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Poly(oligo-oxyethylene methacrylate-*co*-alkali metal acrylamidocaproate) as a single ion conductor

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Summary

The new single ion conductors, poly(oligo-oxyethylene methacrylate-co-alkali metal acrylamidocaproic acid) ($(CH_2CCH_3COO(CH_2CH_2O)_9H)_x$-$(CH_2CHCONH(CH_2)_5COO^-M^+)_{1-x}$), M^+=Li^+,Na^+,K^+, were synthesized and the effects of the cation and the temperature on ionic conductivity were investigated. The alkyl spacer in the alkali metal acrylamidocaproate was introduced to increase the flexibility of the side chain for the complex formation between the ionic groups and the oxygens in PEO unit. The room temperature(30°C) conductivity of the K single ion conductor was found to be 5×10^{-7} S/cm which is the highest value reported for the single ion conductors having carboxylate groups without any additives. The pseudo-activation energy in the VTF equation was not dependent on the type of the cation, which indicates that the ion hopping rate is higher than the string renewal rate in these single ion conductors.

Introduction

Solid polymer electrolytes have received special attention for more than one decade in its potential applications such as rechargeable high-energy density batteries. One of the interesting field in the solid polymer electrolytes is the single ion conductor in which only cation can be mobile under the influence of electric field, and which does not suffer from the passivation problem caused by accumulation of anion on the anode (1). There have been some improvements on the molecular design of the single ion conductor with the basic idea that the high solvating power and the high segmental mobility of the chain are requisites for the high ionic conductivity (1,2~5,9). H. Ohno et al. designed the single ion conductors, poly(oligo-oxyethylene methacrylate-co-alkali metal methacrylate) (2,6) and poly((ω-carboxy)oligo-oxyethylene methacrylate) (3), with this idea and reported the single ion conductions of these materials (2,3,6).

In this work, we synthesized the single ion conductors, poly(oligo-oxyethylene methacrylate-co-alkali metal acrylamidocaproate) $(CH_2CCH_3COO(CH_2CH_2O)_9H)_x$-$(CH_2CHCONH(CH_2)_5COO^-M^+)_{1-x}$ (P(MEO$_9$-AACM)), M^+=Li^+,Na^+,K^+, by radical copoly-

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merization of oligo-oxyethylene methacrylate and acrylamidocaproic acid, and the subsequent neutralization of the carboxylic acid group with various alkali hydroxides. The oligo-oxyethylene methacrylate unit imparts the salt-solvating power and the segmental motion necessary for ionic diffusion, and the alkali metal acrylamidocaproate unit provides the charge carriers for ionic conduction. The alkyl spacer in the alkali metal acrylamidocaproate was introduced to increase the flexibility of the side chain for the complexes formation between the ionic groups and the oxygens in PEO unit. The conductivities of these single ion conductors were investigated, and the relevant mechanism of ionic conduction was discussed.

Experimental

Synthesis and preparation of the single ion conductor

The oligo-oxyethylene methacrylate ($CH_2{=}CCH_3COO(CH_2CH_2O)_9H$) was used as supplied by Aldrich without further purification. The acrylamidocaproic acid was synthesized by condensation reaction of acryloyl chloride ($CH_2{=}CHCOCl$) and 6-aminocaproic acid ($NH_2(CH_2)_5COOH$). The detailed procedure for this reaction can be found elsewhere (10). The copolymer of oligo-oxyethylene methacrylate and acrylamidocaproic acid was obtained by radical copolymerization in water medium with the redox initiator ($K_2S_2O_8$, $NaHSO_3$). The monomer concentration of the reactant solution was 5wt%. The polymerization was carried out for more than 12hrs at 30°C. The unreacted monomer was removed by extraction with diethyl ether. The reaction temperature and the amount of initiator were adjusted carefully; the high initiator concentration and the high reaction temperature often caused gelation during the polymerization. The ratio of initiator and monomer in the reactant solution was $K_2S_2O_8$/$NaHSO_3$/monomer=0.0375/0.015/5(g/g/g).

