

# Highly conductive poly(ethylene oxide)–poly(methyl methacrylate) blends complexed with alkali metal salts

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Solid electrolytes of room temperature ionic conductivity exceeding  $10^{-5} \text{ S cm}^{-1}$  were obtained by complexing NaI, LiI,  $\text{LiBF}_4$  and  $\text{LiClO}_4$  with blends prepared by thermal polymerization of methyl methacrylate in the presence of high molecular weight poly(ethylene oxide). All of the studied samples were thermally stable up to at least  $60^\circ\text{C}$ . Differential scanning calorimetry studies indicated that these electrolytes contained amorphous phases with very low glass transition temperatures. This is due to the plasticizing effect of the grafted copolymers formed during the polymerization. This is supposed to lead to high mobility of the charge carriers in the systems studied.

**(Keywords: blends; electrolytes; complexes; impedance; conductivity)**

## INTRODUCTION

Several papers have recently shown that mechanical properties of polymeric electrolytes based on poly(ethylene oxide) (PEO) can be improved by addition of polymers with high glass transition temperatures ( $T_g$ s) such as polystyrene<sup>1</sup>, poly(acrylic acid)<sup>2</sup> or poly(methyl methacrylate) (PMMA)<sup>3,4</sup>. Our previous investigations<sup>3,4</sup> showed that blends prepared by thermal polymerization of methyl methacrylate (MMA) in the presence of PEO after complexation with NaI exhibited much higher conductivities than polymer electrolytes based on blends prepared by casting a two-component polymer mixture from an appropriate solvent. We have proved that during thermal polymerization of MMA in the presence of PEO some grafted copolymer was formed. The presence of this copolymer might enhance ionic conductivity due to an increase in segmental motion in the amorphous phase of the polymeric electrolytes<sup>4</sup>. In this paper we present new results supporting this hypothesis.

## EXPERIMENTAL

Polymer blends were prepared according to the procedure described elsewhere<sup>3,4</sup>. The dopants used were NaI, LiI,  $\text{LiClO}_4$  and  $\text{LiBF}_4$  (reagent grades). Polymer foils were prepared by a standard casting technique using acetonitrile as solvent. All reagents were carefully dried before use. All experiments were carried out under vacuum. Conductivity of the studied samples was evaluated from impedance spectroscopy experiments. The measurements were performed in the frequency range of  $5\text{--}500 \times 10^3 \text{ Hz}$  applying stainless steel blocking electrodes. To study the thermal behaviour of PEO–PMMA blends differential scanning calorimetry (d.s.c.) experiments were carried out in the temperature range

180–400 K using a UNIPAN 605 scanning microcalorimeter. The heating rate was equal to  $2 \text{ K min}^{-1}$ . The  $^1\text{H}$  nuclear magnetic resonance (n.m.r.) spectra were recorded in  $\text{CDCl}_3$  on a Bruker AM 300 spectrometer.

