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Short communication

Ionic conductivity studies of gel polyelectrolyte based on ionic liquid

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Abstract

Novel lithium polyelectrolyte-ionic liquids have been prepared and characterized of their properties. Poly(lithium 2-acrylamido-2-methyl propanesulfonate) (PAMPSLi) and its copolymer with *N*-vinyl formamide (VF) also has been prepared as a copolymer. 1-Ethyl-3-methylimidazolium tricyanomethanide (emImTCM) and *N*,*N*-dimethyl-*N*-propyl-*N*-butyl ammonium tricyanomethanide (N_{1134}TCM) which are chosen because of the same with the anion of ionic liquid were prepared. The ionic conductivity of copolymer system (PAMPSLi/PVF/emImTCM: 5.43×10^{-3} S cm^{-1} at 25 °C) exhibits about over four times higher than that of homopolymer system (PAMPSLi/emImTCM: 1.28×10^{-3} S cm^{-1} at 25 °C). Introduction of vinyl formamide into the copolymer type can increase the dissociation of the lithium cations from the polymer backbone. The ionic conductivity of copolymer with emImTCM (PAMPSLi/PVF/emImTCM) exhibits the higher conductivity than that of PAMPSLi/PVF/N_{1134}TCM (2.48×10^{-3} S cm^{-1}). Because of using the polymerizable anion it is seen to maintain high flexibility of imidazolium cation effectively to exhibit the higher conductivity. And also the viscosity of emImTCM (19.56 cP) is lower than that of N_{1134}TCM (28.61 cP). Low viscosity leads to a fast rate of diffusion of redox species.

Keywords: Ionic conductivity; Copolymer; Ionic liquid; Imidazolium cation; Quaternary ammonium cation; Tricyanomethanide

1. Introduction

Ionic liquids have the properties of non-volatile, non-flammability, large stable liquid range, low viscosity, superior solvating liquids, hydrophobicity or hydrophilicity, high thermal and electrochemical stability [1–3]. The physical properties at room temperature substituted imidazolium base have been extensively studied for their application as electrolytes for batteries and capacitors [4,5]. In most of these studies, *N*,*N*′-dialkylimidazolium salt, especially 1-ethyl-3-mehyl-imidazolium salt was focused empirically because of low viscosity and correspondingly high ionic conductivity [6].

In my previous research works [7,8] the ionic conductivities of plasticized polymer electrolyte were mentioned. Those plasticized polymer electrolytes showed some problems. They exhibited low conductivity by the low transference numbers of the lithium cations and the volatility of the plasticizer caused the materials to be unstable.

Recently, ambient temperature ionic liquids have been used in polymer electrolyte samples where the ionic liquids play the role of both a charge carrier and a non-volatile plasticizer. Especially, alkyl imidazolium-based ionic liquids are capable of dissolving up to molar concentrations of lithium salt and functioning as the electrolytic material in a lithium battery. The substitution of the methyl group has been shown to increase the electro-chemical stability of the imidazolium by over 0.25 V [7,8]. Poly(lithium2-acrylamido-2-methyl-propanesulfonate) (PAMPSLi) as a water-soluble and proton-conducting polyelectrolyte was widely used. PAMPSLi and poly(*N*-vinyl formamide) (PVF) with ionic liquids (emImTCM: 1-ethyl-3-methyl imidazolium tricyanomethanide, N_{1134}TCM: *N*,*N*-dimethyl-*N*-propyl-*N*-butyl ammonium tricyanomethanide) were used as a new polyelectrolyte system.

In this work, the novel lithium polyelectrolyte with ionic liquid, PAMPSLi/PVF/emImTCM, PAMPSLi/emImTCM,

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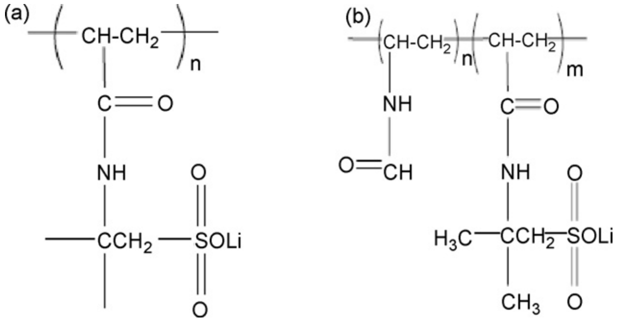


Scheme 1. Structure of (a) PAMPSLi and (b) PAMPSLi/PVF.

PAMPSLi/PVF/N_{1134}TCM PAMPSLi/N_{1134}TCM were prepared and characterized their properties (Scheme 1).

