

High Ionic Conductivity of New Polymer Electrolytes consisting of Polypyridinium, Pyridinium and Aluminium Chloride

Masayoshi Watanabe,^a Shin-ichiro Yamada,^b Kohei Sanui^b and Naoya Ogata^{a,b}

^a Department of Chemistry, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240, Japan

^b Department of Chemistry, Sophia University, Kioi-cho, Chiyoda-ku, Tokyo 102, Japan

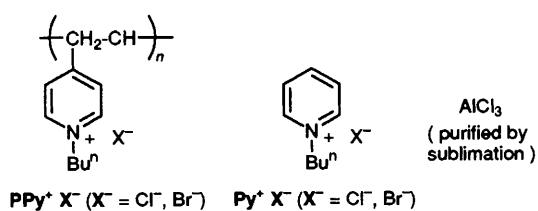
Polymer complexes consisting of polypyridinium, pyridinium and aluminium chloride are found to be a new class of highly conductive polymer electrolytes, which exhibit a high ionic conductivity of 10^{-3} S cm⁻¹ at room temperature within range of the conductivity of electrolyte solutions, in spite of film-forming properties.

Polymer electrolytes¹⁻⁵ have occupied an important position in solid-state ionics, because of their unique properties, such as thin film-forming properties, good processibility, flexibility, light weight, elasticity (plasticity) and transparency as well as relatively high ionic conductivity and wide potential window. Some of these characteristics cannot be attained by hard inorganic solid electrolytes, including inorganic glasses, and thus, polymer electrolytes have been exploited to bridge a gap between fluid electrolyte solutions and hard inorganic solid electrolytes.

Conventional polymer electrolytes, mostly based on poly(ethylene oxide) derivatives, are solid solutions of electrolyte salts in polymers.¹⁻⁵ To date, the highest conductivity range attained at room temperature is 10^{-4} – 10^{-5} S cm⁻¹.¹⁻⁵ The limitation in conductivity may be caused by the following facts:¹⁻⁵ ionic motion in these polymer electrolytes is coupled with the local segmental motion; and the increases in carrier-ion density and mobility are inconsistent, because the carrier generation occurs *via* the interaction of polymer segments with ions, resulting in the increase in the glass transition temperatures with increasing ionic concentration, that is, the increased salt concentration causes the decrease in mobility. The achievement of high carrier-ion density and decoupling of ion transport from matrix polymer motion will considerably enhance the ionic conductivity. We have directed our attention to the fact that mixtures of certain pyridinium^{6,7} or imidazolium salts⁸ and aluminium chloride

(AlCl₃) form room temperature ionic liquids (molten salts), where only ionic species are components of the liquids. Ionic conductivity of the molten salts is fairly high because of considerably high carrier density as well as reasonably high carrier mobility. It has been discovered that polypyridinium or polyimidazolium salts form homogeneous complexes with the ionic liquids (electrolyte salts) and that resulting polymer complexes have high ionic conductivity as well as film forming properties. In this communication, the ion transport properties of polymer complexes based on polypyridinium salts are described.

Sufficiently pure components: poly(1-butyl-4-vinylpyridinium halide) [PPy⁺X⁻, M_r of poly(4-vinylpyridine) before quaternization is 3.58×10^5], 1-butylpyridinium halide (Py⁺X⁻) and AlCl₃ were used to prepare the polymer



Scheme 1

complexes (Scheme 1). The quaternized ratios of poly(4-vinylpyridine) with bromobutane and chlorobutane were found to be unity by NMR spectra.[†] In an argon-filled dry box, Py^+X^- and AlCl_3 were mixed at various compositions to yield ionic liquids (room temperature molten salts). The polymer complexes were made by the dissolution of PPy^+X^- into Py^+X^- - AlCl_3 molten salts at an elevated temperature (*ca.* 150 °C), followed by cooling the mixtures to room temperature. The dissolution of PPy^+X^- greatly increased the viscosity of the mixtures even at 3–5 unit mol%, and the complexes obtained after cooling behaved as viscoelastic solids at room temperature. This viscoelastic nature allowed the complexes to be processed into thin films. When the content of PPy^+X^- is more than 25 unit mol%, nitromethane was added to the molten salts to form homogeneous solutions, and PPy^+X^- was dissolved in the solutions. In order to attain complete dissolution of PPy^+X^- , the least possible amount of ethanol (at most 10 vol% to nitromethane) was added to the solution.[‡] The polymer complex films were obtained by casting the solutions onto poly(tetrafluoroethylene) substrates, followed by evaporation of the solvents in a dry box, and finally the solvents were allowed to evaporate completely under vacuum. The ionic conductivity of these polymer complexes was measured by the complex impedance method (YHP 4192A) with platinum electrodes.

