}]$ greater than 2.2 mol%), higher salt concentration leads to the formation of more transient cross-linkage between macromolecules by the coordination of lithium cations to oligoether oxygen atoms, which results in the increase of microscopic viscosity. Consequently, T_{g1} of the copolyelectrolyte increases sharply. It means that the ion transport by the segmental movement of macromolecules in the polymers becomes difficult, and the ionic conductivity decreases. On the other hand, since the salt concentration of the copolyelectrolytes in the present work is located in the low salt content region ($[\text{Li}^+]/[\text{EO}] < 10 \text{ mol}\%$), the increase of free ion carriers with salt concentration is not sufficient, meaning that the ionic conductivity increases slightly. The counter effects of these two opposite factors results in the decrease of ionic conductivity.

At temperatures above 50°C, the ionic conductivity of P(LiSMOE_n)s increases monotonously with the increase of salt concentration even in the higher salt content range of $[\text{Li}^+]/[\text{EO}]$ greater than 2.2 mol%. This is because the copolyelectrolytes have now become completely amorphous at temperatures higher than the second glass transition temperature (T_{g2}) due to the main chain of the copolyelectrolytes. The segmental motion of polymer macromolecules then

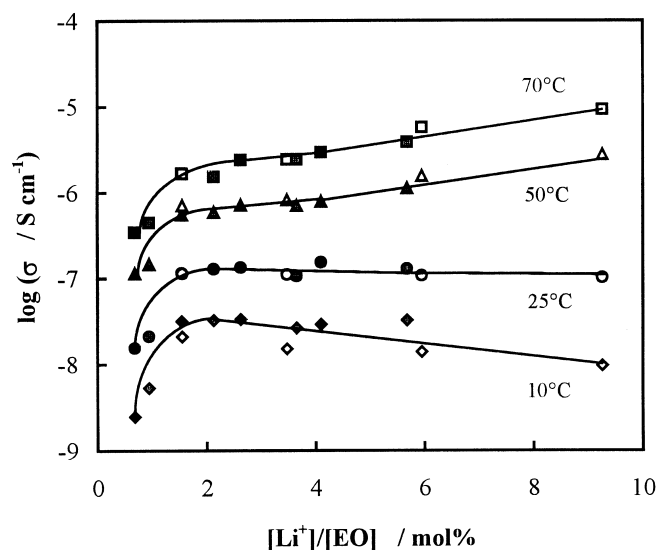


Figure 4. The dependence of isothermal ionic conductivity on salt concentration $[Li^+]/[EO]$ for $P(LiSMOE_n)$ s.

becomes easier. At the same time, higher thermal energy also causes more salts to dissociate and increases the number of free ions. As a result, the ionic conductivity of the copolyelectrolytes is higher at higher temperatures. Meanwhile, with higher salt concentration, there will be more free ions. Therefore, the ionic conductivity of the copolyelectrolytes increases monotonously with salt concentration.

Temperature Dependence of Ionic Conductivity

The effect of temperature on ionic conductivity of $P(LiSMOE_n)$ s is shown in Figure 5. The plots of $\log \sigma$ vs $1/T$ do not give straight lines, suggesting that non-Arrhenius behavior of ion transport occurs in the copolyelectrolytes. For an amorphous polymer electrolyte, the temperature dependence of ionic conductivity generally follows the Vogel-Tammann-Fulcher (VTF) equation [21], namely

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

where σ is the ionic conductivity, A the constant, E_a the apparent activation energy of ion transport, and T_0 the ideal glass transition temperature at which

