Ionic Conductivity in the poly(propylene glycol)-poly(methyl methacrylate)-$LiCF_3SO_3$ System

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The temperature dependence of the ionic conductivity in the PPG-rich part of the ternary system poly(propylene glycol)-poly(methyl methacrylate)-$LiCF_3SO_3$ has been investigated. The highest conductivity values, 3×10^{-5} (ohm cm)$^{-1}$ at 31 °C and 4×10^{-4} (ohm cm)$^{-1}$ at 77 °C, were obtained for samples which had the properties of a pressure sensitive adhesive. The temperature dependence of the ionic conductivity could be well described by the Vogel-Tammann-Fulcher equation.

Key words: Ionic conductivity, polymer electrolyte adhesive, poly(propylene glycol), poly(methyl methacrylate), $LiCF_3SO_3$

Introduction

Ion conducting polymers have attracted considerable attention lately due to their many advantages compared to other solid electrolytes [1–6]. E.g., the plasticity of the material allows for absorbing the volume changes that occur during charge-discharge processes at the electrode-electrolyte interface. Systems based on poly(ethylene oxide) (PEO) and lithium or sodium salts have been studied most thoroughly so far, and it has been shown that the conductivity is highest in amorphous materials. Poly(propylene oxide) (PPO) may be used instead of PEO in order to avoid crystallization, and high ionic conductivities have been reported for high molecular weight PPO complexed with $LiCF_3SO_3$ [1, 2, 4]. In the present paper the system containing poly(propylene glycol) PPG of molecular weight 4000, methyl methacrylate (MMA) and $LiCF_3SO_3$ has been investigated.

Sample Preparation

$LiCF_3SO_3$ stated to be 97% pure (Aldrich Chemical Companby Inc., England) PPG of molecular weight 4000 (Polysciences Inc., USA) and MMA stated to be 99.5% pure (BDH Chemicals Ltd., England) were used. The PPG was filtrated and heated to 140 °C under vacuum for 72 hours before use. The MMA was freeze-dried under vacuum, distilled and after this freeze-dried again.

For most samples the $LiCF_3SO_3$ was dissolved in MMA during stirring, and the solution was then mixed with PPG during continued stirring. For samples with a high salt to MMA ratio, the salt was instead dissolved in PPG during stirring and heating to 50 °C. The solution was in this case cooled to room temperature and then mixed with the MMA under constant stirring because of the volatility of MMA. The $LiCF_3SO_3$ was less soluble in PPG than in MMA, but it was in all cases possible to dissolve the salt. All preparations involving the salt were made in a nitrogen atmosphere. The PPG-MMA-$LiCF_3SO_3$ mixture was freeze-dried and sealed under vacuum. The polymerization process occurred at 40 °C and was completed after about three months.

Experimental

The samples were pressed carefully to cylindrical pellets in a glass tube between two stainless steel electrodes. The pellets were 10 mm in diameter and 1 to 3 mm thick. The complex impedance was measured with a computer controlled HP4274A LCR-meter in the frequency range 100 Hz to 100 kHz, applying a signal of 20 mV. A typical complex impedance plot is shown in Figure 1. The sample temperature was measured with a Platinel II thermocouple. The complex impedance measurements were performed in air or in nitrogen. The X-ray powder diffraction measurements were done using a Philips X-ray diffractometer with

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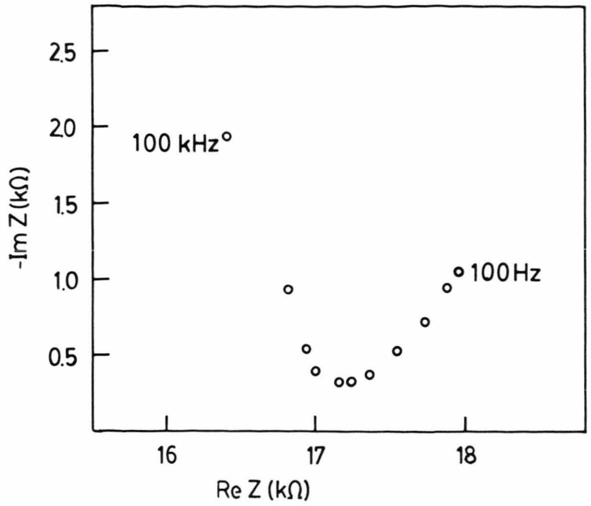

Fig. 1 Complex impedance diagram for a 70 mol% PPG, 20 mol% MMA, 10 mol% LiCF$_3$SO$_3$ sample at 26.2 °C.

