Cationic Conductivity for Poly[Oligo(Oxyethylene) Methacrylate-*co*-Methacryloyl Hexylsulfonic Acid Alkali Metal Salt]

Shengshui Zhang[a]; Zhenghua Deng[b]; Guoxiang Wan[b]

[a] Laboratory of Solid State Ionics, University of Science and Technology Beijing, Beijing, People's Republic of China [b] Chengdu Institute of Organic Chemistry Academia Sincia Chengdu, People's Republic of China

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CATIONIC CONDUCTIVITY FOR POLY[OLIGO(OXYETHYLENE) METHACRYLATE-*co*-METHACRYLOYL HEXYLSULFONIC ACID ALKALI METAL SALT]

SHENGSHUI ZHANG,* ZHENGHUA DENG, and GUOXIANG WAN

Chengdu Institute of Organic Chemistry
Academia Sincia
Chengdu 610015, People's Republic of China

ABSTRACT

Poly[oligo(oxyethylene) methacrylate-*co*-methacryloyl hexylsulfonic acid alkali metal salts], $P(MEO_n–SHMM)$, were prepared as single-cationic conductors. The cationic conductivity of copolymers was deeply influenced by the type of cations, the comonomeric salt concentration, polar group, and mixed ions. An optimum Li^+-ionic conductivity of 2.1×10^{-6} S/cm at 25°C was obtained for the polarity-improved copolymer, $P(MEO_{12}–AM–SHMLi)$, with neither organic plasticizer nor low molecular weight salt.

INTRODUCTION

Polymer-based electrolytes have recently been extensively investigated due to their potential application in electrochemical devices, especially in all-solid-state lithium batteries. As a candidate electrolyte material for lithium batteries, they should have both good conductivity and high Li^+-ionic transference number. These two properties, however, are incompatible with each other, and a conciliation of the contradiction is frequently accompanied by the impairment of conductivity. Most of the polymeric electrolytes reported are anion-mobile, which will lead to dc conductivity decay when dc voltage is applied. The descent of conductivity is

*Present address: Laboratory of Solid State Ionics, University of Science and Technology Beijing, 100083 Beijing, People's Republic of China.
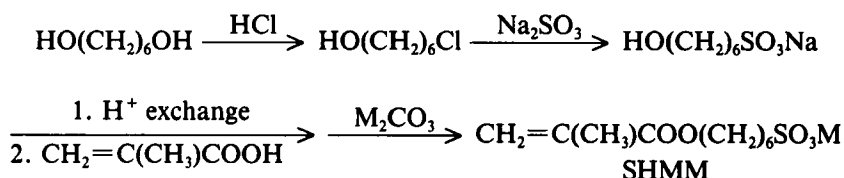
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inconvenient in a lithium battery composed of an Li^+-insertion cathode. It is, therefore, necessary to develop a single-Li^+-conductor for a high performance lithium battery [1, 2]. An effective method to optimize cation transference number is to anchor anions in a macromolecular chain through covalent bonds. Even by using liquid additives such as tetraethylene glycol, conductivities of the single-cationic conductors are generally much lower than those observed in anion-mobile systems due partly to tight ion pairing [3]. In order to improve Li^+-ionic conductivity at ambient temperature, emphasis should be paid to preparing new polymer hosts having a low T_g and a completely amorphous structure together with a salt-solubilizing property. In the present work a series of copolymers with hexylsulfonic anions fixed in a macromolecular chain and oligo(oxyethylene) side chains has been successfully prepared, and they are considered structurally to be a single-cationic conductor. The relationship between the structure and cationic conductivity of copolymers will be discussed.

EXPERIMENTAL

Materials

Oligo(oxyethylene) methacrylates (MEO_n; the number of oxyethylene units n) were prepared from oligo(oxyethylene) monomethyl ethers as suggested by Philippe [4]. Oligo(oxyethylene) monomethyl ethers with different oxyethylene repeating units (where n = 5, 8, 12, 16, 20, or 22, supplied by Kanto Chemical Co.) were dried under vacuum at 120°C for 24 h and then, together with an excess of triethylamine, dissolved in dry toluene. Under an inert atmosphere a slight excess of methacryloyl chloride toluene solution was added dropwise to the above solution at 0°C. This solution was stirred at 0°C for 1 h followed by further reaction at room temperature for another 16 h. The reaction solution was filtered to remove the precipitate formed, and then the filtrate was flowed through a silica gel column to purify the product. The desired MEO_n was obtained by carefully evaporating the product fraction below 30°C under vacuum. The chemical structure was determined with ^{1}H-NMR spectrometry. Typical ^{1}H-NMR results in $CDCl_3$ for MEO_{22}: terminal $-OC\underline{H}_3$, 3.31 (3H); $-OC\underline{H}_2-$, 3.58 (86H); $-COOC\underline{H}_2-$, 4.23 (2H); $>C=C\underline{H}_2$, 5.50, 6.04 (2H); methacrylate $-C\underline{H}_3$, 1.88 (3H) in ppm.

