Ionic conductivity and electric relaxation in the poly(NN-dimethylacrylamide)-$LiClO_4$ system

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The poly(NN-dimethylacrylamide)-$LiClO_4$ system has been investigated regarding ionic conductivity and electric relaxation. This material may contain up to 29 mol% $LiClO_4$ while still being an amorphous and transparent ionic conductor. The conductivity for this composition is of the order of 10^{-9} (ohm cm)$^{-1}$ at room temperature while it increases to $7 \cdot 10^{-7}$ (ohm cm)$^{-1}$ at 100 °C. The activation energy according to the conductivity measurements is 1.1 eV. The system poly(methylmethacrylate)-$LiCF_3SO_3$ was also investigated but only very low ionic conductivities were detected.

Key words: Ionic conductivity, electric relaxation dimethylacrylamide, lithium perclorate, polymer electrolyte.

Introduction

During the last few years the interest for ion conducting polymers has grown rapidly [1–5]. The systems that have been studied most have been based on poly(ethylene oxide) (PEO) and it has been shown that a high ionic conductivity occurs mainly above the glass transition temperature in elastomeric materials, while crystalline materials have low ionic conductivities [3].

In many ion conducting glasses the ionic conductivity increases with increasing amounts of the network modifier [6] i.e. a high conductivity may be obtained by adding a rather large amount of an inorganic salt to the glass. In the present paper we report on studies of the ionic conductivity when $LiClO_4$ is added to a transparent amorphous polymer, poly(NN-dimethylacrylamide) (PDMA). The glass transition temperature for dominantly atactic PDMA is 120 °C [7]. The DMA monomer unit, see Fig. 1, contains one oxygen in the side group rather than in the polymer backbone as is the case for poly(ethylene oxide). The ionic conductivity of the system poly(methyl methacrylate) (PMMA)-$LiCF_3SO_3$ was also studied.

The electrical relaxation has been studied using electric modulus analysis [8–13]. The complex electric modulus M is equal to the inverse of the complex permittivity,

$$M = (\varepsilon)^{-1} = M' + j M'', \tag{1}$$

and the complex modulus is related to the complex impedance Z through

$$M = j \omega C_0 Z, \tag{2}$$

where C_0 is the vacuum capacitance of the cell. Electric modulus measurements have earlier been performed mainly for β-alumina and ion conducting glasses, where it has been shown to be a useful method to study materials with mobile ions [8–13].

Experimental

NN-dimethylacrylamide monomer (Fluka, 98% pure) was freeze-dried and distilled under vacuum. Dried $LiClO_4$ (Ventron, 99.5% pure) was dissolved in the liquid monomer at 90 °C, and the samples was then freeze-dried again to avoid traces of water. The polymerization was performed at a temperature of

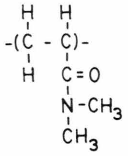

Fig. 1. The poly(NN-dimethylacrylamide) repeat unit.

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40 °C during a few weeks. The PMMA-$LiCF_3SO_3$ samples were prepared in a similar way using 97% pure $LiCF_3SO_3$ (Aldrich Chemical Company Inc., England).

The ionic conductivity measurements were performed using complex impedance analysis [14]. The complex impedance and the electrical modulus were measured in the frequency range 100 Hz to 100 kHz using a computer controlled HP4274A LCR meter. The samples were about 7 mm in diameter and 1–2 mm thick. Graphite electrodes were painted on the sample surfaces using graphite dissolved in alcohol (DAG-580, Acheson, Holland). Another type of electrode that was also used for the PDMA samples was a thin platinum foil which was made to stick to the sample surfaces if these were slightly moistened using a small drop of ethanol. After the application of the graphite or platinum electrodes the sample was dried in vacuum before the measurement was started, since even small amounts of residual solvent may influence the results. Good agreement was obtained between results using the two kinds of electrodes. Wide angle X-ray diffraction measurements have been done using a Philips X-ray diffractometer employing Ni filtered CuKα radiation. All measurements were performed in a nitrogen atmosphere or in vacuum.

Results and Discussion

The electrical conductivity of PDMA samples with 9.4 and 13.5 mol% $LiClO_4$ was negligible, less than 10^{-9} (ohm cm)$^{-1}$ for temperatures between 25 and 115 °C. For samples with 29.4 mol% $LiClO_4$, however, the conductivity was of the order of 10^{-9} (ohm cm)$^{-1}$ at ambient temperature and increased to $7 \cdot 10^{-7}$ (ohm cm)$^{-1}$ at 100 °C. We have not, so far, been able to produce homogenous non-crystalline samples with higher $LiClO_4$ concentration. For all other samples, however, wide angle X-ray diffraction measurements confirmed that the materials were completely amorphous. The temperature dependence of the electrical conductivity for a sample with 29.4 mol% $LiClO_4$ is shown in Figure 2. The average activation energy for this composition, determined from several runs, is 1.07 ± 0.04 eV. The electronic contribution to the total conductivity has been investigated by a dc-polarization method. No detectable electronic conductivity was, however, found.

