Transparent and adhesive polymer electrolyte for smart windows: synthesis, characterization and ionic conductivity measurements

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Transparent, adhesive and viscoelastic polymer electrolytes were synthesized from poly(propylene glycol) (PPG) (molecular weight 2000), poly(methyl methacrylate) (PMMA) and $LiCF_3SO_3$ for smart-window application. The synthesis was carried out by the matrix polymerization method. Methyl methacrylate was polymerized in PPG doped with $LiCF_3SO_3$ using azobisisobutyronitrile as the initiator. Interestingly, the presence of $LiCF_3SO_3$ makes the two otherwise incompatible polymers compatible. Various combinations of the salt and PMMA were tried to make it applicable for smart windows. The PMMA incorporated (up to 8%) by this method appears to form a protective coating for the PPG–salt complex, making it hydrophobic, and also increases the adhesiveness of the polymer electrolyte. The ionic conductivities of these polyelectrolytes were measured as a function of temperature. The plot of conductivity *versus* temperature was found to fit to the Vogel–Tammann–Fulcher equation over the temperature range −20 to 110°C. The glass transition temperature was determined by differential scanning calorimetry. At high O:M ratio (ratio of ether oxygens to alkali-metal cation), PMMA does increase the T_g of the system, as can be expected. However, at low O:M ratio, PMMA does not seem to have any influence on the T_g of the system. The PMMA was isolated from the reaction mixture and characterized by ^1H nuclear magnetic resonance and gel permeation chromatography analysis.

(Keywords: polymer electrolyte: poly(propylene glycol); poly(methyl methacrylate); $LiCF_3SO_3$ salt complexes; synthesis; characterization; ionic conductivity)

INTRODUCTION

The ionic conductivity of solvent-free polyether/alkali-metal systems has been widely studied ever since the pioneering works of Wright *et al.*[1–3] and Armand *et al.*[4,5]. A number of papers and review articles have appeared that discuss the preparation, theory and conducting mechanism in these polyelectrolytes[6–11]. These systems are of great interest because of their application in making high-energy-density solid-state batteries and energy-efficient smart windows.

The objective of the present work was to synthesize a stable, transparent and adhesive polymer electrolyte, which is a critical component for electrochromic-based smart windows. The entire assembly of a smart window is described in detail elsewhere[12]. Poly(propylene glycol) (PPG) of low molecular weight has the advantages of being non-crystalline and having relatively high ionic conductivity when complexed with alkali-metal salts[13–16] and is an excellent base material for the electrolyte for smart-window application. However, the PPG–salt system is hydrophilic and has poor mechanical stability and adhesiveness. In order to improve these properties, poly(methyl methacrylate) (PMMA) was incorporated into the polymer matrix by polymerizing MMA in PPG doped with $LiCF_3SO_3$ using azobisisobutyronitrile (AIBN) as the initiator.

EXPERIMENTAL

Poly(propylene glycol) (mol. wt 2000) was supplied by Dow Chemical USA. The polymer was stringently freeze-dried using freeze–pump–thaw cycles under reduced pressure (10^{-4} Torr) until no more bubbles evolved. Again it was degassed in boiling water to get rid of any residual solvents present in the polymer. Lithium triflate (3M, Industrial and Chemical Division, USA) was dried under vacuum for 24 h at 120°C prior to use. Methyl methacrylate (Fisher Scientific) was distilled over calcium hydride under reduced pressure. AIBN (Aldrich) was used as received. Methanol (Fisher Scientific) and tetrahydrofuran (THF; Fisher Scientific) were distilled before use.

While still under vacuum, the degassed, dried PPG was transferred to a dry-box and the required amount of salt was dissolved directly in it at 80°C without the use of any solvents. This was then transferred to the polymerization vessel, provided with a mechanical stirrer, argon inlet and a septum. It was then kept in a constant-temperature bath at 60°C. The required amount of MMA (weight per cent of the mass of PPG) with 1% of AIBN was injected into the polymerization vessel and the polymerization was allowed to proceed for 24 h under argon atmosphere. The viscosity of the system increased as the polymerization proceeded and the clarity of the product was found to depend upon the amount of salt and PMMA present in the system (*vide infra*). The

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reaction mixture was removed and sealed under argon atmosphere until used.

The polyelectrolyte was repeatedly extracted with hot methanol. PPG and the salt dissolved in hot methanol while the PMMA separated. It was then filtered, washed with hot methanol and dried *in vacuo* prior to characterization.

