PII: S0032-3861(97)10260-9

Polymer Vol. 39 No. 26, pp. 7139–7141, 1998
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0032-3861/97/$ - see front matter

Ion conduction in crosslinked β-cyclodextrin gels

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(Revised 1 April 1997)

Gels of crosslinked β-cyclodextrin have been prepared using dimethylacetamide containing lithium, sodium and potassium triflate salts.

Compositions were adjusted to produce materials with dry surfaces that showed no evidence of solvent leakage. Alternating current conductivity (σ) measurements of ion transport in these systems were made over the temperature range 290–360 K. Systems containing KCF_3SO_3 exhibited the best range of conductivity values from $\sigma = 10^{-4}$ S cm^{-1} (293 K) to $\sigma = 1.8 \times 10^{-3}$ S cm^{-1} (360 K). These systems also show a linear dependence of log conductivity on 1/temperature, with activation energies for ion transport in the range 32–48 kJ mol^{-1}. © 1998 Elsevier Science Ltd.

(Keywords: β-cyclodextrin gels; ion conduction; crosslinked)

Introduction

The first suggestion that polymer-based solid electrolytes could be used in high-energy density batteries was made by Armand and et al.[1] in 1978. This was a consequence of work reported earlier by Wright[2] who demonstrated that sodium and potassium salt complexes with polyethylene oxide were conductive. Since then there has been a vast amount of effort expended on developing a range of solvent-free polymer electrolytes that can also be used in batteries, electrochromic devices and sensors[3,4].

In these polymer–salt solid solutions, ion transport is assisted by the liquid-like chain relaxation processes present in the polymer when it is above its glass transition temperature. This means that conductivity levels tend to be restricted and are also strongly dependent on temperature. Consequently, attention has moved to systems that can provide greater ion mobility, but this usually means that one has to sacrifice the idea that those electrolytes are solvent free. This can be achieved either by adding plasticizers to the polymer[5–7] which will lower the glass transition temperature and increase the ion mobility or use systems where the polymer may act predominantly as a support and play only a minor role in the transport mechanism. Polymer gels[8–11] and porous films[11,12] fall into the latter category.

In the solvent-free polymer electrolytes, the polymer acts as the solvent, usually by complexing the cation, thereby producing the separated charge carriers. The archetypal polymer structure used as an effective solvating agent is polyethylene oxide which has been widely used in various structural forms[3]. Crown ethers are also effective ion-binding agents and these have also been incorporated into polymeric structures to form polymer electrolytes[13,14].

More recently, we have been studying ion conduction in gels formed from cellulose/*N,N*-dimethylacetamide/LiCl mixtures or alternatively using *N*-methyl pyrrolidone as the solvent[11]. These give conductivities around 3.0×10^{-4} S cm^{-1} at ambient temperatures but tend to be sensitive to the salt used. In this paper we report a preliminary study of an alternative anhydroglucose structure which is also in the form of a ring, namely β-cyclodextrin, which is a cyclic structure comprising seven anhydroglucose units linked α-1,4. These can be crosslinked to form a network which can be readily swollen with polar solvents, and conductivity data are reported for cyclodextrin/dimethylacetamide/triflate salt gels.

Experimental section

Samples. A β-cyclodextrin, crosslinked with epichlorohydrin was purchased as polymer beads under the trade name Cavitrin from Scientific Polymer Products. The bead sizes used were 60–100 mesh and the water content as received was ~85%. *N,N*-dimethylacetamide (DMAc) and the (Li, Na, K) CF_3SO_3 salts (all supplied by Aldrich) were purified and dried rigorously using the procedures described elsewhere[15].

Gel preparation. To remove the water a solvent exchange procedure was used. The beads were suspended in methanol and left for several hours, then filtered off and fresh methanol was added. This was repeated five times. Methanol was then removed progressively by suspending the beads in DMAc, again exchanging the solvent five times. Lastly, five successive equilibrations with DMAc/salt mixtures gave the final gel product. Lithium, sodium and potassium triflate were used as the salt component of the gels. After some trial and error, materials which behaved like rubbery solids with dry surfaces could be prepared using the following compositions.

(1) 5 wt% β-cyclodextrin, 5 wt% $LiCF_3SO_3$ and 90 wt% DMAc
(2) 5 wt% β-cyclodextrin, 5.5 wt% $NaCF_3SO_3$ and 89.5 wt% DMAc
(3) 5 wt% β-cyclodextrin, 6.03 wt% KCF_3SO_3 and 88.97 wt% DMAc

These ensured that the gels all contained the same concentration of cation to allow comparison between the systems examined.

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Higher solvent/salt loadings could be obtained, for example, 1.10 wt% cyclodextrin, 4.30 wt% lithium salt and 94.6 wt% DMAc, which gave higher conductivities than those reported here, but the materials produced were highly viscous and opaque, with a wet surface. These loadings did not give significantly better conductivities, which would have justified their use, and measurements were confined to systems 1–3 above.

Conductivity measurements. The a.c. conductivity of each gel sample was measured using a Solartron 1255 frequency response analyser in conjunction with a Solartron 1286 electrochemical interface. Stainless-steel blocking electrodes were used in the measuring cell and the gel samples were placed between these, separated by a compressed doughnut-shaped, Teflon spacer to maintain a constant sample thickness. Gels were prepared and loaded into the measuring cell under anhydrous conditions in a glove box flushed by dry oxygen-free argon. Cells were sealed in the glove box then transferred to the Solartron. The complex impedance, from which the conductivity can be derived, was measured as a function of temperature. The sample was allowed to equilibrate for at least 1 h at each measuring temperature and conductivities were measured on both the heating and cooling cycles to ensure consistency.

