Ionic conduction in poly(*N,N*-dimethylacrylamide) gels complexing lithium salts

S. A. Dobrowski†, G. R. Davies, J. E. McIntyre* and I. M. Ward#
IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK

(Received 30 July 1990; revised 7 December 1990; accepted 7 December 1990)

Ionic conductivities of gel electrolytes prepared from poly(*N,N*-dimethylacrylamide) (PDMA) and lithium salts (perchlorate and trifluoromethanesulphonate), incorporating *N,N*-dimethylacetamide (DMAc) as plasticizer, were studied. The molar mass of the polymer was controlled by use of ethane thiol as a chain transfer agent. The salt-free and salt-containing materials free from added DMAc were tough, non-crystalline, transparent solids. Complexes of high molar mass PDMA and lithium salts, incorporating 60% by weight of DMAc were tacky resins exhibiting bulk ionic conductivities from 2×10^{-4} S cm^{-1} at room temperature to 7×10^{-3} S cm^{-1} at 393 K. Rubbery solids were obtained by crosslinking the highly plasticized gels, and these materials had bulk ionic conductivities above 10^{-3} S cm^{-1} at room temperature.

(Keywords: poly(*N,N*-dimethylacrylamide); gel electrolyte; ionic conductivity)

INTRODUCTION

Solid polymer electrolytes formed by the dissolution of salts in suitable polymers were first studied by Wright[1], but Armand *et al.*[2] were the first to recognize that these materials had practical applications in high energy-density batteries. Whilst several suitable polymer types can be identified, polyethers, exemplified by poly(ethylene oxide) (PEO), have been the favoured materials for dissolving a wide range of lithium and other salts.

A key advance in the study of these materials was the recognition that significant ion transport required the presence of a non-crystalline phase[3,4]. Unfortunately, PEO–salt complexes form partially crystalline solids at room temperature and, therefore, exhibit good ionic conductivities only at temperatures at which they become liquid. There have been many attempts to circumvent this tendency of PEO to crystallize, for example by suitable modification of polymer structure such as in the formation of comb polymers[5,6], networks[7], block copolymers[8] or by blending with low molar mass oligomers or solvents[9]; these studies have been reviewed by Vincent[10].

In this study, poly(*N,N*-dimethylacrylamide) (PDMA) has been explored as a suitable host to lithium salts. The polymer was chosen because it is non-crystalline and because it possesses a coordinating group (tertiary amide) known to form complexes with lithium salts[11,12]. The use of a low molar mass additive (*N,N*-dimethylacetamide) (DMAc) to enhance ionic conductivity was also explored. A preliminary study of ionic conductivity in other poly(*N,N*-dialkylacrylamide)s complexing lithium salts has previously been reported[13,14].

EXPERIMENTAL

Preparation of materials

N,N-dimethylacrylamide (monomer; Aldrich), DMAc (Gold Label; Aldrich) and methyl benzoylformate (Aldrich) were used as received. Anhydrous lithium perchlorate (Aldrich) and anhydrous lithium trifluoromethanesulphonate (triflate) (Aldrich) were heated at 423 K under reduced pressure for at least 24 h before use, and stored under a dry atmosphere of nitrogen.

Poly(*N,N*-dimethylacrylamide) complexes with lithium salts were prepared as follows: accurately known weights of monomer and lithium salt were combined to yield a monomer–salt solution having an amide group to lithium atom ratio of 12:1. Methyl benzoylformate (0.1% on weight of monomer) was added as initiator, and the resultant solution was degassed (two freeze–thaw cycles) before being bulk polymerized between glass cover slips (thickness 0.06 mm) held 1 mm apart in a support frame; polymerization was activated using an ultraviolet (u.v.) light source (Thorn Me/D 250 W; high pressure mercury discharge). The polymerization cell was irradiated for 1 s every 6 s, 20 cm from the source for the first 30 min of polymerization and continuously, 10 cm from the source for a further 30 min. During these steps, the cell was

---

† Chemistry and Chemical Technology, Department of Chemical Engineering, University of Bradford, Bradford BD7 1DP, UK
* Department of Textile Industries, University of Leeds, Leeds LS2 9JT, UK
# To whom correspondence should be addressed

0032-3861/91/162887-05

externally cooled in a rapid stream of nitrogen gas. The resultant transparent polymer plaque was removed from the cell and heated at 353 K under reduced pressure (below 13.3×10^2 Pa) for at least 240 h in an attempt to reduce residual monomer to a minimum.