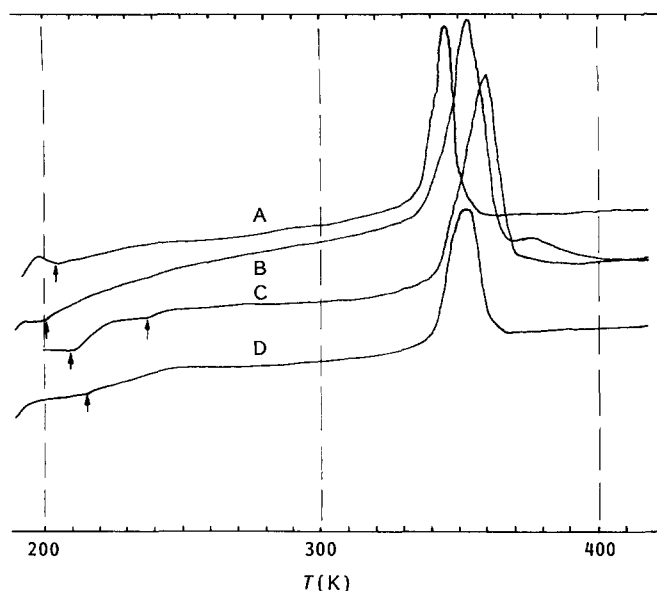
## RESULTS AND DISCUSSION

### *D.s.c. studies on PEO–PMMA blends*

In order to explain the effect of grafted copolymers on the mobility of the charge carriers in polymeric electrolytes it is informative to compare the thermograms of blends prepared by polymerization of MMA in the presence of PEO with those of conventional solvent cast PEO–PMMA blends. Samples with PMMA concentrations of 6, 20, 34 and 43 wt% were taken for d.s.c. investigations. After polymerization was complete the samples were cast from an acetonitrile solution and then crystallized for 30 days at room temperature. D.s.c. curves (*Figure 1*) showed the presence of melting peaks of a crystalline PEO phase at  $\sim 335 \text{ K}$  as well as the glass transition occurring in the temperature range of 200–215 K (*Table 1*). The degree of crystallinity, calculated by comparing the melting heats of the crystalline phase of a blend with those found for pure crystalline PEO, decreased from 68 to 34% with increasing PMMA concentration (*Table 1*). Degrees of crystallinity calculated from X-ray experiments were found to be slightly lower. The melting temperature,  $T_m$ , of PEO crystallites was not significantly suppressed by the presence of PMMA. In fact, a small increase in  $T_m$  (as well as a shift in the base line) was observed in samples containing 34 and 43 wt% of PMMA. Li and Hsu<sup>5</sup> suggested that this effect might result from the presence of a second amorphous phase with a  $T_g$  close to  $T_m$ .

$^1\text{H}$  n.m.r. studies indicated that the PMMA formed in the systems studied had an atactic structure and the mole fractions of isotactic, heterotactic and syndiotactic triads were equal to 0.089, 0.412 and 0.504, respectively. The

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**Figure 1** D.s.c. traces for PEO-PMMA blends prepared by thermal polymerization of MMA in the presence of PEO. Concentrations (wt%) of PMMA: (A) 6; (B) 20; (C) 36; (D) 43

**Table 1** Glass transition temperatures ( $T_g$ ), melting temperatures ( $T_m$ ) and degrees of crystallinity ( $X_c$ ) for PEO-PMMA blends

PMMA (wt%)	Blends prepared by polymerization				Solvent cast blends		
	$T_g$ (K)	$T_m$ (K)	$X_c^a$ (%)	$X_c^b$ (%)	$T_g$ (K)	$T_m$ (K)	$X_c^b$ (%)
6	205	335	68	59	—	338	57
20	200	335	52	52	240	338	48
34	211	334	—	35	248	336	38
43	215	334	34	31	260	336	33

<sup>a</sup> Calculated from d.s.c. studies

<sup>b</sup> Calculated from X-ray experiments

thermograms of conventional blends of PEO and atactic PMMA showed that the method of blend preparation had no significant influence on the  $T_m$  values and degrees of crystallinity.

However, as can be seen from *Table 1*,  $T_g$  values measured for the amorphous phase of the blends prepared by thermal polymerization of MMA in the presence of PEO are much lower than obtained for blends prepared by mixing the polymers, and even lower than the  $T_g$  value measured for pure PEO. This fact indicates the formation of an internal plasticizer increasing the mobility of the polymer chains. The lowest  $T_g$  value was measured for the blend containing 20 wt% MMA. It should be noted that this polymer matrix was found to provide the highest ionic conductivity in electrolytes comprising NaI and PEO-PMMA blends.