2. Experimental

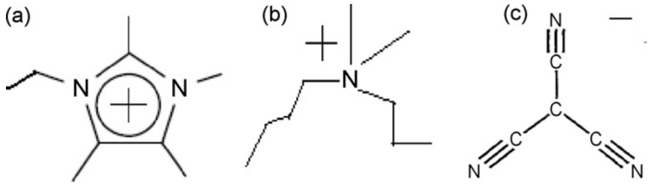
The lithium-2-acrylamide-2-methyl propanesulfonate (AMPSLi) was prepared by the reaction of 2-acrylamide-2-methyl propanesulfonic acid (Aldrich) with lithium carbonate in a water solution placed in an ice bath; this monomer was polymerized at room temperature as the water was removed from the monomer aqueous solution by the water pump. The copolymer poly(lithium2-acrylamido-2-methyl-propanesulfonate (PAMPSLi)/poly(*N*-vinyl formamide) (PVF) was synthesized by polymerization of *N*-vinyl formamide (Aldrich) with AMPSLi at ~80 °C in the presence of a little $K_2S_2O_8$, initiator [9]. The mole ratio of AMPSLi to VF in the copolymer PAMPSLi/PVF is 1:9. The polymer products, PAMPSLi and PAMPSLi/PVF, were dried under vacuum (~80 Torr) at 65 °C for at least 48 h.

2.1. 1-Ethyl-3-methylimidazolium tricyanomethanide (emImTCM)

EmImTCM was prepared as follows: 1-ethyl-3-methylimidazolium bromide (emImBr: 1.84 g, Ag: 5.68 mmol) and AgTCM (2 g, 10.16 mmol) were mixed and stirred at 25 °C for overnight. From the solution, the bromide was filtered and evaporated the filtrate. The pale yellow residue was dissolved in dichloromethane and dried over anhydride magnesium sulfate. Pale yellow liquid (emImTCM) was obtained about 1.5 g. ^{1}H NMR ($CDCl_3$): δ 1.65 (t, 3H, CH_3), 3.98 (s, 3H, CH_3), 4.30 (q, 2H, CH_2), 7.38 (d, 2H, CH), 8.88 (s, 1H, CH). ^{13}C NMR ($CDCl_3$): δ 14.2 (CH_3), 35.7 (CH_3), 44.7 (CH_2), 120.4 (CH), 122.0 (CH). ES-MS: ES$^+$, *m/z* 110.6 emIm$^+$. ES$^-$, *m/z* 89.5 TCM$^-$.

2.2. N,N-Dimethyl-N-propyl-N-butylammonium tricyanomethanide (N_{1134}TCM)

N_{1134}TCM was obtained same method used for emImTCM. *N*,*N*-Dimethyl-*N*-propyl-*N*-butylammonium bromide (N_{1134}Br) and AgTCM were used. AgTCM, emImBr, N_{1134}Br were prepared in our laboratory by the method of Andersen et al. and Konnert et al. [10].



Scheme 2. Structure of (a) 1-ethyl-3-methylimidazolium cation, (b) *N*,*N*-dimethyl-*N*-propyl-*N*-butylammonium cation and (c) tricyanomethanide anion.

^{1}H NMR (CH_2Cl_2): δ 1.03 (m, 6H, CH_3), 1.45 (m, 2H, CH_2), 1.82 (m, 4H, CH_2), 3.08 (s, 6H, CH_2), 3.32 (d, 4H, CH_2), 4.67 (s, CH_2). ES$^+$, *m/z* 144.0 $N_{1134}{}^+$. ES$^-$, *m/z* 89.7 TCM$^-$.

PAMPSLi/emImTCM and PAMPSLi/PVF/emImTCM were mixed with 10 wt% polyelectrolyte and 90 wt% ionic liquid with ethanol and stirred over night. The final products were dried under vacuum (~80 Torr) at 65 °C for at least 72 h. Viscosity was measured using an ASTM Kinematic viscometer size 500 inside a nitrogen dry box, at ambient temperature (23 °C) (flow times were in the order of minutes).

Thermal analysis of samples was performed using a TA instruments differential scanning calorimeter (DSC Q100) at a scanning rate of 10 °C min^{-1} over a temperature range of −150 °C to 150 °C. Glass transition (T_g) and melting points (T_m) were determined as a function of composition. Before the DSC measurement, all samples were dried under vacuum at room temperature for at least 3 days.