Gel electrolytes comprising PDMA complexes with lithium salts and added DMAc were prepared by polymerizing mixtures of monomer–salt–DMAc. In these systems, the total amide group to lithium atom ratio was 12:1; initiator was 0.1% on weight of monomer, i.e. independent of the DMAc content; samples containing 50% or more of plasticizing DMAc were not subjected to the post-polymerization thermal process to avoid loss of solvent from the polymer plaques.

In order to produce polymers with lower molar mass, bulk polymerization of mixtures of monomer and salt was performed as described above, but with the addition as chain transfer agent of thiophenol or ethane thiol. Polymer–salt complexes from monomer–salt–chain transfer agent were prepared.

Gel permeation chromatography (g.p.c.)

Gel permeation chromatography was performed using a Waters 501 HPLC pump, 401 differential refractometer, 745 data module and a single Ultrastyrogel linear column ($M_w = 15 \times 10^3$–5×10^6) maintained at a temperature of 303 K. Samples for analysis were made up as 1% solutions in the eluent, dimethyl formamide, and a flow rate of 1 ml min^{-1} was used.

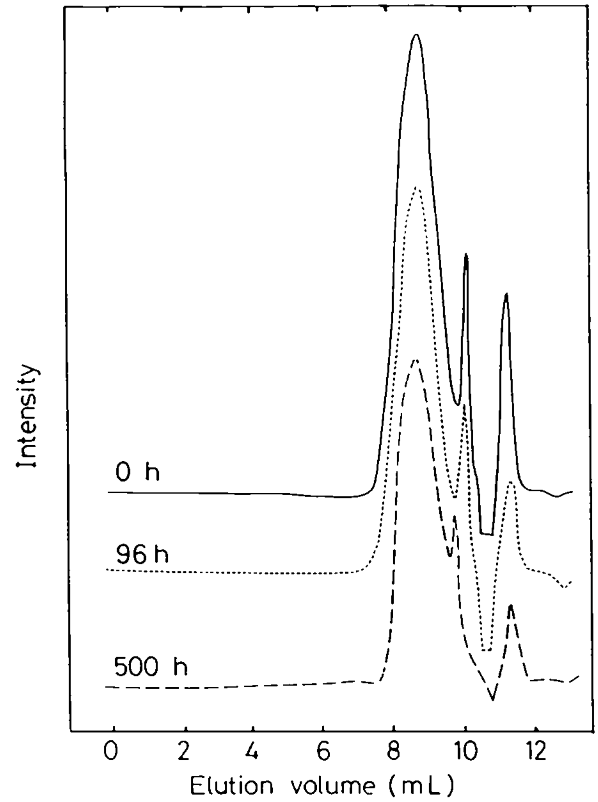

Figure 1 Gel permeation chromatogram of PDMA–lithium trifluoromethanesulphonate; monomer content as a function of duration of post-polymerization heating. Temperature 80°C, pressure < 1.3 kN m^{-2}

Alternating current impedance spectroscopy

Polymer samples (1 mm thick) were pressed between brass (blocking) electrodes and their alternating current conductivity as a function of temperature was measured using an 1172 Slumberger Solartron frequency response analyser. The complex admittance was measured as a function of frequency from 0.1 Hz to 63 kHz. 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. To exclude atmospheric moisture from the samples, all handling and measurement of conductivity was performed in a dry nitrogen atmosphere.

Calorimetry

Glass transition temperatures (T_gs) were determined by differential scanning calorimetry (d.s.c.) using a Perkin-Elmer DSC II operating in the temperature range 143–423 K at a heating rate of 10 K min^{-1}, and by dynamic mechanical thermal analysis (d.m.t.a.) using a Polymer Laboratories DMTA Mark II instrument.

