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A New Polymer Electrolyte Composed of Poly(N-vinylacetamide), Poly(ethylene glycol), and Lithium Trifluoromethanesulfonate

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A new solid composite of poly(N-vinylacetamide), lithium trifluoromethanesulfonate, and poly(ethylene glycol) was prepared and characterized as a polymer electrolyte with high conductivity.

Water-free polymer electrolyte has attracted great attention because of a wide range of practical applications in dry battery, sensor, and other electrochemical devices. So-called polymer electrolytes are generally composed of a water-soluble polymer and a strong electrolyte such as a salt between strong acid and strong base. The water-soluble polymer for a polymer electrolyte is required to be capable of dissolving the electrolyte with high coordination ability to the dissociated ion and letting the ion move through the flexible polymer chain without difficulty.1) High flexibility of a polymer is attainable only above its glass transition temperature(Tg). In accord with these requirements Wright et al. found that the mixture of poly(ethylene oxide)(PEO) and an alkali metal salt such as NaSCN gave a solid composite with moderately high ion conductivity.2)

Further, some attempts have been made to prepare composites with high ion conductivity by adding some amount of plasticizer which makes a polymer chain flexible. As to the composite of polymer/salt/plasticizer systems were reported polyacryronitrile/$LiClO_4$/ethylene carbonate or propylene carbonate,3-5) poly(vinylpyrrolidone)(PVP)/$LiCF_3SO_3$/poly(ethylene glycol)(PEG),6) and poly(vinylene carbonate)/$LiCF_3SO_3$/12-crown-4 7) systems.

In this letter poly(N-vinylacetamide)(PVAA) was paid attention as a new water-soluble polymer for a polymer electrolyte because PVAA and PVP constitute a family of poly(N-vinylamide)s but PVAA has not been evaluated yet for a polymer electrolyte. Lithium trifluoromethanesulfonate and PEG were employed as a strong electrolyte and a plasticizer, respectively, by reference to the PVP/$LiCF_3SO_3$/PEG system.6) The composite of ternary PVAA/$LiCF_3SO_3$/PEG system was characterized as a polymer electrolyte.

N-Vinylacetamide(VAA) was prepared in the pyrolysis reaction of N-(1'-methoxyethyl)acetamide at 550 °C according to the method of Stackman et al. ;8) colorless prism, 70% yield, mp 51 °C (lit.8) 53 °C), IR; 3270, 1670, 1645, 1530 cm^{-1}, ^1H NMR(DMSO-d_6); δ 9.82 (s, 1H), 7.1-6.4(m, 1H), 4.51(d, J=23.4 Hz, 1H), 4.31(d, J=16.2 Hz, 1H), 1.89(s, 3H).

Polymerization of VAA was carried out in 2-propanol at 60 °C with 2,2'-azobisisobutyronitrile according to the method of Dawson et al.9) The polymer obtained as white powder is soluble in water, methanol, and dimethylsulfoxide. Its number-average molecular weight($\overline{M}_n$) was measured to be 110000 by gel permeation chromatography(GPC) using 0.02% aqueous sodium azide solution and pullulan as an eluent and standards, respectively.

A solid composite of the PVAA/$LiCF_3SO_3$/PEG system was prepared as follows. Given amounts of PVAA, $LiCF_3SO_3$, and PEG(average MW=400) were added to somewhat excess of methanol and the mixture was stirred under nitrogen for 3 h to be homogeneous. Some volume of the solution was placed on a glass plate in a vacuum desiccator and then it was set at room temperature under reduced pressure to remove methanol. The film-like solid obtained was further placed at 50 °C under vacuum for 48 h to give a colorless transparent flexible composite.

Table 1 shows the glass transition temperatures(Tg) of the composites with various compositions. All of the composites exhibited each single value of Tg between -18 °C and -54 °C, suggesting that they are very homogeneous.[10,11] A composite of PVAA(1)/$LiCF_3SO_3$(1)/PEG(2) was found to be a flexible film in contrast with a brittle solid composite of PVP(1)/$LiCF_3SO_3$(1)/PEG(2) system.[6]

Table 1. Glass Transition Temperature(Tg) for PVAA/$LiCF_3SO_3$/PEG System

PVAA[a]	$LiCF_3SO_3$[a]	PEG[a]	Tg[b]/°C
1	0	0	190
2	1	0	205
1	1	2	-18
2	1	4	-28
1	1	4	-33
3	1	6	-54

a)The numbers denote mole ratios among VAA repeating unit in PVAA, $LiCF_3SO_3$, and ethylene oxide unit in PEG in the composites. b)Containing experimental error of about 2 °C.

Figure 1 shows the IR spectra in the carbonyl region for PVAA and the composites of the PVAA/$LiCF_3SO_3$/PEG system. PVAA exhibits an absorption peak at 1658 cm^{-1} with a shoulder in the higher frequency side. When added $LiCF_3SO_3$ and PEG, the shoulder made a disappearance and a little bit bathochromic shift was observed by a few cm^{-1}s. Similar changes in the carbonyl absorption were observed for the composite of PVP/ $LiCF_3SO_3$/PEG system by Spindler et al., who suggested an attribution of such changes to the coordination of Li cation to carbonyl group.[6]

Conductivity measurements of the composites were performed on a disk of 10-mm diameter and 0.5-1.5 mm thickness which was prepared under the pressure of 400 kg cm^{-2}. The disk was sandwiched between Pt plates and an a.c. complex impedance response was measured in the temperature range of 40 to 100 °C in the frequency range of 1 Hz to 65 kHz in order to obtain ion conductivity(σ).[12]