Conductivity measurements were carried out in a small conductance cell. The samples were loaded and hermetically sealed in the cell using a SI1260 impedance/gain phase analyzer and Solatron 1296 with Solatron impedance measurement software (v.3.2.0). The cell constants were determined before and after measurements at room temperature using 0.01 M KCl solution. Measurements were taken at 10 °C increments from 25 °C to 65 °C using the Eurotherm 2240E (Scheme 2).

3. Results and discussion

The mole ratio of AMPSLi to VF in the copolymer PAMPSLi/PVF is 1:9. At room temperature, homopolymer (PAMPSLi) and copolymer (PAMPSLi/PVF) were powder, but after the polymers dissolving in ionic liquids, PAMPSLi/emImTCM, PAMPSLi/PVF/emImTCM, PAMPSLi/N_{1134}TCM, PAMPSLi/PVF/N_{1134}TCM (10% polymer + 90% ionic liquid) were changed gel-like samples. Fig. 1 shows the thermal traces of PAMPSLi/emImTCM (a), PAMPSLi/PVF/emImTCM (b), PAMPSLi/N_{1134}TCM (c), PAMPSLi/PVF/N_{1134} _TCM (d). The glass transition temperature(T_g) of PAMPSLi/PVF/emImTCM (−86.63 °C) was slightly lower than that of PAMPSLi/emImTCM (−85.49 °C). The glass transition temperature (T_g) of PAMPSLi/PVF/N_{1134}TCM (−89.7 °C) was also slightly lower than that of PAMPSLi/N_{1134}TCM (−88.1 °C). These DSC results exhibited the glass transition temperature of copolymer-type polyelectrolyte in ionic liquid system is lower than that of homopolymer type. These results are expected that ionic conductivity of copolymer system is higher than that of

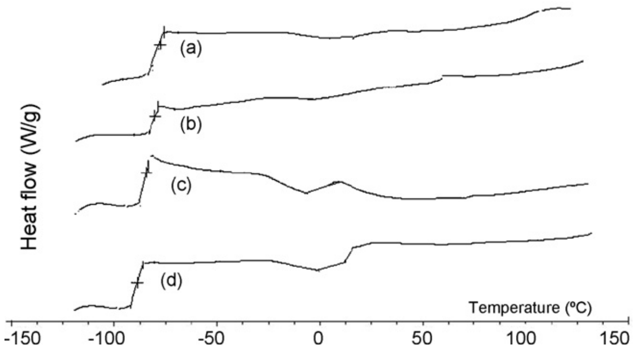


Fig. 1. (a) DSC thermograms of the PAMPSLi/emImTCM, (b) PAMPSLi/PVF/emImTCM, (c) PAMPSLi/N$_{1134}$TCM and (d) PAMPSLi/PVF/N$_{1134}$ TCM.

homopolymer system. But it shows only the little difference of the glass transition temperature, respectively. The glass transition temperature of a pure emImTCM is −85.9 °C and that of a pure N$_{1134}$TCM is −87 °C and the melting point of pure emImTCM and pure N$_{1134}$TCM were −10 °C and 6.5 °C, respectively (not shown here). The glass transition temperature values of a pure emImTCM is −85.09 °C, emImDCA is −104 °C, N$_{1134}$TCM is −87 °C, P$_{13}$TCM is −98 °C and P$_{14}$TCM is −92 °C [10]. Generally, 1-ethyl-3-methyl imidazolium forms exhibit the low viscosity and low melting point. But emImTCM is quite viscous (cP: 19.56) by comparison with related ionic liquids; this presumably reflects strong electrostatic interactions between ions. So, it exhibits the slightly higher glass transition temperature than that of other ionic liquids. The melting point of pure emImTCM and pure N$_{1134}$TCM were −10 °C and 6.5 °C, respectively. But as you can see in Fig. 1, all polymers with ionic liquid samples were not exhibited the melting peak from −150 °C to 150 °C. This means that the presence of polymer in ionic liquids hinders the crystallization of the ionic liquid [9]. Fig. 2 shows that the ionic conductivities of emImTCM, PAMPSLi/emImTCM and PAMPSLi/PVF/emImTCM from 25 °C to 65 °C. The ionic conductivities are increased as the temperature increasing. The ionic conductivity of emImTCM is 20 mS cm^{-1} at 25 °C. This value is superior to that of emImTFSA (8.8 mS cm^{-1}) and N$_{1134}$TCM (8 mS cm^{-1}) but similar to that for emImDCA (22 mS cm^{-1}) [10]. The ionic conductivity of copolymer sample (PAMPSLi/PVF/emImTCM: 5.43×10^{-3} S cm^{-1} at 25 °C) exhibits about over four times higher than that of homopolymer sample (PAMPSLi/emImTCM: 1.28×10^{-3} S cm^{-1} at 25 °C). First of all, higher conductivity of copolymer system than that of homopolymer system seems to be caused by lower T_g. But it showed only the little difference of T_g, respectively. DSC result does not completely explain the conductivity behaviors of polymer electrolyte. So these results needed to be discussed further. The conductivity of polyelectrolyte is proportional to the concentration of charges in the material. If PAMPSLi and PAMPSLi/PVF have a similar environment in the polyelectrolyte, PAMPSLi/emImTCM seems to be higher concentration of lithium cations and exhibit higher conductivity than PAMPSLi/PVF/emImTCM. But PAMPSLi/emImTCM exhibits the lower conductivity than that of PAMPSLi/PVF/emImTCM.

