Ionic conductivities of poly(methoxy polyethylene glycol monomethacrylate) complexes with $LiSO_3CH_3$

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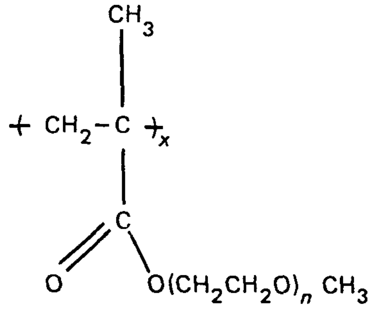
Ionic conductivity values for $LiSO_3CF_3$ complexes with two amorphous poly(methoxy polyethylene glycol monomethacrylates) (PEM) were determined and values as high as $\sim 6 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 373 K and $\sim 2 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ at 293 K were achieved. These values are compared with those obtained for a poly(ethylene oxide) (PEO)–$LiSO_3CF_3$ complex of similar salt concentration with an ether oxygen to Li^+ ion ratio of 18. The conductivity results for the complexes are similar at temperatures > 343 K but at 293 K the values for the conductivities of the PEM–$LiSO_3CF_3$ complexes are approximately two orders of magnitude higher than those for the PEO–$LiSO_3CF_3$ complex. This difference is believed to be due at least in part to the presence of a large amount of crystalline material in the PEO–$LiSO_3CF_3$ complex below 323 K.

(Keywords: polyethylene glycol complexes; electrolyte; ionic conductivity)

INTRODUCTION

Poly(ethylene oxide) (PEO)–lithium salt complexes have been reported to have high ionic conductivities[1–4]. These complexes are semi-crystalline materials with relatively low conductivities at ambient temperatures. A high free volume for polyether–alkali metal salt complexes is believed to be desirable for high ionic conductivities[2,5]. One way of reducing the degree of crystallinity and hence increasing the free volume is to use a crosslinked system. This experiment was carried out by Wright *et al.*[1] who found a value of $\sim 10^{-5}\ \Omega^{-1}\ cm^{-1}$ at 293K for an unsaturated $LiBF_4$ complex with PEO-maleate gels. This value for the conductivity is approximately two orders of magnitude greater than the value for the corresponding semi-crystalline materials.

Another method of producing an amorphous Li–salt complex containing ethylene oxide units is by the use of poly(methoxy polyethylene glycol monomethacrylates),



$$\left[CH_2 - \overset{\displaystyle CH_3}{\underset{\displaystyle O{=}C{-}O(CH_2CH_2O)_n CH_3}{C}} \right]_x$$

where $n \approx 9$ and 22 for PEM9 and PEM22 respectively. These polymers have the added advantage of being soluble in common organic solvents.

The ionic conductivities for complexes of poly(methoxy polyethylene glycol monomethacrylates) with lithium trifluoromethyl sulphonate $LiSO_3CF_3$ are reported here.

EXPERIMENTAL

Preparation of materials

The monomeric methoxy polyethylene glycol monomethacrylates were used as supplied by Polysciences Ltd. $LiSO_3CF_3$ was prepared by neutralizing triflic acid (supplied by Fluorochemicals Ltd.) with lithium hydroxide in aqueous solution. The water was removed on a rotary evaporator and the salt was purified by recrystallization from an acetone/toluene mixture. The salt was dried by heating under vacuum at 413K for twenty four hours.

Polymerization was carried out in 5 to 10% solutions in water under nitrogen at 273K using the redox pair $K_2S_2O_8/FeSO_4$ as the free radical initiator ($\sim 0.2\%$ by weight of monomer). Fifteen to twenty minutes after the addition of initiator the viscosity of the solution appeared to reach a constant value at which time the reaction vessel was opened to the atmosphere and a small amount of hydroquinone was added. The polymers were precipitated in a 0.45 molar solution of potassium sulphate by warming to > 323 K which separated most of the initiator from the polymer. The monomers and hydroquinone are soluble in this hot salt solution. The polymers were then redissolved in acetone to precipitate residual salt which was filtered off. In order to prevent side reactions it is advisable to remove the salt from the polymer solution soon after the precipitation step. The

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polymers were again precipitated in a 50% n-heptane/50% acetone mixture. The monomers and hydroquinone are soluble in this mixture.

To remove the last traces of K_2SO_4 it is necessary to redissolve the polymer in an organic solvent. The salt is removed by decantation or by filtration before removing the solvent by evaporation and then by heating under vacuum at ~353K for 20 h. The limiting viscosity numbers were determined in water at 298K and ranged from 0.6 to 1.26 (100dl g^{-1}). Li-salt complexes were prepared by forming a homogeneous solution of the polymers and $LiSO_3CF_3$ in acetone. The acetone was removed by evaporation and the complexes were dried by heating under vacuum at ~408K for 30 h or by heating under vacuum at ~383K for a few days. Salt concentrations in the PEM9 and PEM22 complexes were both $O/Li^+ \approx 18$, where O/Li^+ is the ratio of the molar concentrations of ethylene oxide units to the molar concentrations of lithium ions.

The drying procedure described above sometimes resulted in a slightly crosslinked product which swelled but did not completely dissolve in water. This enabled us to study the effect of molecular weight differences on the conductivity. Each drying step was carried out in stainless steel equipment in preference to glassware to prevent any reaction with silica in the glass. Silica is known to crosslink polymers with pendant ester groups at elevated temperatures[7].

On two occasions complexes were formed with copolymers prepared from monomer solutions containing the following mixtures: 75% by weight of $n \approx 22$ and 25% of $n \approx 9$; 50% of $n \approx 22$ and 50% of $n \approx 9$. The salt concentrations were both $O/Li^+ \approx 18$, and their conductivity values were determined.