RESULTS AND DISCUSSION

The PDMA–lithium salt complexes prepared by bulk polymerization were found to be tough, transparent solid materials. That these materials were tough is highlighted by the fact that samples polymerized in the bulk, in the form of cylinders, could be machined by high speed lathe.

The degree of crystallinity of the salt-free, and of both the perchlorate and triflate-containing materials was examined by wide-angle X-ray diffraction (WAXS). The WAXS revealed no sharp peaks due to crystalline regions; only a Debye-Scherrer pattern associated with scattering from non-crystalline material was observed in each case, indicating that the polymer is non-crystalline both in the absence and in the presence of the lithium salts.

Gel permeation chromatography of PDMA complexing lithium perchlorate shows three peaks corresponding, from left to right in *Figure 1*, to polymer, salt and monomer; the peaks for salt and monomer were identified by observing the change in peak area produced on addition of a small quantity of each to samples of the polymer solution analysed by g.p.c. *Figure 1* shows that monomer is present after the first stage (u.v.) of polymerization and that the thermal process does indeed cause a reduction in residual monomer, but does not remove it entirely, even after 500 h. An approximate estimate of the quantity of monomer in the polymer samples was made by injecting known amounts of monomer onto the g.p.c. column and by comparing the peak areas for monomer. The monomer content was found to be ~20 wt% in the polymer not subjected to thermal treatment, falling to ~15% after 96 h and ~10% after 500 h of heating under reduced pressure.

The monomer contents of PDMA free from added salt and of the complexes with lithium perchlorate and lithium triflate, determined by thermal gravimetric analysis (t.g.a.) were found to be 12.6, 13.3 and 14.9%, respectively, after the post-polymerization thermal process for 240 h. These values correspond to the steady state per cent weight reduction attained immediately prior to the very rapid fall in weight associated with thermal decomposition of the materials. It is to be noted that at temperatures below the degradation temperatures of the materials

(PDMA–salt free, ~660 K; PDMA–perchlorate, ~590 K; PDMA–triflate, ~650 K), the weight *versus* temperature curves did not show the sudden weight loss that usually accompanies evaporation of a volatile component. Instead, the weight of the materials decreased gradually over a very wide temperature range beginning well before and continuing well beyond the normal boiling point of the monomer (~470 K at atmospheric pressure).

The overall picture suggests that the escape of volatiles does not occur suddenly. This type of behaviour suggests that diffusion rates of the monomer are exceptionally slow in these tough materials even above the boiling point of the monomer and the T_g of the polymer. The idea that monomer can somehow be 'trapped' is strengthened by d.s.c. studies of the PDMA–salt complexes containing low molar mass solvent (DMAc), a solvent which in several ways is closely related to the monomer in chemical structure and composition. These studies have shown that up to between 30% and 40% of added DMAc can be incorporated into the PDMA–salt DMAc system before the d.s.c. thermograms exhibit the endothermic distortion in the trace at ~438 K that is characteristic of boiling of DMAc, suggesting that DMAc is tenaciously bound into the materials.

The presence of unpolymerized monomer will act to plasticize the polymer and reduce the T_g. It is desirable to know by how much T_g is reduced by the presence of unpolymerized monomer. The T_g, measured by d.s.c., for PDMA–triflate free from added solvent (DMAc) (but incorporating ~15% of unpolymerized monomer) was found to be 318 K. The T_gs for monomer and solvent-free (hereinafter plasticizer-free) PDMA–triflate complexes (prepared by the conventional route of solvent casting thin films from solutions of polymer plus salt), however, are reported to be 415 and 425 K for amide group to lithium atom ratios of 15:1 and 11:1, respectively[15]. These data imply that the presence of ~15% of unpolymerized monomer results in a significant reduction in T_g, i.e. of the order of 100 K.

The T_gs were found to rise on addition of inorganic electrolyte to PDMA free from added DMAc. For example, T_gs measured by d.m.t.a. (taken from the maximum in tan δ) and d.s.c. respectively, were 301 and 302 K (salt-free), 313 and 312 K (perchlorate) and 322 and 318 K (trifluoromethanesulphonate). It has been suggested that the phenomenon of an increase in T_g on addition of inorganic electrolytes to polymers containing electronegative donor atoms is indicative of intermolecular coordination between cation and donor atoms[16,17].