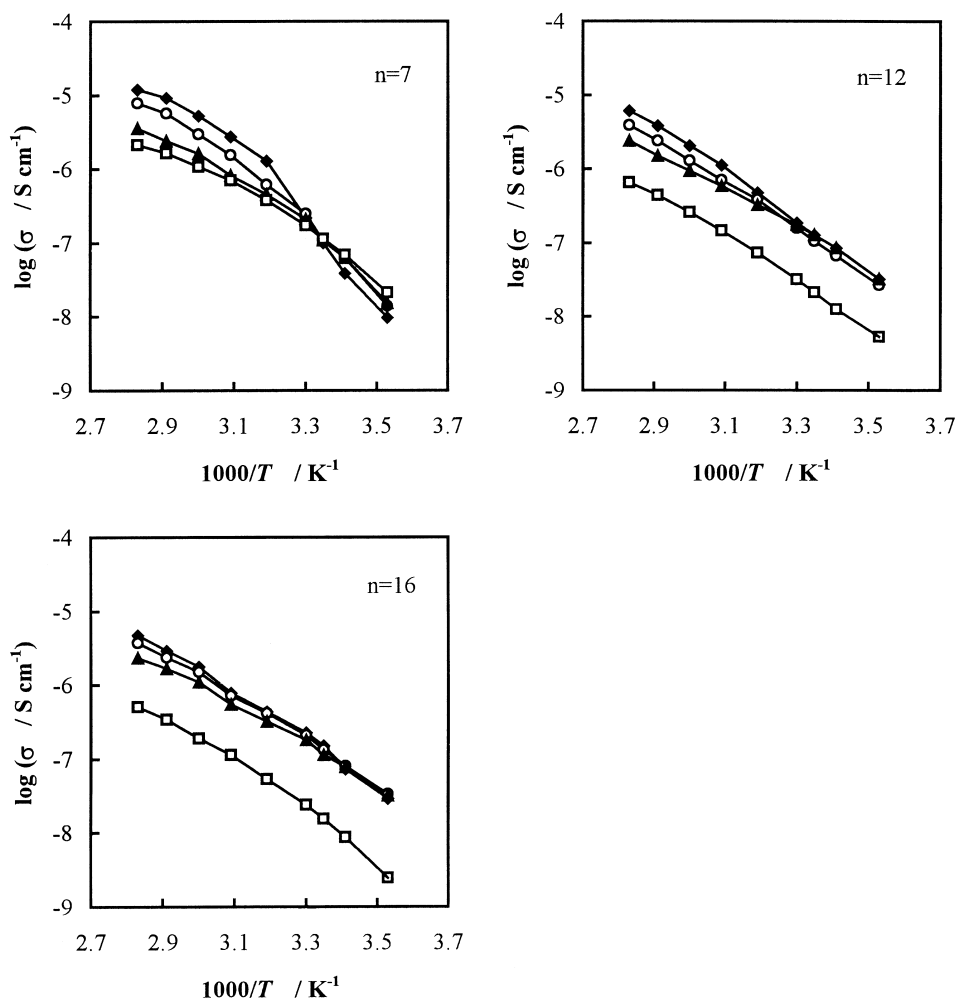


Figure 5. Temperature dependence of ionic conductivity of P(LiSMOE_n)s. [LiSPMI]/[MOE_nM]: (◆) 0.4:0.6, (○) 0.3:0.7, (▲) 0.2:0.8 and (□) 0.1:0.9.

the configurational entropy disappears. Following the Adam-Gibbs analysis, T_0 can be taken as 50 K below the measured T_g [22]. As mentioned above, there are two glass transitions in these copolymer electrolytes, T_{g1} and T_{g2} . It would be unreasonable to take T_{g2} as the T_g value used in VTF equation because in the temperature range below T_{g2} and above T_{g1} , the oligoether side chains of the copolyelectrolytes are still mobile. Therefore, T_{g1} has been adopted to fit the ionic conductivity data in the VTF equation.