^{1}H n.m.r. was taken on a Brüker AM 250 MHz instrument. Gel permeation chromatography was used to determine the molecular-weight distributions of the PMMA. These measurements were performed at 25°C using THF as the eluent (flow 1 ml $\min^{-1}$), on a Waters 590 GPC equipped with a model R-401 DRI detector. The detector was connected to an IBM-compatible microcomputer for data acquisition. The system was operated with four PL-gel columns with 100 000, 1000, 500 and 100 Å pore sizes. Both polystyrene (Pressure Chemical Co. and Polymer Laboratories) and PMMA (Polymer Laboratories) standards were used in calibrating the system. A universal calibration was used.

The water content of the polymer electrolyte samples determined by a 684 Karl Fischer Coulometer (Metrohm Ltd, Switzerland) was found to be less than 1%. Thermogravimetric analysis on degassed PPG using a Perkin–Elmer TGAA-7 showed a change in weight of 0.06% after raising the temperature from 30 to 150°C at 20°C $\min^{-1}$.

The glass transition temperature (T_g) of the polymer blend was measured using a Dupont 900 Differential Scanning Calorimeter on sample sizes of 5–10 mg, with a heating rate of 10°C $\min^{-1}$. Measurements were made under nitrogen atmosphere. The ionic conductivity of these polyelectrolytes was determined using the complex impedance method. The samples were sandwiched between two stainless steel electrodes and placed in a temperature-controlled furnace. The impedance measurements were carried out on a computer-interfaced HP 4192A impedance analyser over the frequency range 5 Hz to 13 MHz.

RESULTS AND DISCUSSION

The various compositions used to produce polyelectrolytes for practical use for smart windows are listed in *Table 1*. The clarity of the system was found to depend upon the amount of salt and PMMA present in the system. When MMA was polymerized in PPG in the absence of salt, the system turned cloudy irrespective of the MMA concentration. The system also remained cloudy at low salt concentration (O:M = 25:1, where O:M indicates the ratio of ether oxygens to alkali-metal cation) for 4% and 8% PMMA concentration. However, the samples having O:M = 16:1 were clear for both the PMMA concentrations. Another interesting observation was that the salt need not necessarily be added to the system prior to the polymerization. The system turned out clear even when the salt was added after the polymerization and the amount of salt required was found to depend on the PMMA content. Thus a study involving the incremental addition of salt to the cloudy mixture of PPG–PMMA revealed the system to become clear at O:M = 18:1 for the system containing 4% PMMA. From the foregoing results, it is evident that the salt plays an important role in making these polymers compatible. It is well known that the lithium cation binds with the ether oxygens of the polyether molecules and that the viscosity increases dramatically with increasing salt concentration[17,18]. This has been explained by the intermolecular and intramolecular bonding of chains through the lithium cation. The PPG–PMMA–salt blends are very stable and do not phase aggregate even after long periods of storage. This can be the result of ionic interactions between the alkali-metal cation, the ether oxygens of PPG and the ester group of PMMA side group, where lone pairs of electrons are available for bonding. This conclusion is further supported by the fact that the amount of salt needed for compatibilization of the polymers is increased with increasing amount of PMMA. A detailed study on the morphology of these polyelectrolytes using scanning electron microscopy is in progress.

Table 1 Compositions of polymer electrolytes

Sample No.	PPG	O:M ratio	PMMA (%)	Appearance
1	2000	–	4	Cloudy
2	2000	25:1	4	Cloudy
3	2000	25:1	8	Cloudy
4	2000	16:1	4	Clear
5	2000	16:1	8	Clear
6	2000	8:1	4	Clear
7	2000	8:1	8	Clear

Table 2 T_g of the polyelectrolytes and molecular weights of PMMA obtained by g.p.c. analysis

Sample No.	T_g (°C)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
2	−55.9	163 000	2.10
3	−45.5	200 000	3.06
4	−50.2	113 000	2.40
5	−31.6	173 000	1.73
6	−23.3	161 000	1.90
7	−24.8	194 000	1.73

The viscosity of the system increases with increasing amount of PMMA since the molecular weight of PMMA increases with increasing amount of MMA converted (*Table 2*). The samples containing PMMA were generally found to be sticky in nature. Also it was noted that the adhesive characteristics of the mixture were enhanced as the amount of PMMA in the system increased. Although no quantitative measurements were made to account for this enhancement, qualitatively one could observe the difference between samples with increasing amounts of PMMA. This conclusion was based upon the way in which each sample adhered to the walls of the reaction vessel and the degree of difficulty of removal after polymerization. We also studied qualitatively the capacity of each sample to hold two glass plates together in shear and tension.

The glass transition temperatures of the electrolytes determined by d.s.c. are given in *Table 2*. At the salt concentration sufficient to make the system compatible (O:M = 16:1), the PMMA affects the T_g of the system. At lower salt concentrations, the effect of PMMA on the T_g of the system is not as pronounced because the system is only partially compatible. However, at high salt concentrations, where the salt appears to play a more dominant role, the effect of PMMA on the T_g was found to be nullified.

