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Studies on comb-like polymer blend with poly(ethylene oxide)—lithium perchlorate salt complex electrolyte

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Comb-like polymer having poly(ethylene oxide) (PEO) side chain was synthesized from the macromer poly(ethylene glycol) ethyl ether methacrylate (PEGEEM). Copolymers of PEGEEM with hydrophobic methyl methacrylate (MMA) of varying compositions were also synthesized. The copolymers were characterized by ^{1}H n.m.r. Hybrid film of polyelectrolyte was prepared from these polymers with PEO and $LiClO_4$ by the solution cast technique. Ionic conductivities were studied by the impedance method for these hybrid films with respect to MMA percentage and salt concentration. It was found that the conductivity at high frequency semi-circle (σ_h) was independent of MMA concentration, while the bulk (σ_d) conductivity was higher than the PEO–salt complex up to 20–30% of the MMA concentration. The salt variations in hybrid films showed that the ionic conductivity for (ethylene oxide), EO/Li = 8 was lower than that for EO/Li = 12 and 20. © 1997 Elsevier Science Ltd.

(Keywords: macromer; copolymer; hybrid films)

Introduction

The discovery of polymeric electrolytes by Wright and Armand[1,2], has led to intensified research in the synthesis of polymer electrolytes with high ionic conductivity and dimensional stability[3–9]. Among these, poly(ethylene oxide) (PEO) based lithium conductive electrolytes have been found to be attractive[10,11]. Ionic conduction in solvent free polymer electrolytes primarily occurs in the amorphous phase[12]. The conductance of PEO–salt complex electrolyte is poor at room temperature because of the semi-crystallinity and hence research is targeted at development of newer amorphous systems[13,14].

Recently, comb-like amphiphilic polymer with hydrophilic PEO side chains have gained interest[15]. These polymers simultaneously provide the main chain rigidity and the pendant hydrophilic PEO as side chains impart flexibility. Thus, these amorphous polymers have the desired combination of structural strength and low T_g.

In the present study we report on the synthesis of a comb-like polymer having PEO side chains derived from the macromer poly(ethylene glycol) ethyl ether methacrylate (PEGEEM). Copolymers of PEGEEM with hydrophobic methyl methacrylate (MMA) of varying compositions were also synthesized. Polyblends of PEO with homopolymer poly[(poly ethylene glycol ethyl ether) methacrylate] (PEGEEP) as well as with copolymers of PEGEEM and MMA were prepared by solution casting. The ionic conduction of lithium perchlorate ($LiClO_4$) complexes of these polyblends were studied.

Experimental

Materials. PEO ($M_n = 400000$), $LiClO_4$ and monomers of PEGEEM (MW = 246) and MMA were procured from Aldrich Chemical Co., USA. The initiator, azobis isobutyronitrile (AIBN) was from Fluka, Switzerland. Toluene was from S.D. Fine Chem., India.

The monomers were distilled before use, PEO was used after drying under reduced pressure at 40°C for 12 h and $LiClO_4$ was used after vacuum drying at 120°C for 20 h. Acetonitrile of reagent grade from Ranbaxy, India was used as received.

Polymerization. The polymers were synthesized by radical polymerization in toluene at 65°C for 24 h. In a typical experiment the monomer, PEGEEM 15 ml was added to toluene (75 ml) and was purged with oxygen free nitrogen gas for 5 min. The initiator, AIBN, 1 wt% with respect to monomer, was added and the flask containing this solution was stoppered. The polymerizations were carried out by keeping the flask in a water bath set at 65°C. After 24 h of polymerization, the flasks were cooled to ambient temperature. The toluene was then distilled off under vacuum and the polymers were precipitated by pouring into cold petroleum ether 60–80 followed by filtration and drying under vacuum. The yields were in the range 80–85%. Copolymers of differing molar compositions of MMA/PEGEEM (0/100, 20/80, 30/70, 40/60, 50/50 and 75/25) were synthesized in a similar manner. The total volume of the monomer mixture was kept constant at 15 ml.

Electrolyte preparation. The homo/copolymer–$LiClO_4$ electrolytes (hybrid films) were prepared as follows. PEO/PEGEEP (homopolymer)/PEGEEM/MMA (copolymer) and $LiClO_4$ were dissolved in acetonitrile at desired ratios as described in *Table 1* and magnetically

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Table 1 Nomenclature and details of composition

Sl. No.	EO/Li = 12 polymer electrolyte	Text description
1	PEO–$LiClO_4$	PEO–salt complex
2	$[(PEO)_{0.45}\{PEGEEP\}_{0.55}]$–$LiClO_4$	Hybrid A–salt complex
3	$[(PEO)_{0.45}\{(PEGEEM)_{0.8}$ $(MMA)_{0.20}\}_{0.55}]$–$LiClO_4$	Hybrid B–salt complex
4	$[(PEO)_{0.45}\{(PEGEEM)_{0.70}$ $(MMA)_{0.30}\}_{0.55}]$–$LiClO_4$	Hybrid C–salt complex
5	$[(PEO)_{0.45}\{(PEGEEM)_{0.60}$ $(MMA)_{0.40}\}_{0.55}]$–$LiClO_4$	Hybrid D–salt complex
6	$[(PEO)_{0.45}\{(PEGEEM)_{0.50}$ $(MMA)_{0.50}\}_{0.55}]$–$LiClO_4$	Hybrid E–salt complex
7	$[(PEO)_{0.45}\{(PEGEEM)_{0.25}$ $(MMA)_{0.75}\}_{0.55}]$–$LiClO_4$	Hybrid F–salt complex