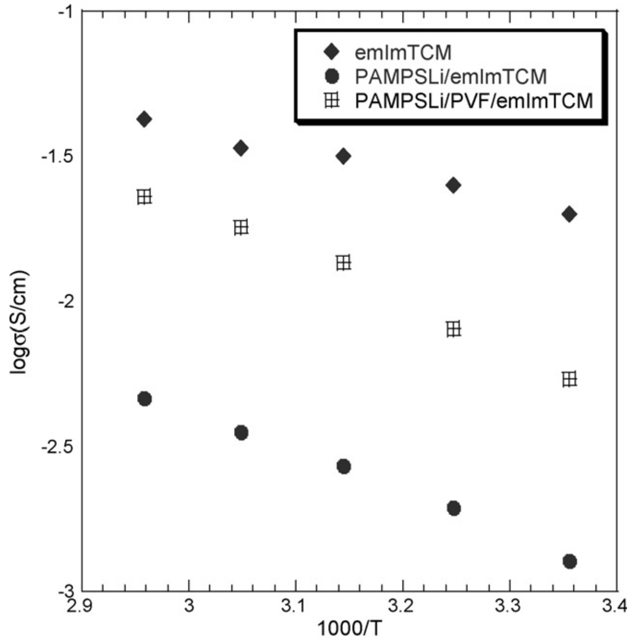


Fig. 2. Conductivity of emImTCM, PAMPSLi/emImTCM and PAMPSLi/PVF/emImTCM as a function of temperature.

This behavior of higher conductivity of copolymer sample can explain by free lithium cations dissociated from the polymer backbone and reducing repulsion of anions. Therefore, these result support that introduction of vinyl formamide into the copolymer type can increased the dissociation the lithium cations from the polymer backbone. The role of vinyl formamide in copolymer is needed investigation further. Fig. 3 shows conductivity of N$_{1134}$TCM, PAMPSLi/N$_{1134}$TCM and PAMPSLi/PVF/N$_{1134}$TCM from 25 °C to 65 °C. Despite the glass transition temperature (T_g) of a pure N$_{1134}$TCM (−87 °C) is lower than that of emImTCM (−85.09 °C), N$_{1134}$TCM exhibits the lower conductivity than that of emImTCM.

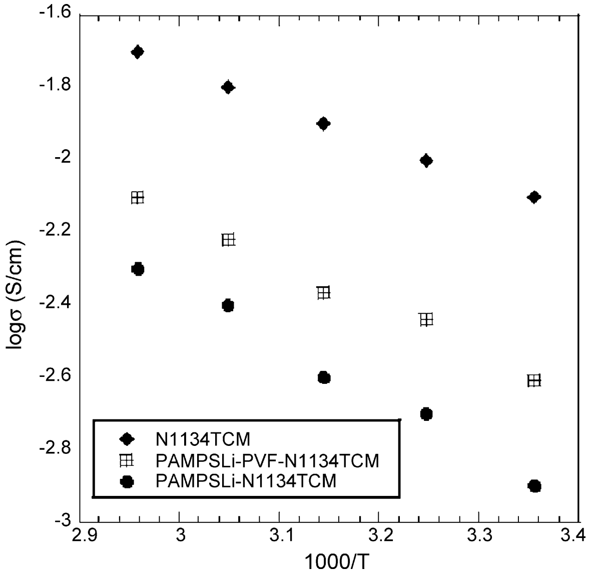


Fig. 3. Conductivity of N$_{1134}$TCM, PAMPSLi/N$_{1134}$TCM and PAMPSLi/PVF/N$_{1134}$TCM as a function of temperature.