The carboxylic acid groups in the resulting polymer were neutralized with various alkali hydroxides by titration. Phenolphthalein was used as an indicator. 0.1N LiOH, NaOH and KOH were used as titrants.

Conductivity measurement

The stainless steel electrode was used in the preparation of the cell for impedance measurement. A thin layer of the aqueous solution of P(MEO_9-AACM) was spread over the one side of the electrode and the solvent was evaporated under atmosphere. The cast film was further dried under vacuum at 70°C for more than 12hrs to completely remove the residual solvents. The one side coated cell was squeezed by the other stainless steel electrode. The thickness of the film was about 15μm. It should be noted that the single ion conductors were slightly crosslinked during the solvent removal. This is attributed to the spontaneous gelation of oligo-oxyethylene methacrylate unit (11).

Impedance measurements were taken over the frequency range of 1Hz~10MHz using the Solatron SI1255 frequency response analyzer. The data were transmitted to the personal computer from the frequency response analyzer through GPIB. The conductivity was obtained from the bulk resistance found in the complex impedance plot.

Results and discussion

Structural characterization of the single ion conductor

Fig. 1 shows the ^1H NMR spectra of the copolymers of oligo-oxyethylene methacrylate and acrylamidocaproic acid. The detailed peak assignments are given in this figure. These assignments were based on the spectra of homopolymer of poly(oligo-oxyethylene methacrylate) and poly(acrylamidocaproic acid). The peaks at 1.05, 1.21, 1.51, 2.28 and 3.08ppm correspond to the methylene proton of alkyl spacer in acrylamidocaproic acid unit. The protons in PEO unit are found at 2.8~4.5ppm. The methyl group in methacrylate unit is observed at 0.81ppm. The broad peaks ranged from 1.4 to 2.2ppm correspond to the methylene protons of the main chain. The peaks from the double bond were not found in these spectra, indicating that the unreacted monomer was completely removed by extraction. From the relative peak area of the methylene unit of the alkyl spacer in the acrylamidocaproic acid and that of the PEO unit in the oligo-oxyethylene metharylate, the copolymer composition was determined. The composition of the acrylamidocaproic acid unit in the copolymer was found to somewhat exceed the feed composition.

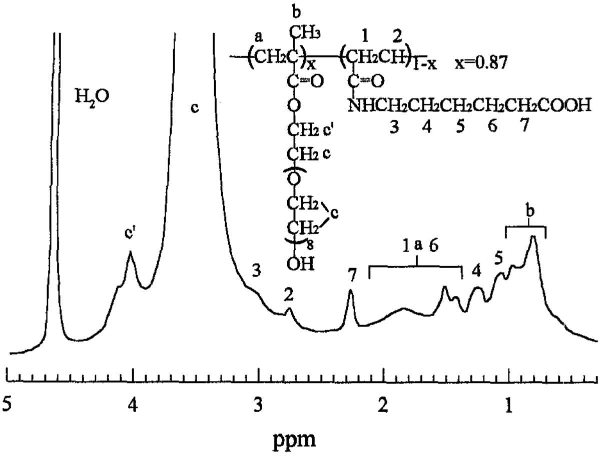

Fig. 1 ^1H NMR spectrum of poly(oligo-oxyethylene methacrylate-co-acrylamidocaproic acid)

Fig. 2 shows the FTIR spectrum of the unneutralized copolymer of which composition is (oligo-oxyethylene methacrylate)/(acrylamidocaproic acid)=0.67/0.33. The C=O stretching peak of ester in oligo-oxyethylene methacrylate unit is found at 1728cm^{-1}. The peaks at 1655cm^{-1} and 1542cm^{-1} correspond to the amide I and amide II bands from the acrylamidocaproic acid unit respectively. The strong peak shown at 1117cm^{-1} is due to C–O–C stretching of the oxyethylene unit. It was observed that the peaks at 1655cm^{-1} and 1542cm^{-1} (amide I and II) were more intense for the copolymer with the higher content of the acrylamidocaproic acid unit.

The unneutralized and neutralized copolymers were completely amorphous, which was evidenced by the absence of melting peaks in the DSC thermograms.