Ni-filtered CuK$_\alpha$ radiation. The samples were in this case applied to the platinum sample holder as a film of thickness 0.5 mm. All X-ray measurements were performed under vacuum.

Results and Discussion

This investigation has been concentrated on the PPG-rich part of the ternary system, where the highest ionic conductivity values are expected. Samples of the binary system PMMA-LiCF$_3$SO$_3$ are solid and practically non-conducting [7], while samples with high PPG concentrations are ion conducting viscous liquids. We have investigated a region in the ternary system from liquid-like to the completely solid samples obtained with 65 mol% PPG, 20 mol% MMA and 15 mol% LiCF$_3$SO$_3$. The ionic conductivity is, in general, reasonably high at room temperature in the liquid-like samples but low in the solid samples. In the concentration range between liquid and solid the samples have the properties of a pressure sensitive adhesive, i.e. they are permanently sticky and deformable at room temperature, and they adher to surfaces upon mere contact. A typical compositon for an ion conducting adhesive material is 70 mol% PPG, 20 mol% MMA and 10 mol% LiCF$_3$SO$_3$ within a range of a few mol%. The highest ionic conductivities of these adhesives were found to be 3×10^{-5} (ohm cm)$^{-1}$ at 31 °C and 4×10^{-4} (ohm cm)$^{-1}$ at 77 °C. Ionic conductivities of the different samples are shown in Table 1, and the temperature dependence of the conductivity for a 70 mol% PPG, 20 mol% MMA, 10 mol% LiCF$_3$SO$_3$ sample is shown in Figure 2. The solid curve in the figure shows a least squares fit to the Vogel-Tammann-Fulcher (VTF) equation [8–10],

$$\sigma = A T^{-1/2} \exp\{-E/k_B(T-T_0)\}, \quad (1)$$

where T_0 is the ideal glass transition temperature. A good fit to the VTF equation could be obtained but since the temperature range of the measurements was limited the scatter in the fitted values is rather large.

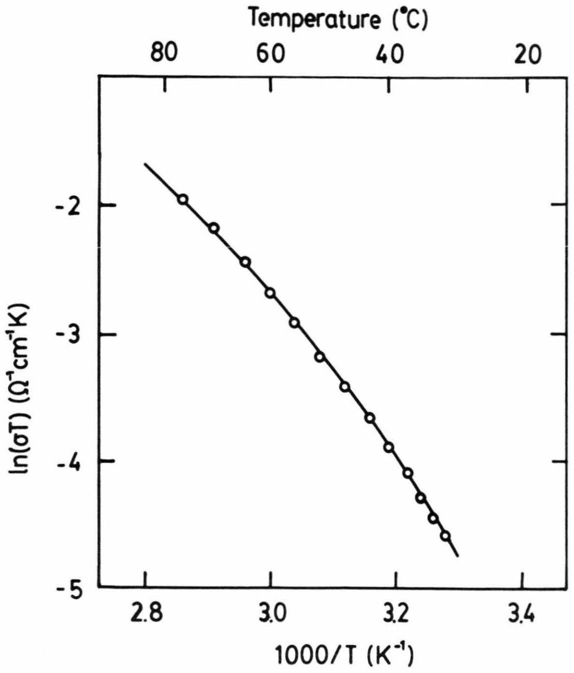

Fig. 2. Temperature dependence of the ionic conductivity σ of a 70 mol% PPG, 20 mol% MMA, 10 mol% LiCF$_3$SO$_3$ sample recorded during a decreasing temperature run. The solid line is least squares fitted to the VTF-equation (1).

Table 1. Ionic conductivities at 315 K for different PPG-MMA-LiCF$_3$SO$_3$ samples.

PPG	MMA (mol%)	Salt	σ (ohm cm)$^{-1}$
75	20	5	1.2×10^{-5}
73	20	7	0.64×10^{-5}
70	20	10	7.3×10^{-5}
65	20	15	0.008×10^{-5}
83	10	7	1.7×10^{-5}
78	15	7	0.18×10^{-5}
73	20	7	0.64×10^{-5}
68	25	7	0.28×10^{-5}

For the pressure sensitive adhesive samples the degree of stickiness and the ionic conductivity both increased somewhat after heating to 80°C. Both these factors are of importance for battery operation since, e.g., a high degree of stickiness may improve the electrode-electrolyte interface properties during charging and discharging. The samples showed no signs of crystallinity according to a wide-angle X-ray diffraction study.

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