The T_gs were found to fall on incorporation of solvent (DMAc) into the PDMA salt complexes. *Figure 2* shows that for PDMA–lithium trifluoromethanesulphonate, the T_g (d.s.c. values) falls by ~35 K (i.e. from 318 to 283 K) on inclusion of 30% DMAc, and by ~80 K (i.e. from 283 to 202 K) on inclusion of a further 30% DMAc. The reduction in T_g with increasing content of DMAc is consistent with plasticization of the polymer.

The polymers were also characterized for molar mass. Gel permeation chromatography revealed that bulk polymerization of monomer–salt mixtures yielded materials having molar masses around 1.5×10^6. The molar masses given here are polystyrene equivalent values obtained from a calibration curve; a more rigorous treatment for molar mass and polydispersity has not been carried out.

Ethane thiol was found to be an effective agent in the control of molar mass. It was possible to reduce the molar mass of PDMA from the value given above to 670000, 116000 and 17000 by use of 0.25, 2.5 and 20%, respectively, of ethane thiol on the weight of monomer.

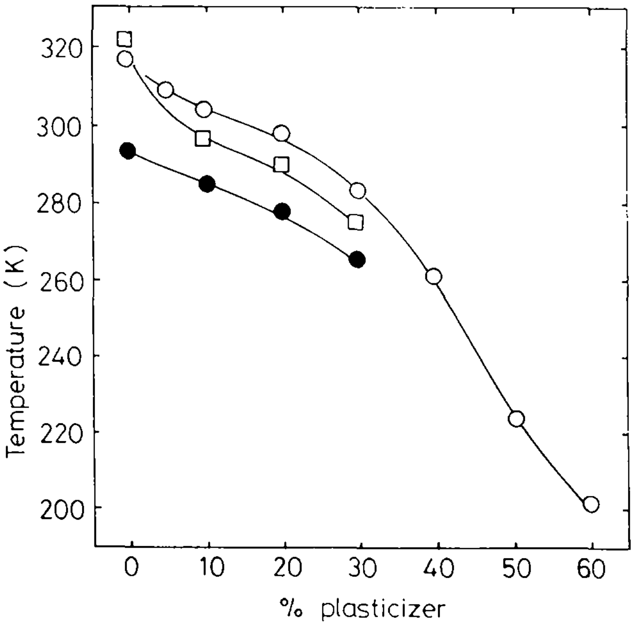

Figure 2 Glass transition temperature *versus* weight per cent of DMAc in PDMA–lithium trifluoromethanesulphonate. Carbonyl:lithium = 12. Maxima in: (□) tan δ; (●) log E''; (○) T_g from d.s.c.

In contrast to ethane thiol, thiophenol was found to be a much less effective agent in the control of molar mass. The use of 20 wt% of the agent resulted in a lowering of molar mass to around 8×10^5.

Bulk ionic conductivities for the PDMA–salt–DMAc complexes are shown in *Figures 3* and *4* for lithium perchlorate- and lithium triflate-containing samples, respectively. Comparison of *Figures 3* and *4* shows that the conductivities of the perchlorate-containing samples are generally slightly higher than those for the triflate-containing samples. Opposite behaviour has been observed elsewhere[18] for complexes of poly(methoxy oligoethylene glycol monomethacrylate) with these salts; the behaviour observed in the present study might be due to slight differences in the content of unpolymerized monomer in the samples. These data show that ambient temperature conductivities from 2×10^{-4} rising to 7×10^{-3} S cm^{-1} are possible with 60% added plasticizer. Except for the materials free from DMAc, which show a discontinuity in the curve at ~370–380 K, the conductivities are typical of amorphous materials in that they exhibit characteristic VTF or WLF behaviour[19].