Conductivity of the single ion conductors

Fig. 3 represents the Arrhenius plot of ionic conductivities of the single ion conductors. The room temperature conductivity of the K single ion conductor of which ionic content is $O/K^{+}=30$ is found to be 5×10^{-7} S/cm. This value is the highest value among the previously reported single ion conductors having carboxylate groups. Since the polymeric mediums were identical to the other single ion conductors containing carboxylate groups (2,3,6), the enhancement of ionic conductivity would be attributed to the structural characteristic of the alkali metal acrylamidocaproate unit. On account that the oxygen and the alkali metal cation should be properly coordinated for dissociation of ion pair, more flexible side chains are preferable, and thereby the incorporation of the alkyl spacer could lead to the relatively high ionic conductivity.

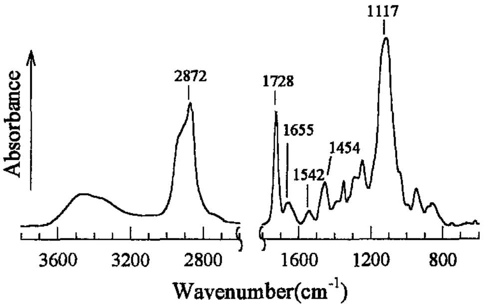

Fig. 2 FTIR spectrum of poly(oligo-oxyethylene methacrylate -co-acrylamidocaproic acid)

The Li, Na, and K single ion conductors of which ionic content was $O/M^{+}=30$ show higher ionic conductivities than those of $O/M^{+}=18$ and 60 as shown in Fig. 3. This is due to the two opposite effects of ionic group on conductivity. The ionic conductivity is proportional to the number of charge carrier and the mobility of the charge carrier, and the increase in ionic content affects these two parameters in opposite direction. As the more ionic groups are incorporated into the polymer chain, the number of charge carrier would be increased, while the ion dipole interaction between the dissociated ions and the oxygens in PEO and the ion-ion interaction between the ion pairs would reduce the mobility of the chain. For $O/M^{+}=30$, the gain in the number of charge carrier is overwhelmed by the loss in the chain mobility compared to $O/M^{+}=60$, and the gain in chain mobility overcomes the loss in the number of charge carrier compared to $O/M^{+}=18$.

From the comparison of the single ion conductors with different cations, it was found that the P(MEO_9-AACNa) showed the higher ionic conductivities than the P(MEO_9-AACLi) for $O/M^{+}=60$, whereas for the higher ionic contents($O/M^{+}=30$ and 18) the P(MEO_9-AACLi) revealed the higher ionic conductivity than the P(MEO_9-AACNa). Considering only the number of charge carrier, i.e. free ion, P(MEO_9-AACNa) should show higher ionic conductivity than P(MEO_9-AACLi), since the sodium carboxylate has lower dissociation energy. Besides the number of the charge carrier, it should be also considered which single ion conductor has higher segmental mobility that is indicated by the value of T_g. For the lower ionic content(O/M^+=60), the T_g's of the Li single ion conductor and the Na single ion conductor were −45°C and −43°C respectively, indicating the small difference in chain mobility. However, the Na single ion conductor showed the larger increase in T_g with ionic content than the Li single ion conductor. The T_g's of the Na and the Li single ion conductors at the ionic content of O/M^+=30 were −39°C and −44°C and at the ionic content of O/M^+=18, −31°C and −42°C respectively. At high ionic content, the Na single ion conductor is more restricted in chain mobility than the Li single ion conductor and thus reveals the lower conductivity. The lower mobility for the larger cation is a consequence of the more ion-dipole interaction between the free ions and the oxygens in PEO unit due to the higher dissociation. In that reason, the K single ion conductors show the higher T_g than those of the Na and the Li single ion conductors with the same ionic content.

For all the ionic content investigated, the K single ion conductors show higher conductivites than those of the Na and the Li single ion conductors with the same ionic content, though the T_g's of the K single ion conductors are higher than those of the Na and the Li single ion conductors. This represents that the fraction of the free ion in K single ion conductor is much higher than those of the other single ion conductors.