Conductivity measurements

The samples were pressed between stainless steel electrodes and conductivity measurements were carried out using a 1172 Solartron frequency response analyser. The complex admittance was measured as a function of frequency from 10^{-1} to 10^4 Hz. Due to the blocking nature of the electrodes, the real part of the admittance rose with increasing frequency to a frequency independent plateau. The value at the plateau was used to calculate the bulk conductivity.

RESULTS AND DISCUSSION

Poly(methoxy polyethylene glycol monomethacrylates)

PEM9 shows no sign of crystallinity at ambient temperatures and above. A Differential Scanning Calorimetric (d.s.c.) investigation of a quenched sample of PEM9 showed a glass transition temperature of ~210K. PEM22 began to show signs of crystallization when left standing at ambient temperatures for 2 to 3 h. D.s.c. analysis revealed that this material melts over the temperature range 303 to 323K. PEM22 was prepared by a free radical polymerization and is expected to possess little stereoregularity which would prevent crystallization by the main chain of the polymer. The side groups of the PEM22 are believed to crystallize. This phenomenon has been observed previously for poly(alkyl methacrylates) containing long side groups[6].

Addition of Li-salt to PEM22 causes a large decrease in the rate of crystallization. Signs of crystallization begin to appear after two or more days, the rate being dependent on the temperature of the surroundings.

Conductivity results

Conductivity measurements were carried out on PEM22–$LiSO_3CF_3$ complexes before any crystalline material had formed. The results are shown in *Figure 1*. Values of $\sim 2.5 \times 10^{-4}\,\Omega^{-1}\,cm^{-1}$ at 373 K and $\sim 5 \times 10^{-6}\,\Omega^{-1}\,cm^{-1}$ at 293 K for the PEM9–$LiSO_3CF_3$ complex, and $\sim 6 \times 10^{-4}\,\Omega^{-1}\,cm^{-1}$ at 373K and $2 \times 10^{-5}\,\Omega^{-1}\,cm^{-1}$ at 293K for the PEM22–$LiSO_3CF_3$ complex were obtained. No significant differences in the conductivity values for the crosslinked systems and those prepared from polymers with relatively low limiting viscosity numbers were observed.

These values are compared in *Figure 1* with results reported previously[4] for a poly(ethylene oxide)–$LiSO_3CF_3$ complex with $O/Li^+ = 18$. The conductivity values for the PEM9 and PEM22–$LiSO_3CF_3$ complexes are approximately two orders of magnitude higher than the value for the PEO–$LiSO_3CF_3$ complex at 293K. However, the conductivities at elevated temperatures are similar. A d.s.c. analysis of the PEO–$LiSO_3CF_3$ complex revealed that almost all the crystalline material in the PEO–$LiSO_3CF_3$ complex melts at ~338K. This transition corresponds to the knee in the conductivity plot at this temperature shown in *Figure 1*. The difference in conductivity of the PEM–$LiSO_3CF_3$ complexes and the PEO–$LiSO_3CF_3$ complex at 293K is believed to be due at least in part to the presence of a large amount of crystalline material in the PEO–$LiSO_3CF_3$ complex.

A conductivity value for a PEM9 sample containing no added Li-salt was obtained and a value of $10^{-7}\,\Omega^{-1}\,cm^{-1}$ at 373K was observed. The impurities present are therefore expected to have a negligible effect on the conductivity of the Li-salt complexes. Nevertheless, this value is relatively high and may be attributed to traces of potassium sulphate from the preparation of the polymer as discussed above.

PEM9–PEM22 copolymer complexes

The presence of units containing $n \approx 9$ did not prevent crystallization at concentrations down to 50% by weight

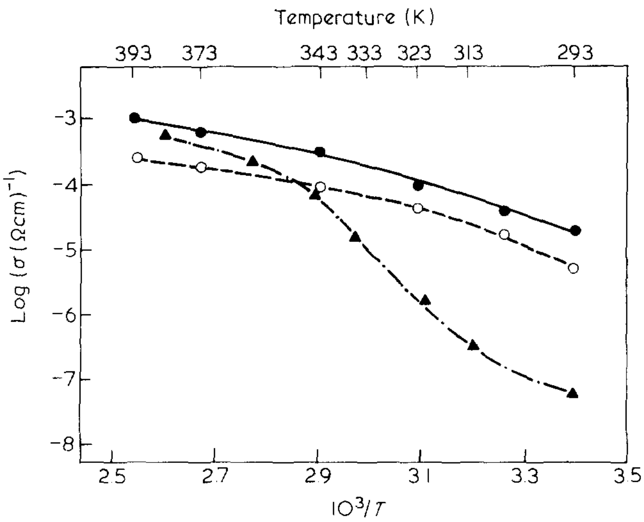

Figure 1 Log conductivities vs. reciprocal temperatures for the PEM9–$LiSO_3CF_3$ (○), PEM22–$LiSO_3CF_3$ (●) and PEO–$LiSO_3CF_3$ (▲) complexes

of the monomer with $n \approx 22$. The conductivity values obtained for the Li–salt complexes were intermediate between the conductivity results for the PEM22–$LiSO_3CF_3$ and PEM9–$LiSO_3CF_3$ complexes.

Future work should investigate other poly(methoxy polyethylene glycol monomethacrylates) with *n* values less than 22 which may not crystallize at ambient temperatures. In addition, poly(methoxy polyethylene glycol acrylates) should have lower glass transition temperatures than the methacrylate analogues so the ionic conductivities of the Li–salt complexes of these and other polymers with more 'flexible' backbones are of interest.

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