#### D.s.c. and conductivity studies on electrolytes based on PEO-PMMA blends

The blend characterized by the lowest  $T_g$  value was complexed with some lithium and sodium salts. As can be seen from *Table 2* the  $T_g$  values of electrolytes shift to higher temperatures in comparison with those found for the pristine blend. However, these changes are much smaller than in analogous systems containing pristine

PEO as the polymer matrix<sup>6</sup>. We suggest that the grafted copolymer of ethylene oxide and MMA formed during preparation of the blends increases the distance between PEO chains and hence diminishes a crosslinking effect of added salts resulting from the interactions between alkali metal cations and oxygen atoms in distinct PEO chains. (A similar effect was recently observed in electrolytes comprising lithium triflate and random copolymers of ethylene oxide with ethoxyethyl glycid ether<sup>7</sup>). Systematic changes in  $T_g$  values with concentration of a salt are not observed. This may be due to the formation of several amorphous phases of different segmental mobility of PEO chains which are not fully separated. Two distinct  $T_g$  values in the low temperature region (at 209 and 241 K, respectively) are observed in the sample containing 10 mol% of LiClO<sub>4</sub> with respect to ethylene oxide monomeric units (*Figure 2*).

The melting point of the PEO crystalline phase decreases significantly after doping with lithium salts (*Table 2*). A decrease in  $T_m$  and increase in  $T_g$  values indicate that the degree of PEO crystallinity for lithium electrolytes is lower than that for uncomplexed blends. In some complexes with LiClO<sub>4</sub> the melting peak of the crystalline phase of the PEO-salt complex is observed but its intensity is very small. The melting point of this phase is ~50 K lower than those observed for (PEO)<sub>n</sub>LiClO<sub>4</sub> complexes. Addition of NaI to the blend causes a small increase in  $T_g$  and hardly affects the  $T_m$  and degree of crystallinity. These effects are probably due to the weaker coordination of sodium cations rather than lithium cations by ether-type ligands.

Values of ionic conductivity versus reciprocal temperature obtained for the studied electrolytes are shown in *Figures 3* and *4*. At salt concentration equal to 10 mol% with respect to ethylene oxide monomeric units the room temperature conductivity of all samples was  $>10^{-5}$  S cm<sup>-1</sup> (*Figure 3*). Conductivity increases in the order: NaI < LiBF<sub>4</sub> < LiI < LiClO<sub>4</sub> with respect to the type of added salt. The highest value (measured for the sample containing LiClO<sub>4</sub>) was equal to  $6.6 \times 10^{-5}$  cm<sup>-1</sup> at 20°C. Further investigations performed on electrolytes of various LiClO<sub>4</sub> concentration showed that 10 mol% of the added salt was an optimum value (*Figure 3*). All of the studied samples were mechanically stable at least up to 60°C and some of them even up to 100°C. The conductivities at 100°C were  $\sim 10^{-3}$  S cm<sup>-1</sup>.

Taking into account the d.s.c. data the lower conductivity of samples containing NaI than those containing lithium salts seems to result mainly from a higher amorphous phase content in the lithium

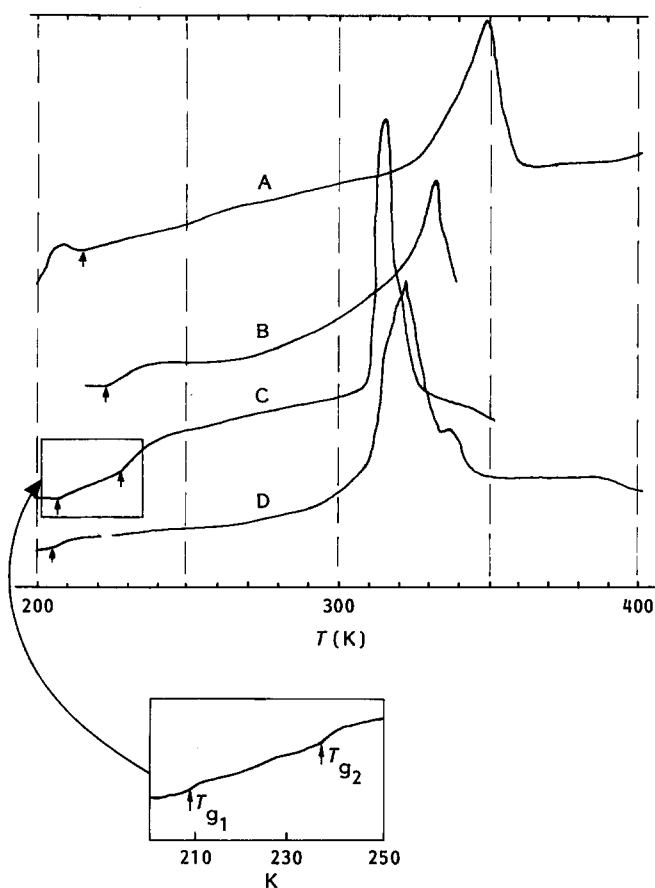
**Table 2** D.s.c. data for alkali metal electrolytes based on PEO-PMMA blends<sup>a</sup>