Methacryloyl hexylsulfonic acid alkali metal salts (SHMM) were synthesized according to the following route:

$$HO(CH_2)_6OH \xrightarrow{HCl} HO(CH_2)_6Cl \xrightarrow{Na_2SO_3} HO(CH_2)_6SO_3Na$$

$$\xrightarrow[\text{2. } CH_2=C(CH_3)COOH]{\text{1. } H^+ \text{ exchange}} \xrightarrow{M_2CO_3} CH_2=C(CH_3)COO(CH_2)_6SO_3M$$
$$SHMM$$

6-Chlorohexanol was prepared as described in the literature [5]. The product was a colorless liquid with the boiling point 100–102°C/9 mmHg.

Sulfonation of a 6-chlorohexanol with sodium sulfite was carried out in the presence of a phase-transfer catalyst at reflux temperature with vigorous stirring. The colorless flakes of sodium 6-hydroxyhexane sulfonate (mp 240–241°C) were

obtained by evaporating the solution to dryness and extracting the solid residue repeatedly with 95% ethyl alcohol. The yield was about 75–80%.

Analysis. Calculated for $C_6H_{13}O_4SNa$: C, 35.28%; H, 6.27%; S, 15.72%. Found: C, 34.84%; H, 6.40%; S, 15.92%.

Sodium 6-hydroxyhexane sulfonate was turned to the corresponding free acid with an H^+-type cation-exchange resin, and the resulting acid was esterified with a slight excess of methacrylic acid in the presence of an inhibitor (hydroquinone). Water formed during the reaction was withdrawn from the reactor by means of azeotropic distillation with toluene. After cooling, the reaction mixture was neutralized with alkali metal carbonate. The product was precipitated by the addition of diethyl ether and recrystallized twice from methanol. The yield was about 80–85%. Typically, the chemical structure of the SHMLi was checked with the ^{1}H-NMR spectrum in D_2O: $-OC\underline{H}_2-$, 4.1 (2H); $-CH_2CH_2C\underline{H}_2C\underline{H}_2CH_2CH_2-$, 1.4 (4H); $>C=C\underline{H}_2$, 5.6, 6.2 (2H); $-OCH_2C\underline{H}_2-$ and $-C\underline{H}_2CH_2SO_3Li$, 1.7 (4H) in ppm; IR spectrum: 1725 ($\nu_{C=O}$), 1640 ($\nu_{C=C}$), 1340 ($\nu_{as\,S=O}$), 1165 ($\nu_{s\,S=O}$), 870 ($\delta =C\underline{H}_2$), 1280 ($\nu_{as\,CO-O}$) cm^{-1}.

Analysis. Calculated for $C_{10}H_{17}O_5SLi$: C, 46.88%; H, 6.64%; S, 12.50%. Found: C, 47.23%; H, 6.78%; S, 12.41%.

Copolymerization was carried out in dry methanol solution with 2,2'-azobisisobutyronitrile as initiator at 60°C for 24 h. After concentrating, the resulting copolymers were precipitated on addition of 20 times their volume of diethyl ether and dried at 100°C under vacuum for 24 h. The composition of copolymers thus obtained was determined from the results of elemental analyses, and expressed in terms of the ratio (M/O) of cation to ether oxygen atoms. The analysis of a typical copolymer $P[(MEO_{12})_{1-x}-SHMLi_x]$ with an x value of 0.335 (i.e., M/O = 0.042) is as follows. Calculated: C, 53.96; H, 8.53; S, 2.13%. Found: C, 55.12; H, 7.25; S, 2.13%. The copolymer films, which were semitransparent elastomers at room temperature, were easily prepared by solution casting technology.

Measurements

All measurements were carried out in a dry nitrogen atmosphere.