Preliminary data on the effect of molar mass on the bulk ionic conductivities of PDMA–lithium triflate complexes free from added plasticizer are shown in *Figure 5*. The data suggest that the conductivity is highest in the polymers of lowest molar mass. Whilst this trend is to be expected, the large difference in the conductivities of the polymers having molar masses of 3.4×10^5 and 1.5×10^6 was not expected. Studies elsewhere[20] have shown that conductivities of PEO–salt complexes are independent of molar mass when the molar mass exceeds $\sim 3 \times 10^4$. The differences in the observed conductivities might be due to differences in the content of unpolymerized monomer in the samples.

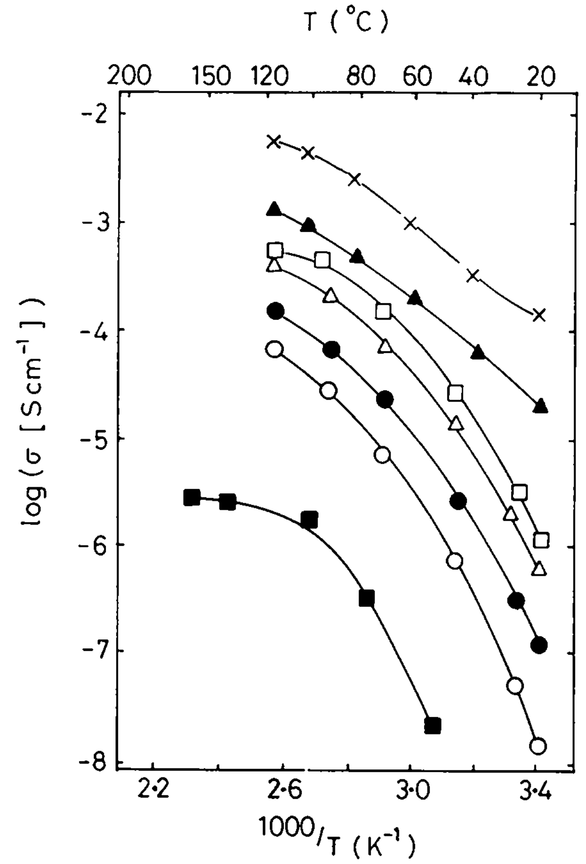

Figure 3 Log conductivity *versus* reciprocal temperature for PDMA–DMAc–lithium perchlorate gels. Carbonyl:lithium = 12. DMAc (%): (■) 0; (○) 10; (●) 20; (△) 30; (□) 40; (▲) 50; (×) 60

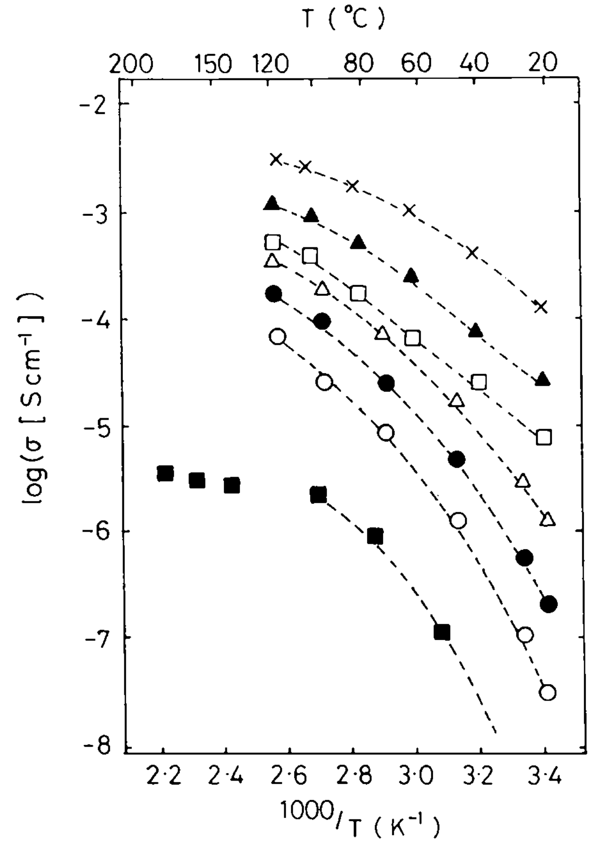

Figure 4 Log conductivity *versus* reciprocal temperature for PDMA–DMAc–lithium trifluoromethanesulphonate gels. Carbon:lithium = 12. Symbols as in *Figure 3*