Figure 2 shows plots of log σ vs. 1/T for the composites of various composition of PVAA(1) /$LiCF_3SO_3$(1)/PEG(2), PVAA(2)/$LiCF_3SO_3$(1)/PEG(4), and PVAA(3)/$LiCF_3SO_3$(1)/PEG(4) system together

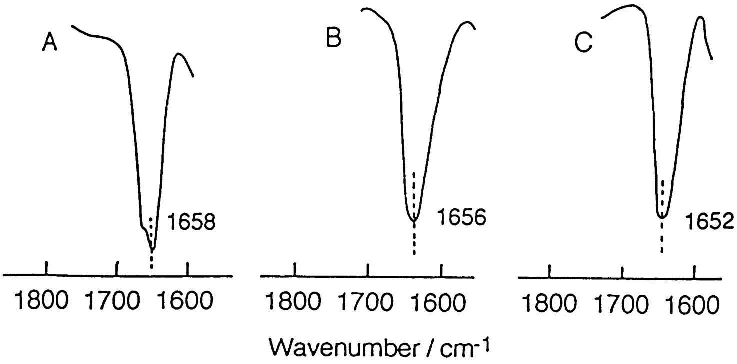

Fig.1. Infrared spectra in the carbonyl region for PVAA and PVAA/$LiCF_3SO_3$/PEG composites: (A)PVAA; (B)PVAA(2)/ $LiCF_3SO_3$(1)/PEG(4); (C)PVAA(1)/$LiCF_3SO_3$ (1)/PEG(2).

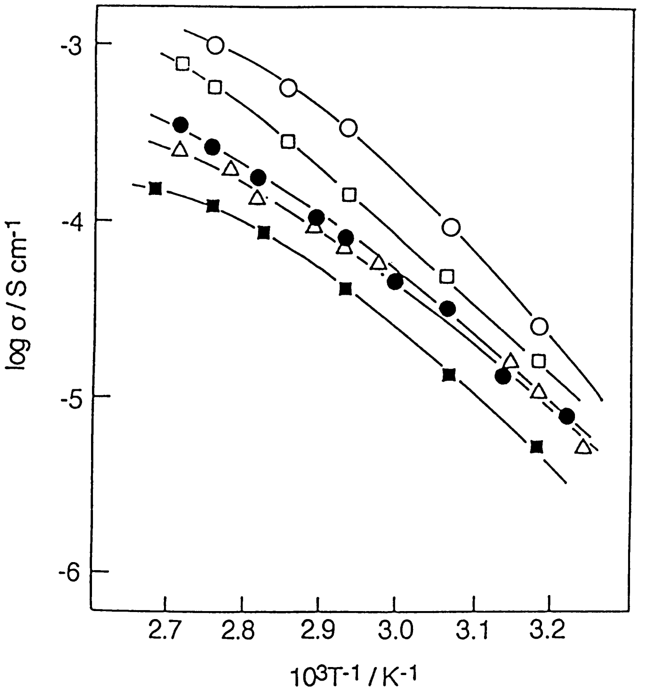

Fig. 2. log σ - 1/T plots for PVAA and PVP composites; (○)PVAA(1)/$LiCF_3SO_3$(1)/PEG(4), (□)PVAA(2)/ $LiCF_3$-SO_3(1)/PEG(4), (●)PVAA(1) /$LiCF_3SO_3$(1)/ PEG(2), (■) PVAA(3)/$LiCF_3SO_3$(1) /PEG(6), and (Δ)PVP(2)/ $LiCF_3$-SO_3(1)/PEG(4).

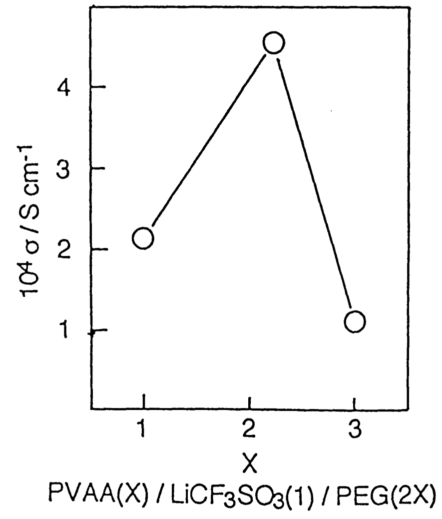

Fig. 3. Plot of ionic conductivity for PVAA/$LiCF_3SO_3$/PEG composites at 80 °C.

with the corresponding one for the composite of PVP(2) /$LiCF_3SO_3$(1)/PEG(4) system. It was pointed out that the plots for the PVAA composites, as well as that for PVP composite, display convex curves that is characteristic of an electrolyte in very amorphous state.[13)] The conductivity for the composite of PVAA(2)/$LiCF_3SO_3$(1) /PEG(4) system is higher than that of PVP(2)/$LiCF_3SO_3$(1)/PEG(4) system, suggesting that the ions on the polymer chain of the former move more easily than ones on the latter do.

Figure 3 shows the conductivities of fixed composition ratio of PVAA(X)/$LiCF_3SO_3$(1)/ PEG(2X) vs. various X values. It was found that the maximum conductivity appears at X=2. The more amount the plasticizer leads the more flexible the polymer chain, but the less the ion concentration. Ion conductivity for the composite is determined by both the mobility of the ion carrier and the concentration of the carrier. Therefore, the balance between them affords the maximum of the conductivity.

Finally, the composite of PVAA, $LiCF_3SO_3$, and PEG system gave an amorphous solid polymer electrolyte with high conductivity. The composite with the composition of PVAA(2)/$LiCF_3SO_3$(1)/PEG(4) was found to show maximum in ion conductivity and furthermore to be a little bit higher in conductivity than the corresponding PVP composite, indicating that PVAA is useful for a polymer electrolyte as well as PVP.

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