It was found that the ionic conductivity of the complexes was much affected by the composition of each component,[§] and the highest conductivity measured was about $10^{-3} \text{ S cm}^{-1}$ at room temperature (Fig. 1). The conductivity measurements here were limited to the polymer complexes consisting of PPy^+Br^- , Py^+Br^- and AlCl_3 . The conductivity of higher than $10^{-3} \text{ S cm}^{-1}$ is comparable to that of the molten salts, not including PPy^+Br^- , and is much higher than that of conventional polyether-based polymer electrolytes by a factor of 10^2 to 10^3 , and closely approaches the conductivity of ordinary fluid electrolyte solutions. When the composition of the molten salt is the same, the ionic conductivity of the polymer complexes monotonically increased with increasing the content of the molten salt (Fig. 2). The increase in the content of the molten salt increases the number of carrier ions and/or their mobility.

The complexation of PPy^+X^- with Py^+X^- - AlCl_3 molten salts has been explored by fast atom bombardment (FAB) mass, Raman and IR spectroscopy. In the molten salts themselves ($0.4 < \text{AlCl}_3/\text{Q}^+\text{Cl}^- < 2$; Q^+ : quaternized pyridinium or imidazolium salt), the following important ionic reactions (acid–base equilibrium) have been generally re-

[†] The quaternization reactions were carried out in \bar{N},\bar{N} -dimethylformamide at refluxing temperatures of bromobutane and chlorobutane for 7 days. The ring protons of pyridine in ^1H NMR spectra before the quaternization, appeared at δ 8.33 (2H, m) and 6.40 (2H, m) from SiMe_4 in CDCl_3 , completely shifted to δ 8.77 (2H, m) and 7.76 (2H, m) from SiMe_4 (external standard) in D_2O after the quaternization.

[‡] Solvolysis reaction of AlCl_3 with ethanol readily occurred if ethanol was added to AlCl_3 before making the molten salts. However, when ethanol was added to the molten salts diluted by nitromethane, the evolution of hydrogen chloride was not observed as far as checked by litmus test. Although the addition of ethanol was not preferable in terms of the possibility of the solvolysis reaction, it was necessary to obtain the homogeneous polymer solutions.

[§] The exact reason for the abrupt drops in the conductivity for the polymer complexes of PPy^+Br^- - Py^+Br^- - AlCl_3 10:40:50 and 10:50:40 at *ca.* 0 and -10°C , respectively, is still not clear. We suspect that these drops correspond to the melting points of the molten salts, since the melting points of molten salts consisting of approximately equimolar mixtures of pyridinium or imidazolium salts and AlCl_3 are generally much higher than those of 1:2 and 2:1 eutectic mixtures.^{6,8}

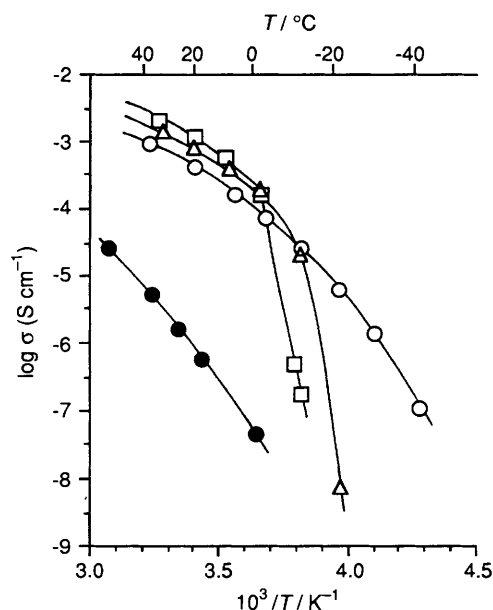


Fig. 1 Temperature dependence of ionic conductivity for polymer complexes: \circ , PPy^+Br^- - Py^+Br^- - AlCl_3 10:30:60; \square , PPy^+Br^- - Py^+Br^- - AlCl_3 10:40:50; \triangle , PPy^+Br^- - Py^+Br^- - AlCl_3 10:50:40; \bullet , PPy^+Br^- - Py^+Br^- - AlCl_3 30:35:35

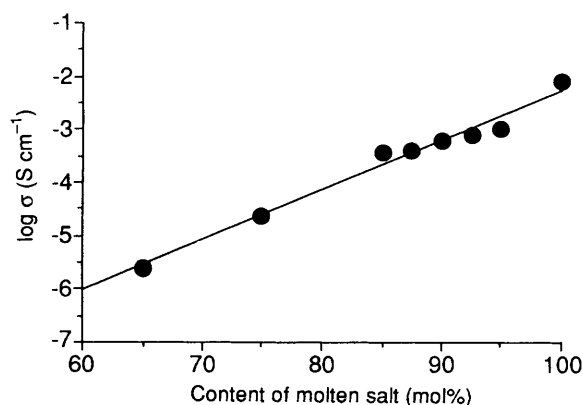
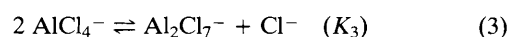
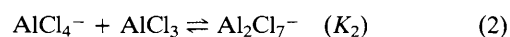
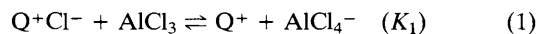