	Concentration (mol%)	$T_g$ (K)	$T_m$ (K)	$T_m^b$ (K)	$X_c^c$ (%)
NaI	10	213	332		51
LiBF <sub>4</sub>	10	224	322		31
LiClO <sub>4</sub>	3	216	320		
LiClO <sub>4</sub>	5	238	315	382	
LiClO <sub>4</sub>	10	209, 241	313	383	30
LiClO <sub>4</sub>	15	227	312		
LiClO <sub>4</sub>	25	232			

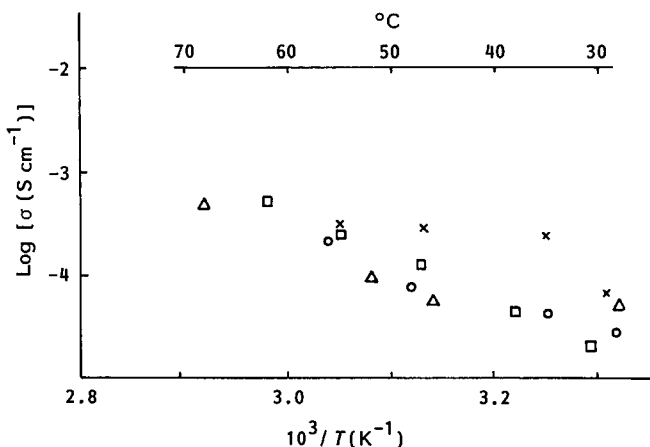
<sup>a</sup> 20 wt% of PMMA

<sup>b</sup> Melting temperature of the PEO-LiClO<sub>4</sub> complex

<sup>c</sup> Calculated from d.s.c. studies



**Figure 2** D.s.c. curves for PEO-PMMA blend (prepared by thermal polymerization of MMA in the presence of PEO) based electrolytes. Concentration of the added salts is equal to 10 mol% with respect to ethylene oxide monomeric units. PMMA concentration is equal to 20 wt%. Sample doped with: (A) NaI; (B) LiBF<sub>4</sub>; (C) LiClO<sub>4</sub>. (D) PEO + 30 wt% of the grafted phase doped with NaI (10 mol%)

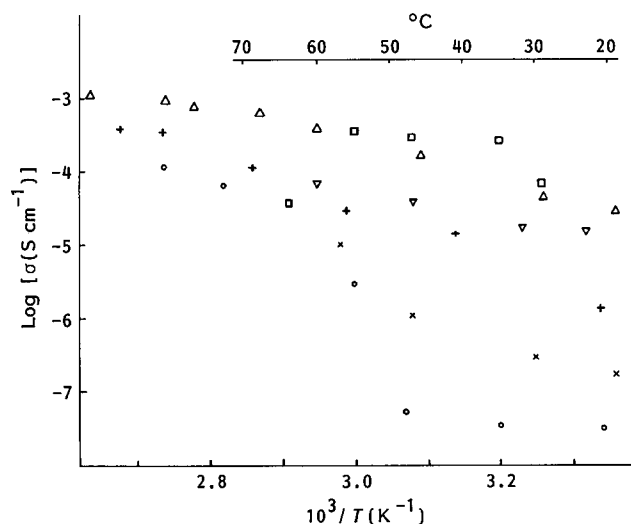


**Figure 3** Changes in conductivity *versus* reciprocal temperature for PEO-PMMA (20 wt%) blend based electrolytes doped with various alkali metal salts. Concentration of the added salts is equal to 10 mol% with respect to ethylene oxide monomeric units. Sample doped with: (○) LiBF<sub>4</sub>; (×) LiClO<sub>4</sub>; (△) LiI; (□) NaI

electrolytes. However, the difference in the conductivity of various lithium electrolytes is attributed to the properties of the amorphous phase. Electrolytes with the highest room temperature conductivity contain phases with the lowest  $T_g$  and thus the highest segmental mobility of PEO chains.