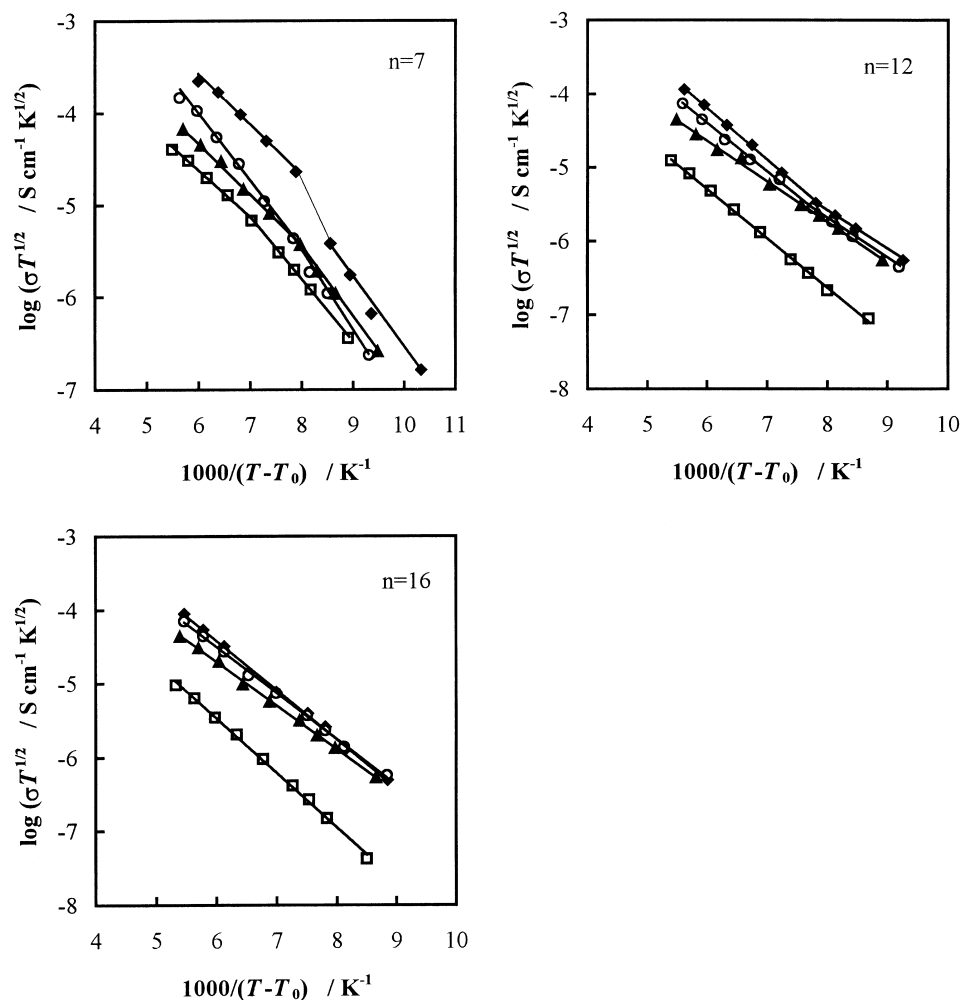


Figure 6. Correlation between $\log(\sigma T^{1/2})$ and $1/(T-T_0)$ in VTF equation for P(LiSMOE_n)s. [LiSPMI]/[MOE_nM]: (◆) 0.4:0.6, (○) 0.3:0.7, (▲) 0.2:0.8 and (□) 0.1:0.9.

Figure 6 illustrates the VTF plots of $\log(\sigma T^{1/2})$ vs reciprocal $(T-T_0)$ $[1/(T-T_0)]$ for the copolyelectrolytes. It is seen that the correlation between $\log(\sigma T^{1/2})$ and $1/(T-T_0)$ for P(LiSMOE₇)s and P(LiSMOE₁₂)s with [LiSPMI]/[MOE₁₂M] of 0.4:0.6 and 0.3:0.7 shows two inflected straight lines and each line has a linear regression factor above 0.99, while that for other copolyelectrolytes gives only one straight line. The results indicate that the temperature dependence of ionic conductivity for these copolyelectrolytes follows

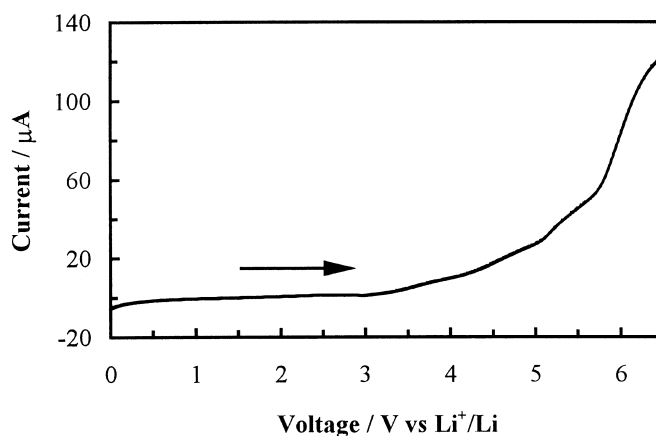


Figure 7. Voltammetric curve of a typical copolyelectrolyte, P(LiSMOE₁₆) with [LiSPMI]/[MOE₁₆M] of 0.4:0.6, measured with a scan rate of 10 mV s⁻¹ at room temperature.