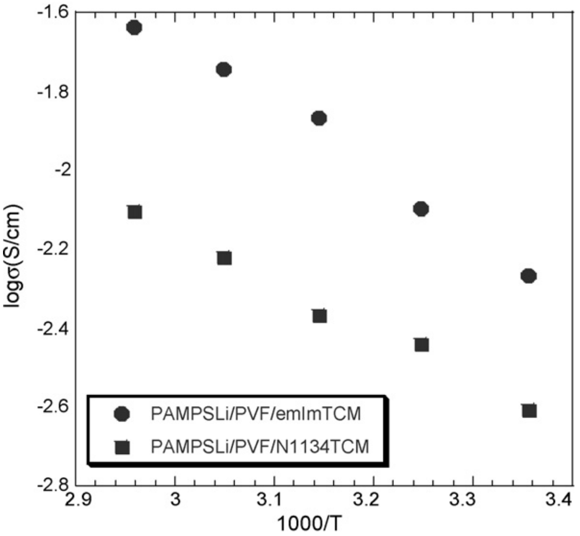


Fig. 4. Conductivity of PAMPSLi/PVF/emImTCM and PAMPSLi/PVF/N_{1134} TCM as a function of temperature.

This result supports that reducing the ionic conductivity of some cyano-containing quaternary ammonium seems to have got to do with the intrinsic miscibility of the ionic liquid solutions. As you can see from Fig. 3, the ionic conductivity of copolymer system also exhibits higher conductivity than that of homopolymer system. Fig. 4 shows the conductivity of PAMPSLi/PVF/emImTCM and PAMPSLi/PVF/N_{1134}TCM as the function of temperature. Despite the glass transition temperature of PAMPSLi/PVF/N_{1134}TCM is lower than that of PAMPSLi/PVF/emImTCM, the ionic conductivity of PAMPSLi/PVF/N_{1134}TCM exhibits lower than that of PAMPSLi/PVF/emImTCM. Some quaternary ammonium cation contributed to increase the conductivity of the solution, while cyano-containing quaternary ammonium and lithium salts decreased the related to the intrinsic miscibility of the ionic liquid solutions [11]. Moreover, the ionic conductivity of PAMPSLi/PVF/emImTCM exhibits fairly higher than that of PAMPSLi/PVF/N_{1134}TCM. The conductivity is changed by the mobility of the ions and ion-pairing phenomenon. Generally, 1-ethyl-3-methyl imidazolium forms exhibit the low viscosity and low melting point [12]. EmImTCM exhibits the lower viscous by comparison with that of N_{1134}TCM. The viscosity of the ionic liquid and its hydrophilicity are critical to achieving high conductivity. The viscosity of N_{1134}TCM (28.61 cP) is higher than that of emImTCM (19.56 cP). This high viscosity leads to a slow rate of diffusion of redox species. Moreover, using the polymerizable anion is seemed to maintain high flexibility of imidazolium cation effectively to exhibit the higher conductivity. So, the ionic conductivity of polyelectrolyte with emImTCM exhibits the higher conductivity (5.43×10^{-3} S cm^{-1}) than that of polyelectrolyte with N_{1134}TCM (2.48×10^{-3} S cm^{-1}).

4. Conclusions

The glass transition temperature (T_g) of a pure emImTCM is −85.09 °C and that of a pure N_{1134}TCM is −87 °C and the melting point of pure emImTCM and pure N_{1134}TCM were −10 °C and 6.5 °C, respectively. The viscosity of N_{1134}TCM (28.61 cP) is higher than that of emImTCM (19.56 cP). The ionic conductivity of copolymer system (PAMPSLi/PVF/emImTCM: 5.43×10^{-3} S cm^{-1}, PAMPSLi/PVF/N_{1134}TCM: 2.48×10^{-3} S cm^{-1}) exhibits the higher conductivity than that of homopolymer system (PAMPSLi/emImTCM: 1.28×10^{-3} S cm^{-1}, PAMPSLi/N_{1134}TCM: 1.25×10^{-3} S cm^{-1}). This behavior of higher conductivity of copolymer sample can explain by free lithium cations dissociated from the polymer backbone and reducing repulsion of anions. Therefore, these result support that introduction of vinyl formamide into the copolymer type can increase the dissociation the lithium cations from the polymer backbone. The reason why the ionic conductivity of PAMPSLi/PVF/emImTCM is higher than that of PAMPSLi/PVF/N_{1134}TCM is that emImTCM exhibits the lower viscous by comparison with that of N_{1134}TCM. The viscosity of the ionic liquid and its hydrophilicity are critical to achieving high conductivity. This high viscosity leads to a slow rate of diffusion of redox species. Moreover, using the polymerizable anion is seemed to maintain high flexibility of imidazolium cation effectively.

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