*D.s.c. and conductivity studies on samples of isolated grafted copolymer*

The grafted copolymer was isolated from the blend containing 20 wt% MMA monomeric units according to the procedure described elsewhere<sup>4</sup>. According to the results from infra-red spectroscopy it contained 88 wt% ethylene oxide and 12 wt% MMA monomeric units. Conductivity and d.s.c. experiments were performed on the electrolytes prepared by doping this copolymer with NaI (10 mol% with respect to ethylene oxide monomeric units) and on a polymer blend prepared from the isolated copolymer (30 wt%) and PEO (70 wt%). The blend was additionally doped with NaI (10 mol%). The results of these studies are summarized in Table 3. The first system was characterized by two  $T_g$  values (222 and 255 K) and low ambient temperature ionic conductivity ( $< 10^{-7} \text{ S cm}^{-1}$  at room temperature). In contrast, the second system exhibited only one very low  $T_g$  value (207 K) and high ionic conductivity  $1.4 \times 10^{-4} \text{ S cm}^{-1}$  at 20°C. These experiments showed that the grafted copolymer itself was not a good ionic conductor. Its effect on conductivity of polymeric electrolytes resulted apparently from decreasing the interactions between PEO chains and increasing their segmental mobility. However, in order to explain the mechanism of ion transport in this type of electrolyte further investigations are necessary especially concerning the quantitative determination of the crystalline and amorphous phase concentrations.



**Figure 4** Changes in conductivity *versus* reciprocal temperature for PEO-PMMA (20 wt%) - LiClO<sub>4</sub> electrolytes. Samples of various salt concentrations (mol%) with respect to ethylene oxide monomeric units: (○) 2; (×) 3; (△) 5; (□) 10; (+) 15; (▽) 25

**Table 3** D.s.c. and conductivity ( $\sigma$ ) data for isolated grafted copolymer (1) and its blend with PEO (2)<sup>a</sup>

	$T_g$ (K)	$T_m$ (K)	$T_{m1}$ (K)	$\sigma$ (at 20°C) (S cm <sup>-1</sup> )
1	222, 255	316	386	$10^{-7}$
2 <sup>b</sup>	207	321	389	$1.4 \times 10^{-4}$

<sup>a</sup> Inorganic additive NaI (concentration equal to 10 mol% with respect to ethylene oxide monomeric units)

<sup>b</sup> 30 wt% of the grafted copolymer

#### ACKNOWLEDGEMENT

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#### REFERENCES

- 1 Gray, F. M., MacCallum, J. R. and Vincent, C. A. *Solid State Ionics* 1986, **18&19**, 252
- 2 Tsuchida, T., Ohno, H., Tsunami, T. and Kobayashi, N. *Solid State Ionics* 1983, **11**, 227
- 3 Przyłuski, J., Such, K., Floriańczyk, Z., Wyciślik, H. and Wieczorek, W. *Synth. Met.* 1990, **35**, 241
- 4 Such, K., Floriańczyk, Z., Przyłuski, J. and Wieczorek, W. 'Proc. II Int. Symposium on Polymeric Electrolytes, Siena, June, 1989' (Ed. B. Scrosati), Elsevier, 1990, pp. 119–127
- 5 Li, X. and Hsu, L. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 1331
- 6 Cowie, J. M. G. 'Polymer Electrolytes Reviews 1' (Eds J. R. MacCallum and C. A. Vincent), Elsevier, Amsterdam, 1987, Ch. 2; and references cited therein
- 7 Ballard, D. G., Chesire, P., Mann, T. S. and Przeworski, J. E. *Macromolecules* 1990, **23**, 1256