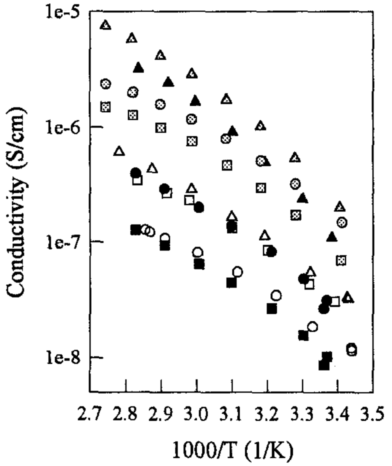

Fig. 3 Temperature dependence of ionic conductivity in P(MEO$_9$-AACM)

M= ○ Li; □ Na; △ K

O/M$^+$= ▭ 60; ▨ 30; ■ 18

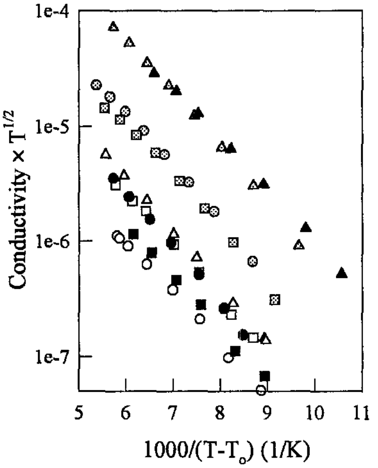

Fig. 4 VTF plot for P(MEO$_9$-AACM)

M= ○ Li; □ Na; △ K

O/M$^+$= ▭ 60; ▨ 30; ■ 18

The curvature in the Arrhenius plot(Fig.3) shows that the ionic conduction obeys the VTF relation rather than Arrhenius relation. The empirical VTF equation given in eqn. (1) describes the transport properties in a viscous matrix, where T is temperature, and T_o corresponds to the thermodynamically limited glass transition, below which there is no further entropy loss caused by the configurational change in polymer, A and B are empirical constants related to the number of charge carriers and conduction activation energy, respectively.

$$\log \sigma = T^{-1/2} A \exp[-B/(T-T_o)] \qquad (1)$$

According to the configurational entropy model of Gibbs et al., the T_o is predicted to be approximately 50K below the T_g. Fig. 4 shows the VTF plots of the single ion conductors. The linear relations are observed, representing that the ionic conduction in these single ion conductors is well described by VTF relation. Their slope values are quite comparable among each other. Table 1 lists the value of B for the various single ion conductors. These values are ranged from 1013 to 1125. There is not a significant change in the B values with the type of the cation.

Table 1. Values of B in VTF equation for P(MEO$_9$-AACM)

Ionic content (O/M$^+$)	M=Li	Na	K
60	1027	1067	1096
30	1062	1058	1105
18	1125	1031	1013

Dynamic bond percolation(DBP) theory (12~17) provides an useful concept for understanding this behavior. The DBP theory assumes a solid-state type jumping of ions along short strings of sites which occasionally connect together according to a liquid-state-type self-diffusion mechanism of the sites themselves. The DBP theory can be generalized to cover a multitude of situations. It reduces to the Arrhenius equation if the fraction of sites which percolated is large. If the faction of the sites which percolated is small and the host polymer is governed by free-volume theory, the result of DBP theory is simply the VTF equation. In this case, the parameter B applies either to the polymer host or to the ions according to the relative rates of ion hopping and string renewal: if the renewal rate is faster, ion parameters should be used, if ion hopping is faster, the parameters used are those of the polymer. Physically, the renewal event describes a motion of polymer segment which frees a pathway for the ions to move and the hopping event involves the change of the coordination shell by breaking one bond and forming a new one and thus the ion-dipole interaction significantly affects the rate of ion hopping. With the DBP theory, the weak dependency of B on the type of the cation presumably can be interpreted as such that the ion hopping rate is higher than that of string renewal in P(MEO$_9$-AACM), which is the usual case for the ionic conduction in polymeric medium (1).

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