Conductivity was measured as described elsewhere by using a 1.10-kHz ac conductometer [6]. A disk sample with a diameter of 10 mm was sandwiched between stainless steel electrodes. The cell was kept in a temperature-controlled dry box, and the conductivity was determined at each temperature after equilibration for 20 min following each incremental rise.

A Perkin-Elmer DSC-7 Differential Scanning Calorimeter was used to evaluate the glass transition temperature (T_g) at a heating rate of 10°C/min. The T_g was taken as the temperature at the midpoint of the baseline shift observed during the transition from the glass to the rubberlike state.

RESULTS AND DISCUSSION

Composition Dependence of Cationic Conductivity

The composition dependence of the cationic conductivity is shown in Fig. 1 for the $P(MEO_{12}-SHMM)$ system with different cations. A maximum cationic conductivity is observed in each system. The variation tendency of the maximum
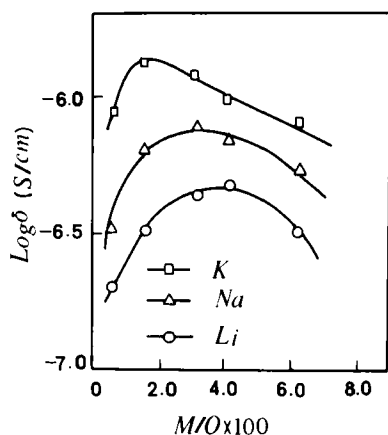
FIG. 1. Composition dependence of cationic conductivity for the copolymer P(MEO$_{12}$-SHMLi) at 25°C.

conductivity against the electrolyte content is similar to that observed in the system of poly[oligo(oxyethylene) methacrylate-co-alkali metal methacrylate], abbreviated as P(MEO$_7$-MAM) [2]. An increase of electrolyte content gradually increases the number of carrier ions. However, the increasing microviscosity of the conduction column also arises from the added electrolyte due to the ion–dipole interaction between metal ion and ether oxygen atoms; it hinders the mobility of carrier ions. The compensation of these two factors determines the conductivity maxima. As seen from Fig. 1, the conductivity maxima for different cations increase in the order of increasing cationic radius, i.e., K > Na > Li, but the corresponding electrolyte contents decrease in the same order. This fact can be attributed to the influence of the cationic radius on the dissociation energy of the added electrolyte and on the coordination energy of the cation with ether oxygen atoms in the P(MEO$_n$-SHMM)s. It is known that the dissociation energy of the salts and the coordination energy of complexes decrease with increasing radius of the cation. When a cation with a large radius is used in a polymer electrolyte, the maximum conductivity of the electrolytes should increase and shift toward the lower salt content side. The conductivity of P(MEO$_{12}$-SHMM) is greatly affected by the dissociation energy of the comonomeric salt (SHMM), especially in the content regions close to the optimum electrolyte content, similar to the results of the P(MEO$_7$-MAM) [2]. As compared with other single-ionic conduction systems containing no polar liquid additive [2, 3], at room temperature the cationic conductivities of the copolymers investigated here are relatively higher due probably to a more proper n value in the MEO$_n$ and to a lower dissociation energy of the sulfonic acid salts in the comonomers.

Mixed-Ion Effect of Cationic Conductivity

It has been reported that the mixed ions deeply influence the conductivity of such conductive inorganic glass as sodium silicate/potassium silicate glass [7]. A similar behavior is also observed in copolymer systems but not as drastically as in the former, as shown in Fig. 2. In order to clarify the reasons for the mixed-ion
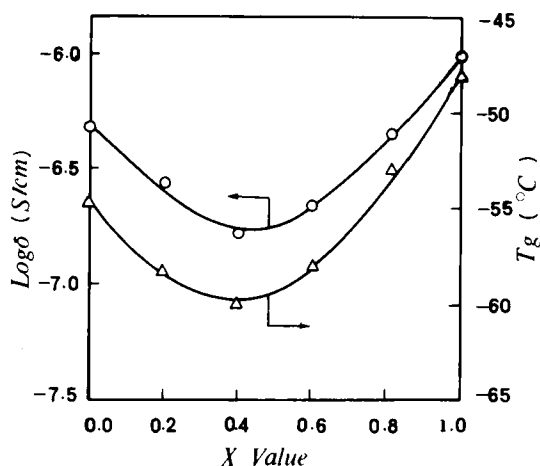
FIG. 2. Mixed-ion effect on cation conductivity at 25°C and T_g for copolymer P[MEO$_{12}$-xSHMK-(1 − x)SHMLi], all with M$_{total}$/O = 0.042.