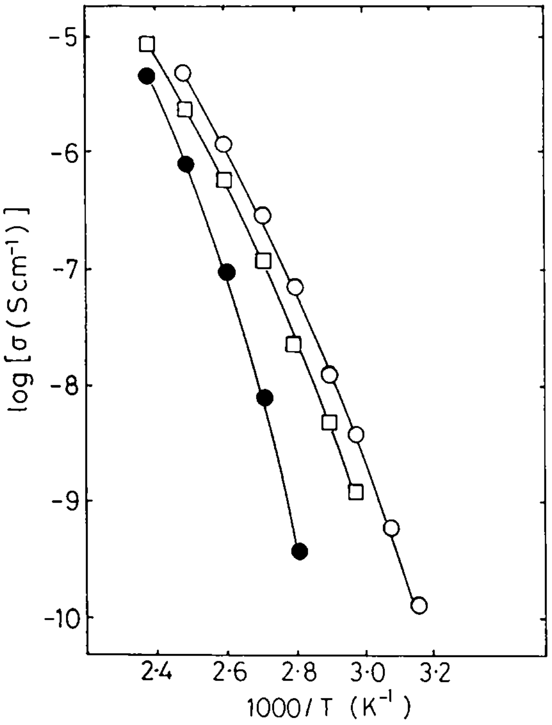

Figure 5 Log conductivity *versus* reciprocal temperature for PDMA–lithium trifluoromethanesulphonate; effect of molar mass of PDMA. Carbonyl:lithium = 12. M_n: (○) 17000; (□) 340000; (●) 1500000

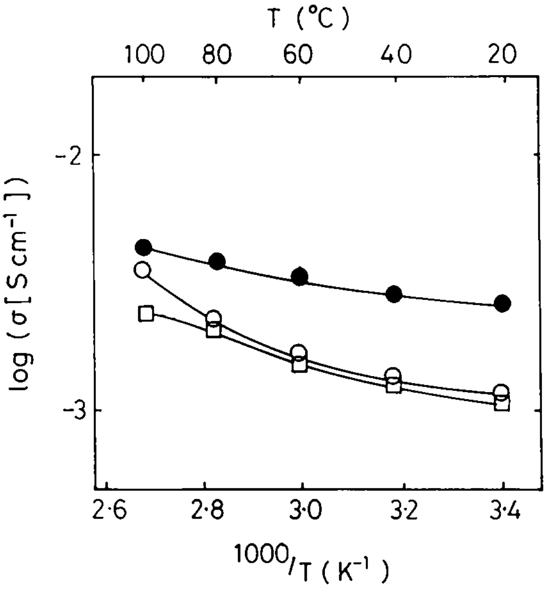

Figure 6 Log conductivity *versus* reciprocal temperature for crosslinked PDMA–DMAc–lithium perchlorate gels. Crosslinker: *N*,*N*-methylenebisacrylamide. Carbonyl:lithium = 12. (○) 60% DMAc: 10% crosslinker; (□) 70% DMAc: 20% crosslinker; (●) 80% DMAc: 30% crosslinker

It is clear that ionic conductivity can be improved if polar plasticizer is incorporated in the PDMA–salt complexes. As the content of added plasticizer is increased to ~50–60%, however, the material loses its solidity. Since it is advantageous to retain solidity, it was thought that crosslinking of the polymer might be a useful way of retaining solidity in materials that would be able to contain even higher levels of added plasticizer. *Figure 6* shows the conductivities of a number of PDMA–lithium perchlorate–DMAc complexes in which the polymer is crosslinked with *N*,*N*′-methylenebisacrylamide. These materials were transparent, rubbery solids and all had ambient temperature conductivities above 10^{-3} S cm^{-1}. The curves imply an increased activation energy at higher temperatures.

CONCLUSIONS

PDMA of very high molar mass complexed with lithium salts is a very tough material that can incorporate a high level of added plasticizer. Materials containing between 10% and 20% of added DMAc can be machined by lathe; further incorporation of DMAc (up to ~50%) gives rise to materials of increasing flexibility, and still further amounts produce a tacky, viscous resin. Materials retaining solidity yet containing even higher contents of added plasticizer can be made with crosslinked samples.