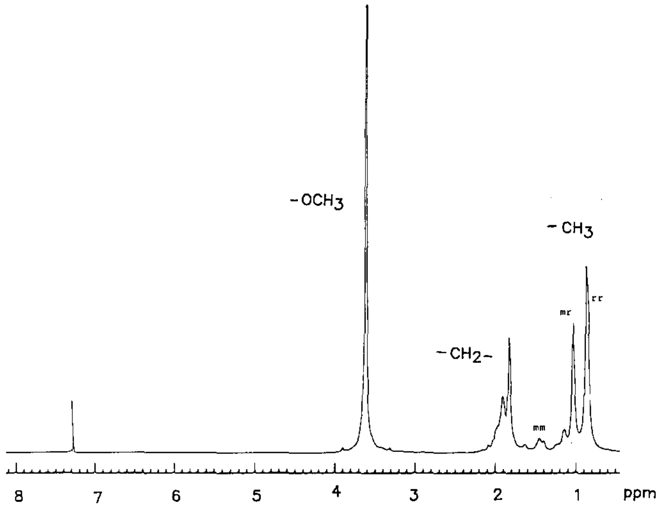

Figure 1 ^{1}H n.m.r. spectrum of poly(methyl methacrylate)

Table 3 Ionic conductivities and VTF parameters for the polymer electrolyte

Sample No.	σ (S cm^{-1}) at 301 K	A	B	T (K)
2	6.35×10^{-6}			
3	4.88×10^{-6}			
4	5.99×10^{-6}	0.026	899	194
5	4.97×10^{-6}	0.451	1051	187
6	1.34×10^{-6}	0.667	1335	199
7	1.10×10^{-6}	0.232	1224	203

It was also of interest for us to see whether the PPG $LiCF_3SO_3$ electrolyte acts as a template inducing stereoregularity into the PMMA produced. The PMMA was separated from the system with hot methanol and the tacticity was determined by ^{1}H n.m.r.[19]. A typical spectrum is given in *Figure 1*. However, it was found that the PMMA obtained was atactic with the dyad concentrations i = 5%, s = 55% and h = 45% similar to that obtained by free-radical polymerization. This composition did not vary much from sample to sample. Hence, we believe that the polymerization is mainly taking place within the bulk of the matrix.

The molecular weight of the PMMA isolated was determined by g.p.c. analysis, which is given in *Table 2*. The molecular weights obtained were in the range 110 000–200 000. With increasing amount of PMMA, the $\bar{M}_n$ increases. The polydispersity was in the range 1.5–3 for most of the samples.

The ionic conductivity of the samples at 28°C is given in *Table 3*. The maximum conductivity was obtained for the sample having O:M = 25:1 and 4% PMMA. However, this sample was cloudy. Among the clear samples the maximum conductivity was observed for the sample containing O:M = 16:1 and 4% PMMA. The conductivity decreased with increasing amount of PMMA. This can be expected for two reasons: (1) for these ranges of $\bar{M}_n$ a PMMA–salt complex has conductivities several orders of magnitude less than PPG–salt complexes of the same O:M ratio, and (2) the increase in viscosity with increasing amount of PMMA in the system hinders segmental mobility, which subsequently lowers the conductivity.

The presence of PMMA in these electrolytes increased the hydrophobicity quite dramatically. The ionic conductivity of the polymer electrolytes without any PMMA increased gradually upon storage. This can be attributed to water being absorbed by the samples from the atmosphere. This was further confirmed by deliberately exposing the samples to water vapour, when the ionic conductivity increased by an order of magnitude[20]. However, with the incorporation of PMMA, the polymer electrolytes were found to be much more stable and resistant to atmospheric moisture. The ionic conductivity was fairly stable even after months of storage without any undue precautions, especially with the polyelectrolytes containing lower salt and greater PMMA contents. PMMA is thus expected to form a protective coating for the PPG–salt mixture. This aprotic polymer electrolyte system is a potential component for smart-window applications[12]. A detailed study of this applicability is in progress.

The ionic conductivity of the clear samples was measured as a function of temperature (see *Figure 2*). Temperatures were varied from −20 to 110°C. The full curves represent the least-squares fits to the Vogel–Tammann–Fulcher (VTF) equation[21–23]:

$$\sigma = AT^{-1/2} \exp[-E/kB(T - T_0)]$$

where A is a pre-exponential factor, E is the pseudo-activation energy and T_0 is the ideal transition temperature. As can be observed, there is a good fit to this equation. The VTF parameters for these samples are given in *Table 3*.