effect, the dependence of T_g for P[MEO$_{12}$-xSHMK-(1 − x)SHMLi], all with the same ratio value of 0.042 in terms of total alkali metal ion to ether oxygen atoms, on the cationic component was investigated (Fig. 2). It is seen from Fig. 2 that both conductivity and T_g reach the lowest point at an x value of about 0.5. When the total salt content in the copolymer is kept constant, the T_g of the cation-containing copolymers is mainly influenced by the interaction of ether oxygen atoms with dissociated cations among the comonomeric salts. As suggested by the relationship of T_g with the cation content, it is reasonable to consider that the formation of ion-pair clustering among the dissociated cations is the main reason for the mixed-ion effect of the conductivity. In the absence of other cations, P(MEO$_{12}$-SHMK) exhibits higher conductivity than that for P(MEO$_{12}$-SHMLi) because of the higher dissociation degree of potassium salt, as reflected by higher T_g even at the same M/ O value. With the mixture of lithium ions to P(MEO$_{12}$-SHMK) or potassium ions to P(MEO$_{12}$-SHMLi), both the T_g and conductivity of the copolymers are correspondingly decreased, suggesting a probable assumption that the dissociated ions gather gradually to ion clustering when mixed ions are introduced into the system.

Relationship between Side-Chain Length and Cationic Conductivity

Figure 3 indicates that the n value in MEO$_n$ deeply affects the conductivity of P(MEO$_n$-SHMLi). Long side chains impede their mobility, and then slow down ion transport. This phenomenon is a little similar to the crosslinking effect of the added lithium salts in the lithium salt complexes of polyethers such as poly(ethylene oxide). Moreover, the oxyethylene crystals unfavorable for ion transfer will be formed when n exceeds 12, as confirmed by DSC results [8]. On the other hand, short side chains also lead to poor conductivity due mainly to the excessive inert poly(methacrylate) main chain regions that hinder the conduction column for cation transport. Thus, an optimum n value for the Li$^+$-ionic conductivity is yielded in which the polymer has not only a low T_g and an amorphous structure, but also enough ether
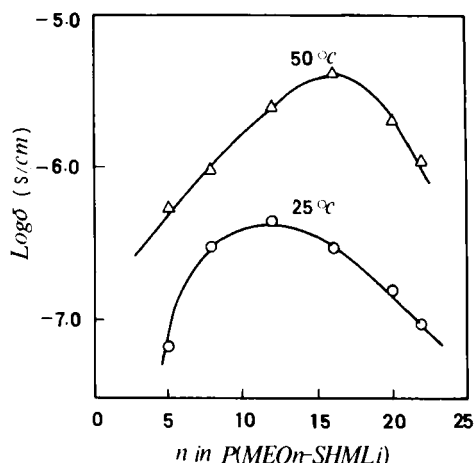
FIG. 3.   Isothermal conductivity as a function of side-chain length for the copolymer P(MEO$_{12}$-SHMLi), all with Li/O = 0.042.

oxygen concentration for solubilizing comonomeric salts [9]. It can be seen from Fig. 3 that P(MEO$_{12}$-SHMLi) exhibits the highest conductivity over the n range between 5 and 25 at room temperature. The result is in agreement with that observed in the blend complex (PMEO$_n$/PSHMLi) system [9], and similar to that for the bi-ionic PMEO$_n$-LiClO$_4$ complexes with high salt content regions [2]. With rising ambient temperature, oxyethylene crystal in the polymeric side-chains melts and the segmental motion responsible for ion conduction accelerates. Consequently, the most proper n value shifts toward a relatively larger value. The copolymer with the maximum conductivity at 50°C, for instance, turns to P(MEO$_{16}$-SHMLi) from the original P(MEO$_{12}$-SHMLi) at 25°C even at the same comonomeric salt content. The fact is ascribable to the differences in the dissociation degree of comonomeric salts and in the microviscosity of the copolymer matrix resulting from the elevated temperature.