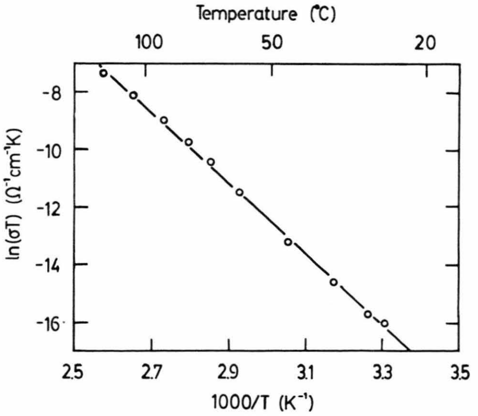

Fig. 2. Temperature dependence of the ionic conductivity for a PDMA sample containing 29.4 mol% $LiClO_4$.

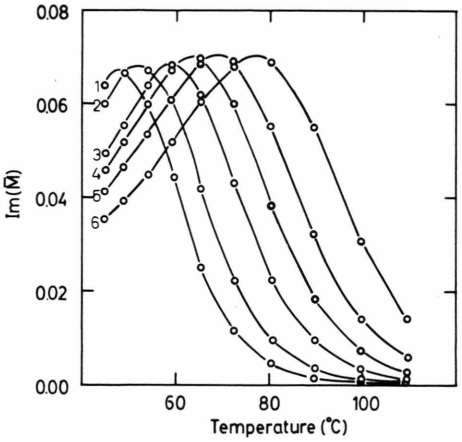

Fig. 3. Temperature dependence of the imaginary part of the complex electric modulus for a PDMA sample containing 29.4 mol% $LiClO_4$. The numbers refer to the frequencies (1) 2 kHz, (2) 4 kHz, (3) 10 kHz, (4) 20 kHz, (5) 40 kHz and (6) 100 kHz.

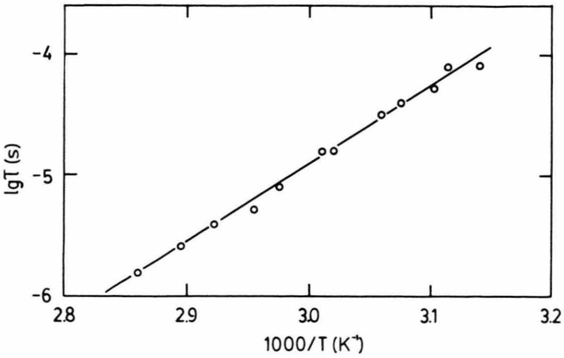

Fig. 4. Electric relaxation time as a function of temperature for the sample in Figure 3.

The real and imaginary parts of the electric modulus have been studied as a function of frequency and temperature. In Fig. 3 the temperature dependence of the imaginary part of the complex modulus is shown. The relaxation time calculated from the relaxation peak is shown as a function of temperature in Fig. 4, where results obtained from plots of the imaginary part of the modulus as a function of log (frequency) as well as of temperature are included. The average activation energy calculated from the relaxation time plots is 1.2 eV. The difference between the activation energies obtained from conductivity and relaxation measurements is, however, not significant since the error in the relaxation measurements is relatively large. The width at half-height of the relaxation peaks as a function of frequency exceeds the Debye value of 1.144 decades as is the case for many other ionic conductors. Typical values for the width are of the order of 2.4 decades, and the peak is unsymmetrical, broader on the high frequency side than on the low frequency side.

The PMMA-$LiCF_3SO_3$ samples were all transparent and amorphous, but the ionic conductivities were very low, below 10^{-8} even at temperatures as high as 150 °C. The compositions investigated covered the range 9 to 29 mol% $LiCF_3SO_3$.

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[1] M. Armand, J. Chabagno, and M. Duclot, in: Fast Ion Transport in Solids, eds. P. Vashishta, J. N. Mundy, and G. K. Shenoy, North Holland Publ. Co., New York 1979, p. 131.
[2] M. Armand, Solid State Ionics **9 & 10,** 745 (1983).
[3] M. Armand, Ann. Rev. Mater. Sci. **16,** 245 (1986).
[4] M. Armand, in: Polymer Electrolyte Reviews 1, eds. J. R. MacCallum and C. A. Vincent, Elsevier, London 1987, p. 1.
[5] G. T. Davis and C. K. Chiang, in: Conducting Polymeric Materials, ed. H. Sasabe, Chemical Marketing Co., Tokyo 1984, p. 244.
[6] M. D. Ingram, Phys. Chem. Glasses **28,** 215 (1987).
[7] Y. Mohajer, G. L. Wilkes, and J. E. McGrath, J. Appl. Polymer Sci. **26,** 2827 (1981).
[8] P. B. Macedo, C. T. Moynihan, and R. Bose, Phys. Chem. Glasses **13,** 171 (1972).
[9] I. M. Hodge, M. D. Ingram, and A. R. West, J. Electroanal. Chem. and Interfacial Electrochem. **58,** 429 (1975).
[10] I. M. Hodge, M. D. Ingram, and A. R. West, J. Electroanal. Chem. **74,** 125 (1976).
[11] D. P. Almond and A. R. West, Solid State Ionics **3/4,** 73 (1981).
[12] U. Strom and K. L. Ngai, Solid State Ionics **9/10,** 283 (1983).
[13] H. Jain and K. L. Ngai, in: Relaxations in Complex Systems. Eds. K. L. Ngai and G. B. Wright, U.S. Department of Commerce, Springfield 1985, p. 221.
[14] B.-E. Mellander and A. Lundén, in: Materials for Solid State Batteries. Eds. B. V. R. Chowdari and S. Radhakrishna, World Scientific Publ. Co., Singapore 1986, p. 161.