Fig. 2 Ionic conductivity of polymer complexes at 33 °C as a function of content of molten salt (Py^+Br^- - AlCl_3 2:1)

ported, eqns. (1)–(3),⁹ where K_1 – K_3 are equilibrium constants



of the reactions. Since both K_1 and K_2 are quite large, whereas K_3 is quite small, the only cationic species existing in the systems are Q^+ . On the contrary, anionic species vary depending on the composition. At $\text{AlCl}_3/\text{Q}^+\text{Cl}^-$ being unity (neutral melt), AlCl_4^- is the only existing anionic species. At $\text{AlCl}_3/\text{Q}^+\text{Cl}^- < 1$ (basic melt), Cl^- is left in addition to the formation of AlCl_4^- , while Al_2Cl_7^- is formed in addition to AlCl_4^- at $\text{AlCl}_3/\text{Q}^+\text{Cl}^- > 1$ (acidic melt). FAB mass spectra (JEOL JMS-SX102A) of negative ions for the polymer complexes consisting of PPy^+Br^- , Py^+Cl^- and AlCl_3 (10:40:50) revealed the formation of AlCl_3Br^- ($m/z = 212$) in addition to AlCl_4^- ($m/z = 169$), indicating that PPy^+Br^- takes part in the ionic equilibrium reactions. Also, Raman and IR spectra for the polymer complexes of PPy^+Cl^- - Py^+Cl^- - AlCl_3 (10:40:50) indicated the formation of AlCl_4^- . We presume at present that PPy^+X^- is involved in the ionic

reactions, in the same way that Py^+X^- is in ionic liquids, and exists as PPy^+ in the polymer complexes. It should be noted that the acid–base equilibrium of the electrolytes is not kept constant in Fig. 2.

The high ionic conductivity of the polymer complexes may be caused by the large number of carrier ions as well as their high mobility, because they consist of only ionic species, including polypyridinium ions, and Py^+X^- – AlCl_3 functions not only as carrier-ion source but also as a plasticizing electrolyte toward PPy^+X^- , presumably resulting in decoupling of the segmental motion and the ionic motion. The present polymer complexes are completely different from conventional polyether-based polymer electrolytes and a new class of highly conductive polymer electrolytes. It has also been reported, for instance in the LiClO_4 –ethylene carbonate–polyacrylonitrile system,¹⁰ that a compatible polymer to a liquid electrolyte solution does not reduce appreciably the conductivity while imparting good mechanical properties. However, the polymers in the present system not only give the polymer complexes film forming properties but also participate in the ionic equilibrium reactions. Consequently, changing the composition of the polymer, the ionic transport number of the resulting polymer complexes would be controlled, because the macromolecular ions are not as mobile as the monomeric ions. Further study is now in progress.

This research is partially supported by a Grant in Aid for Scientific Research (No. 03750655) from the Ministry of

Education, Science and Culture, and by Iketani Science and Technology Foundation.

Received, 1st February 1993; Com. 3/00598D

References

- 1 *Polymer Electrolyte Reviews 1 and 2*, ed. J. R. MacCallum and C. A. Vincent, Elsevier Appl. Sci., London, 1987 and 1989.
- 2 M. B. Armand, *Ann. Rev. Mater. Sci.*, 1986, **16**, 245.
- 3 C. A. Vincent, *Prog. Solid State Chem.*, 1987, **17**, 145.
- 4 M. Watanabe and N. Ogata, *Br. Polym. J.*, 1988, **20**, 181.
- 5 M. A. Ratner and D. F. Shriver, *Chem. Rev.*, 1988, **88**, 109.
- 6 F. H. Hurley and T. P. Wier, Jr., *J. Electrochem. Soc.*, 1951, **98**, 203.
- 7 R. J. Gale, B. Gilbert and R. A. Osteryoung, *Inorg. Chem.*, 1978, **17**, 2728; J. Robinson and R. A. Osteryoung, *J. Am. Chem. Soc.*, 1979, **101**, 323.
- 8 J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263; A. A. Fannin, Jr., D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes and J. L. Williams, *J. Phys. Chem.*, 1984, **88**, 2614.
- 9 R. A. Osteryoung, *Organic Chloroaluminate Ambient Temperature Molten Salts*, in *Molten Salt Chemistry*, ed. G. Mamantov and R. Marassi, Reidel, Dordrecht, 1987, pp. 329–364 and references cited therein.
- 10 M. Watanabe, M. Kanba, K. Nagaoka and I. Shinohara, *J. Polym. Sci., Polym. Phys. Ed.*, 1983, **21**, 939.