Polarity Effect on Cationic Conductivity

Aside from the low microviscosity and the completely amorphous structure, the polarity of polymer hosts is important for high conductivity because a higher polarity of the polymer matrix will promote the dissociation of dissolved salts. Previous results show that polar groups (PG) attached to copolymeric chains can improve the cationic conductivity of the PG-containing copolymers because of its restraining the formation of oligo(oxyethylene) crystals and increasing the polymeric polarity responsible for salt dissociation [9, 10]. On the other hand, excessive PG, which increases the T_g of the copolymer and blocks the conduction column, will impair conductivity. The combination of the above factors leads to an optimum PG content, and this content is connected with the PG used. In this work, acrylamide (AM) was chosen as the PG to improve both Li$^+$-ionic conductivity and the mechanical properties of the copolymers owing mainly to its polarity and high cohesion energy. The AM effect of T_g and conductivity is illustrated in Fig. 4. At
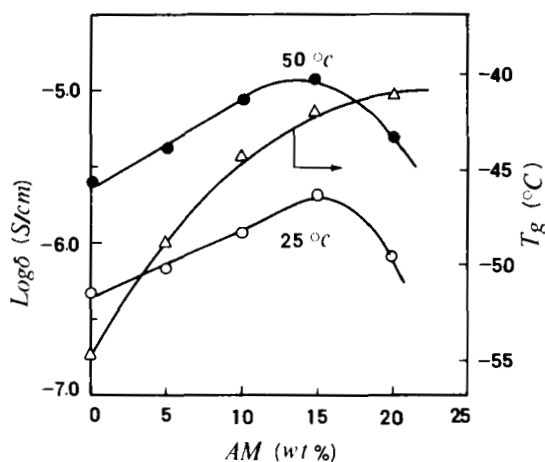
FIG. 4. The effect of AM content on Li^+-ionic conductivity and T_g for the copolymer P(MEO$_{12}$-AM-SHMLi), all with Li/O = 0.042.

first the increase of the AM component causes a rapid rise in T_g, due probably to the H-bonds between AM and ether oxygen atoms in the PMEO$_{12}$. However, the conductivity of the corresponding copolymers was also increased, suggesting that AM groups promote the dissociation of the SHMLi. With increasing AM content, the T_g closes gradually to a plateau and conductivity reaches a maximum value. When AM content equals 15 wt%, a maximum conductivity of 2.1×10^{-6} S/cm at 25°C is observed for the AM-containing copolymer P(MEO$_{12}$-AM-SHMLi) with an Li/O value of 0.042, even without the use of low molecular weight plasticizers. A further increase in AM content causes a rapid decrease in conductivity, although
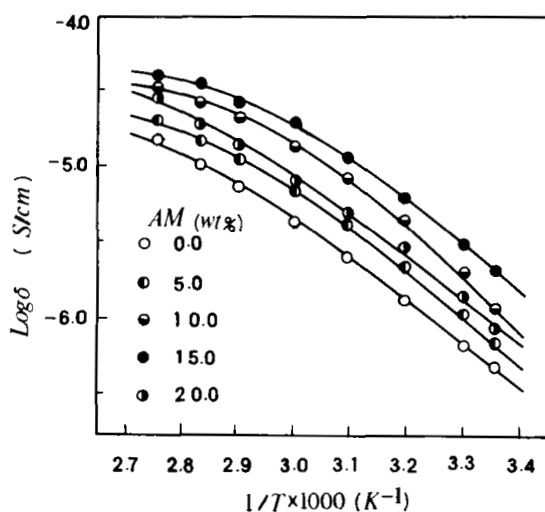

FIG. 5. Arrhenius plots of Li^+-ionic conductivity for the copolymer P(MEO$_{12}$-AM-SHMLi), all with Li/O = 0.042.

the T_g remains constant. The temperature dependences of ionic conductivities for the AM-containing copolymers with different AM content show curved Arrhenius plots, as shown in Fig. 5, suggesting that cation transport occurs in the amorphous regions. This is typical for ion migration in a solid polymeric matrix. Thus it is clear that cation conduction is affected by segmental motion of the polymer matrix. The improvement of the Li^+-cationic conductivity observed in the AM-containing copolymers may be partly attributed to the increased polarity of the polymer matrix.

CONCLUSION

Based on oligo(oxyethylene) methacrylate (MEO_n) and methacryloyl hexylsulfonic acid alkali metal salts, copolymers with single-cationic conductivity were successfully synthesized. Their conductivity was greatly affected by cation species, mixed-ion effect, polar groups, and n value in the MEO_n. The copolymers exhibit high conductivity at room temperature even without the addition of other liquid additives. The temperature dependences of cationic conductivities show curved Arrhenius plots, suggesting that cationic transport occurs in the amorphous regions. An optimum Li^+-ionic conductivity of 2.1×10^{-6} S/cm at 25°C was obtained for the acrylamide-modified copolymer.

ACKNOWLEDGMENT

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