Results and discussion

Conductivity (σ) measurements were made on the gels over a temperature range of 294–360 K and there was no evidence of solvent leakage in the samples with dry surfaces, despite the high DMAc loadings. The data are displayed in *Figure 1* as log σ against reciprocal temperature.

Samples with the KCF_3SO_3 salts exhibited the highest conductivity levels over the complete temperature range with a room temperature conductivity of 10^{-4} S cm^{-1}. This decreased as the size of the cation decreased with (Na^+) $\sigma = 6.3 \times 10^{-5}$ S cm^{-1} and (Li^+) $\sigma = 2 \times 10^{-5}$ S cm^{-1}. The temperature dependence of the log σ was essentially linear and best described by the Arrhenius equation. Comparable data for solvent-free polymer systems are usually curved, reflecting the fact that ion conduction depends on relaxation processes in the polymer chains, which become more facile as the temperature is increased. A linear dependence, such as we observed here, is much more characteristic of low-viscosity liquid electrolytes[16] and is similar to the data reported for macroporous polyethylene (PE) films supporting liquid–salt mixtures[12].

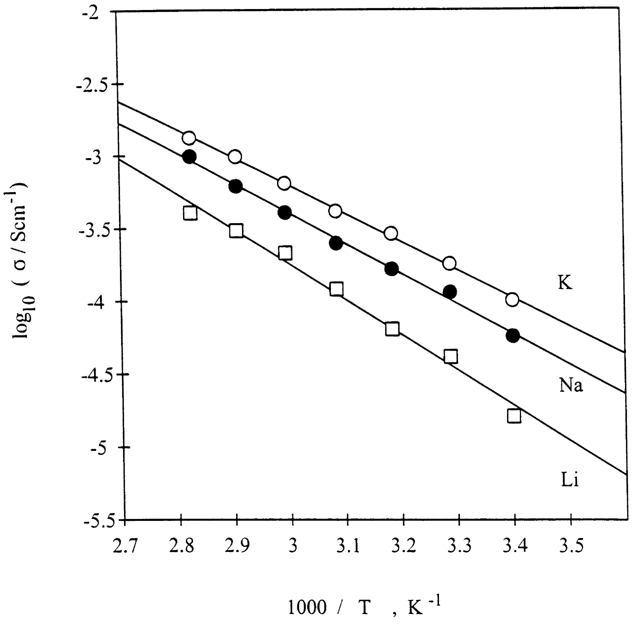

Figure 1 Temperature dependence of the conductivity in β-cyclodextrin/DMAc gels containing $LiCF_3SO_3$ (□); $NaCF_3SO_3$ (●); and KCF_3SO_3 (○)

Activation energies, E_a, were calculated using the Arrhenius equation and are listed in *Table 1*. The values are of the same order of magnitude as those obtained for conduction in the PE/electrolyte films reported elsewhere[14] but lower than values estimated for solvent-free polymer electrolytes[15,17–19]. Of course, these may not be directly comparable. For most solvent-free polymer electrolytes, the use of the Arrhenius equation would give activation energies that varied with temperature, as the temperature dependence of conductivity is non-Arrhenius and best described using a Vogel–Tamman–Fulcher equation. Consequently, the activation energy in these cases should only be calculated using a specific model, and the Adam–Gibbs–DiMarzio[20,21] approach has been applied in this respect. The activation energy calculated using this model is that required to rearrange a small side-chain segment in space at a given salt concentration, but whether this is directly comparable with the activation energy calculated from the Arrhenius equation is not clear.

It is sufficient to say that Arrhenius behaviour is observed in this system, and in device operation it is desirable to have a low dependence of conductivity on temperature, so that over an environmental range of temperatures, the difference in, say, switching times, is minimised. Many solid polymer electrolytes have a quite strong dependence of σ on T because of the mechanistic nature of the ion transport process. This is improved when liquid, low-viscosity media are used, and the systems reported here have relatively low values which are, in effect, proportional to the activation energies E_a. These decrease as the cation size increases.

The observations suggest that the β-cyclodextrin network does not participate greatly in the ion conduction process but has a more passive role in the system, providing only the necessary gel structure to hold the liquid phase. This behaviour has been reported for other polymer/solvent/salt systems[22,23] that also gave log σ–T^{-1} responses which were described adequately by the Arrhenius equation. Comparable cellulose gels[11] had conductivities which were similar to those reported here, again suggesting that the polymer provided the support for the liquid electrolyte and ion transport was through the solvent with little or no participation from the polymer.

While cyclodextrins can form host–guest complexes, these usually involve inclusion of a non-polar molecule in the hydrophobic interior of the cyclodextrin torus[24]. There are only a few examples of the formation of metal–cyclodextrin complexes, but the metal cation tends to bond external to the torus using the exposed hydroxyl groups, such as with the sandwich-type complexes formed by Cu^{2+} ions[25]. Thus, the differences in conductivity observed here, when the cations increase in size, probably reflect the

Table 1 Activation energies for β-cyclodextrin gels

Electrolyte	E_a (kJ mol^{-1})
$LiCF_3O_3$/DMAc	47.9
$NaCF_3SO_3$/DMAc	38.2
KCF_3SO_3/DMAc	32.0

decreasing lattice energies of the salts in the order $LiCF_3SO_3 > NaCF_3SO_3 > KCF_3SO_3$, and the weakening solvation shell as the cation size increases, rather than any assistance from complexation with the cyclodextrin units.

The results obtained are promising and further work is in progress to examine the effect of changing the carrier solvent and the salt concentration in these surface dry gels.

Acknowledgements

The authors wish to thank the Engineering and Physical Sciences Research Council (EPSRC) for a studentship (granted to G. H. Spence).

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