Both g.p.c. and t.g.a. indicate that the PDMA–salt complexes contain ~15–20% of unpolymerized monomer. Attempts to remove this monomer by prolonged heating under reduced pressure have been remarkably ineffective; ~10% of monomer remains in the samples after extended heat treatment.

It was not expected that materials containing such a high level of unpolymerized monomer would retain such excellent mechanical characteristics. Moreover, the ability of the materials to incorporate higher levels of added plasticizer and still retain good mechanical characteristics was also unexpected.

The ionic conductivities of the materials free from added plasticizer are not particularly impressive. Ionic conductivity increases with increasing content of added plasticizer, and a high content of added plasticizer in the crosslinked materials makes very high ionic conductivities (above 10^{-3} S cm^{-1} at ambient temperature) possible. These results are useful in showing how high ionic conductivities can be achieved in samples with good mechanical properties.

It is possible to produce complexed PDMA in a wide range of molar masses by use of ethane thiol as a chain transfer agent. The polymers having the lowest molar mass exhibit the highest ionic conductivities.

REFERENCES

1 Wright, P. V. *Br. Polym. J.* 1975, **7**, 319

2 Armand, M. B., Chabagno, J. M. and Duclot, M. Paper presented at Second International Conference on Solid Electrolytes, St Andrews, 1978

3 Berthier, C., Gorecki, W., Minier, M., Armand, M. B., Chabagno, J. M. and Rigaud, P. *Solid State Ionics* 1983, **11**, 91

4 Weston, J. E. and Steele, B. C. H. *Solid State Ionics* 1981, **2**, 347

5 Bannister, D. J., Davies, G. R., Ward, I. M. and McIntyre, J. E. *Polymer* 1984, **25**, 1600

6 Hall, P. G., Davies, G. R., McIntyre, J. E., Ward, I. M., Bannister, D. J. and Le Brocq, K. M. F. *Polym. Commun.* 1986, **27**, 98

7 MacCallum, J. R., Smith, M. J. and Vincent, C. A. *Solid State Ionics* 1984, **11**, 307

8 Nagaoka, K., Naruse, H., Shinohara, I. and Watanabe, M. *J. Polym. Sci., Polym. Lett. Edn.* 1984, **22**, 659

9 Kelly, I., Owen, J. R. and Steele, B. C. H. *J. Power Sources* 1985, **14**, 13

10 Vincent, C. A. *Prog. Solid State Chem.* 1987, **17**, 145

11 Blecher, L., Lorenz, D. H., Lowd, H. L., Wood, A. S. and Wyman, D. P. in 'Handbook of Water Soluble Gums and Resins' (Ed. R. L. Davidson), McGraw-Hill, New York, 1980

12 Spindler, R. and Shriver, D. F. *Macromolecules* 1986, **19**, 347

13 Dobrowski, S. A., Davies, G. R., Ward, I. M. and McIntyre, J. E. Paper presented at Third International Conference on New Polymeric Materials, Cambridge, 1988

14 Dobrowski, S. A., Davies, G. R., Ward, I. M. and McIntyre, J. E. Paper presented at Second International Symposium on Polymer Electrolytes, Siena, 1989

15 Ibbett, D. personal communication

16 Wetton, R. E., James, D. B. and Whiting, W. *J. Polym. Sci., Polym. Lett. Edn* 1976, **14**, 577

17 Cowie, J. M. G. Paper presented at First International Symposium on Polymer Electrolytes, St Andrews, 1987

18 Hall, P. G., Davies, G. R., Ward, I. M. and McIntyre, J. E. unpublished results

19 Vogel, H. *Phys. Z.* 1921, **22**, 645; Tammann, V. G. and Hesse, H. *Z. Anorg. Allg. Chem.* 1926, **156**, 245; Fulcher, G. S. *J. Am. Ceram. Soc.* 1925, **8**, 339

20 Leng, S. F. *PhD Thesis*, University of Leeds, 1989