the VTF behavior, and moreover, a special dual VTF behavior is obeyed for copolyelectrolytes with shorter oligoether side chain and higher salt concentration. The phenomenon of an inflected VTF line also exists in the nearly alternating comblike copolymers formed by the same two monomers [11]. Armand *et al.* [23] and Lin *et al.* [19] have reported similar results for a partially crystalline PEO-LiI system and methyl vinyl ether/maleic anhydride copolymers, respectively. It is found that the VTF intersections for P(LiSMOE₇)s and the two P(LiSMOE₁₂)s are around 35°C, close to their second glass transition temperatures. It is, therefore, quite obvious that the dual VTF behavior in these copolyelectrolytes is due to their second glass transition process. However, the VTF plots for P(LiSMOE₁₆)s and P(LiSMOE₁₂)s with [LiSPMI]/[MOE₁₂M] of 0.2:0.8 and 0.1:0.9 do not show dual VTF relationship. It is probably because the ionic conductivity of these copolyelectrolytes is very poor with such a low lithium salt concentration. Thus, the second glass transition does not make the ionic conductivity increase faster. As a result, the temperature dependence of ionic conductivity exhibits a normal VTF behavior.

Electrochemical Stability Window of P(LiSMOE_n)s

The electrochemical stability window of P(LiSMOE_n)s was studied using voltammetry. Figure 7 shows a voltammetric result of a typical copolyelectrolyte, P(LiSMO₁₆) with [LiSPMI]/[MOE₁₆M] of 0.4:0.6, measured

between 0 and 7 V vs Li⁺/Li on a stainless steel (SS) electrode at a scan rate of 10 mV s⁻¹ at room temperature. As stated in the experimental section, the decomposition voltage was assumed to be that at which a sharp anodic current from the baseline (*ie*, > 20 μA cm⁻²) began to flow through the cell. It can be obtained from Figure 7 that the decomposition voltage, *i.e.*, the anodic potential, of the P(LiSMOE_n) on a SS electrode is up to 4.6 V vs Li⁺/Li. A decomposition voltage greater than 4.5 V is an important feature for a polymer electrolyte because it would make it suitable to be used in many lithium and lithium ion batteries. It is, therefore, illustrated that P(LiSMOE_n)s have a good electrochemical stability window.

Since the anion groups (-SO₃⁻) are covalently bonded onto the macromolecular chains of the copolyelectrolytes, the anions can scarcely migrate in the copolyelectrolytes. The ionic conduction is based on the motion of lithium cations. Therefore, the lithium ion transference number can be regarded to be unity.

CONCLUSION

Poly[lithium-*N*(4-sulfophenyl) maleimide -co- methoxy oligo(oxyethylene) methacrylate] [P(LiSMOE_n)] with three different oligoether side chains and different salt concentrations were synthesized as solid comb-like copolyelectrolytes. They are essentially random copolymers, with blocks of MOE_nM recurring sporadically in between the salt units of *N*(4-sulfophenyl) maleimide. The salt concentration influences not only the structure of the copolyelectrolytes, but also their thermal behavior and ionic conductivity. All the copolyelectrolytes have two glass transitions in the studied temperature range, one for the oligo(oxyethylene) side chain and another for the main chain of the polymer host. At temperatures below 50°C, the ionic conductivity of the copolyelectrolytes exhibits a peak value at [Li⁺]/[EO] = 2.2 mol%. At temperatures above 50°C, however, the ionic conductivity increases monotonously with salt concentration. The highest conductivity at 25°C is 1.6 × 10⁻⁷ S cm⁻¹ at [Li⁺]/[EO] = 2.2 mol%. The temperature dependence of ionic conductivity of the copolyelectrolytes follows the VTF behavior, and moreover, a dual VTF behavior is observed for copolyelectrolytes with shorter oligoether side chain and higher salt concentration. Voltammetric results demonstrate that these copolyelectrolytes have a reasonably good electrochemical stability window.

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