CONCLUSIONS

A viscoelastic, transparent and adhesive polyelectrolyte, which is a crucial component for smart-window application, was synthesized from PPG (mol. wt 2000), PMMA and $LiCF_3SO_3$ by matrix polymerization. This was achieved without the use of any solvent. The presence of PMMA in the system forms a loose elastomeric network and increases the stability, hydrophobicity and adhesive properties. Clarity of the system depends upon the amount of PMMA and $LiCF_3SO_3$ present in the system. The PMMA isolated from the system was characterized by ^{1}H n.m.r. and g.p.c. analysis and is found to be formed by free-radical polymerization. Ionic conductivity was measured over a temperature range of −20 to 110°C and found to fit the VTF empirical equation.

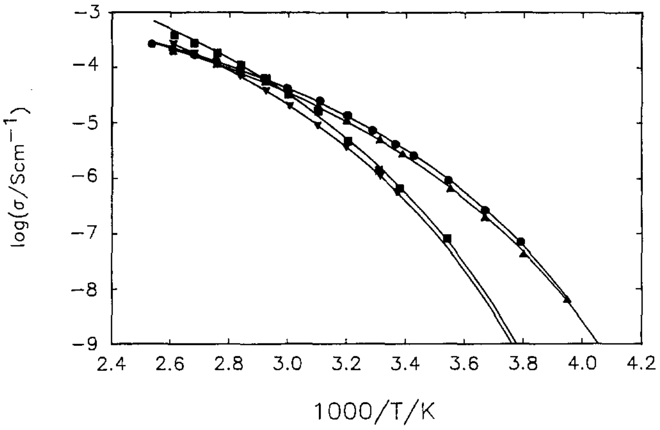

Figure 2 Temperature dependence of the ionic conductivity of sample 4 (●), sample 5 (▲), sample 6 (■) and sample 7 (▼). The full curves show least-squares fits to the VTF equation

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REFERENCES

1 Fenton, D. E., Parker, J. M. and Wright, P. V. *Polymer* 1973, **14**, 589
2 Wright, P. V. *Br. Polym. J.* 1975, **7**, 319
3 Wright, P. V. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 955
4 Armand, M. B., Chabagno, J. M. and Duclot, M. J. in 'Fast Ion Transport in Solids' (Eds. P. Vashishta, J. N. Mundy and G. K. Shenoy), North-Holland, Amsterdam, 1979, pp. 131–136
5 Armand, M. B., Chabagno, J. M. and Duclot, M. J. Extended Abstracts, Second International Conference on Solid Electrolytes, St Andrews, Scotland, 1978
6 MacCallum, J. R. and Vincent, C. A. in 'Polymer Electrolyte Reviews-1' (Eds J. R. MacCallum and C. A. Vincent), Elsevier, London, 1987, p. 23
7 Cameron, G. G. and Ingram, M. D. in 'Polymer Electrolyte Reviews-2' (Eds J. R. MacCallum and C. A. Vincent), Elsevier, London, 1989, p. 157
8 Ratner, M. A. and Shriver, D. F. *Chem. Rev.* 1988, **88**, 109
9 Armand, M. *Solid State Ionics* 1983, **9** & **10**, 745
10 Ratner, M. A. and Shriver, D. F. MRS/Bulletin, 1989, p. 39
11 Wright, P. V. *J. Macromol. Sci.–Chem.* 1989, **26**(A), 519
12 Anderson, A. M., Granqvist, C.-G. and Stevens, J. R. in 'Large-Area Chromogenics: Material and Devices for Transmittance Control' (Eds C. M. Lampert and C.-G. Granqvist), Vol. IS4, SPIE International Society for Optical Engineering, Washington, 1990, p. 471
13 Wetton, R. E., James, D. B. and Whiting, W. *J. Polym. Sci., Polym. Lett. Edn.* 1976, **14**, 557
14 James, D. B., Wetton, R. E. and Brown, D. S. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 1978, **19**, 347
15 Watanabe, M., Ikeda, J. and Shinohara, I. *Polym. J.* 1983, **15**(1), 65
16 Watanabe, M., Ikeda, J. and Shinohara, I. *Polym. J.* 1983, **15**(2), 175
17 Eisenberg, A., Ovans, K. and Yoon, H. N. in 'Ions in Polymers' (Ed. A. Eisenberg), American Chemical Society, Washington DC, 1980, p. 267
18 Wixwat, W., Fu, Y. and Stevens, J. R. *Polymer* 1990, **32**, 1181
19 Bovey, F. and Tiers, G. V. D. *J. Polym. Sci.* 1960, **44**, 173
20 Wixwat, W., M.Sc. Thesis, University of Guelph, Ontario, 1990
21 Vogel, H. *Phys. Z.* 1921, **22**, 645
22 Tammann, V. G. and Hesse, W. Z. *Anorg. Allg. Chem.* 1926, **156**, 245
23 Fulcher, G. S. *J. Am. Ceram. Soc.* 1925, **8**, 339