PEO = linear poly(ethylene oxide), $M_n = 400\,000$; PEGEEM = poly(ethylene glycol) ethyl ether methacrylate; MMA = methyl methacrylate; PEGEEP = comb-shaped poly and poly(ethylene glycol) ethyl ether methacrylate; hybrid A = poly blend of PEO 45 wt% and PEGEEP homopolymer 55 wt%; hybrid B = poly blend of PEO 45 wt% and copolymer of PEGEEM–MMA 80–20 are 55 wt%; hybrid C = poly blend of PEO 45 wt% and copolymer of PEGEEM–MMA 70–30 are 55 wt%; hybrid D = poly blend of PEO 45 wt% and copolymer of PEGEEM–MMA 60–40 are 55 wt%; hybrid E = poly blend of PEO 45 wt% and copolymer of PEGEEM–MMA 50–50 are 55 wt%; hybrid F = poly blend of PEO 45 wt% and copolymer of PEGEEM–MMA 25–75 are 55 wt%

stirred at 25°C for 10 h inside an argon filled glove chamber maintained at a relative humidity of less than 2%. The slurry was cast on to a polypropylene dish. The cast hybrid film was dried initially inside the glove chamber at ambient temperature for 16 h and was later transferred to a vacuum chamber for further drying at 40°C for 48 h.

Polymer/film characterization. ^1H n.m.r. of PEGEEM/MMA copolymers were taken in $CDCl_3$. The ionic conductivities of the hybrid films (polymer electrolytes) were measured at 25°C in argon atmosphere by impedance measurements between 20 Hz and 1 MHz using a Hewlett–Packard 4284A Impedance Analyser. The film (16 mm in diameter) was sandwiched between a stainless steel electrode for impedance measurements. D.s.c. measurements of homo/copolymers and polymer electrolyte films were made with a Mettler DSC-30, in the temperature range of −100°C to +100°C in dynamic mode at 10°C min^{-1} after an initial annealing for 5 min at 100°C.

Results and discussion

The synthesized monomers and polymers were readily soluble in methanol and acetone but insoluble in water. The n.m.r. spectrum results show that the copolymer does not contain any unreacted monomers as evidenced by the absence of peak at $\delta = 5$–6 (C=C bond of monomer). The protons of dioxyethylene units (OCH_2CH_2O) are assigned at $\delta = 3.7$, $-COOCH_2-$ at $\delta = 4.1$, CH_3- at $\delta = 0.9$, and $-CH_2-$ at $\delta = 1.2$. In MMA units, CH_3O- at $\delta = 3.6$, and $-CH_2-$ at $\delta = 1.8$. Similar results were reported by other workers for this type of system[15–18]. I.r. spectra also did not show any peak corresponding to the vinylic bond (C=C)[19].

Ionic conductivity. The impedance (Z' vs. Z'') plots were plotted for all polymer electrolytes (hybrid films). In the case of PEO- and hybrid-A-salt (EO/Li = 12 [units]) complexes (see *Table 1*), the curves had a single semi-circle whereas the other polymer electrolytes (hybrid B to F) had two semi-circles. The conductivities σ_d and σ_h were calculated from the impedance values where the curve approached the real axis at low and high frequencies, respectively. Thus, σ_d represents the total bulk conductivity. These results are presented in the form of conductivities ($\sigma = \sigma_d$ and σ_h) vs. MMA percentage in *Figure 1*. The conductivity, σ_h, for all other electrolytes synthesized from copolymers [hybrid (B–F)] was found to be practically independent of MMA concentration and this value was comparable to the conductivity of hybrid-A-salt complex. The bulk conductivity (σ_d) of linear PEO–salt complex is lower than that of the hybrid-A–salt polymer electrolytes. This result is consistent with the work of others for the comb-like polymers[20]. The synthesized polymer (PEGEEP) has pendant flexible ethylene oxide units which aids the ionic conduction. The bulk conductivity (σ_d) decreases with increase in MMA ratio. The high conductivity is optimized at MMA ratio up to 20–30%.

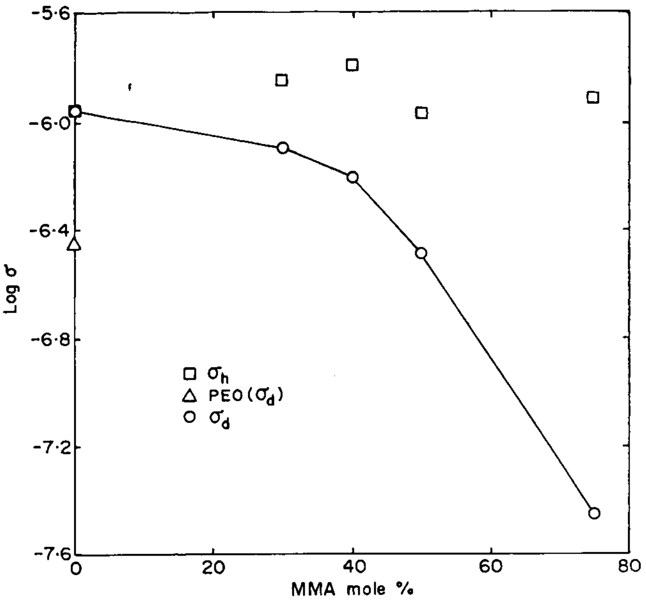

Figure 1 The conductivities ($\sigma = \sigma_d$ and σ_h) vs. MMA mol% in the hybrid homo/copolymer–salt complexes. (The bulk conductivity, σ_d and the high frequency conductivity, σ_h of the hybrid–salt complexes of homo/copolymers at room temperature were calculated from the complex impedance plots corresponding to the low and high frequency semi-circles respectively)

The d.s.c. gives a single T_g for all the polymers and polymer electrolytes[19] which support the homogeneity in the system. The homogenous system is known to give a single semicircle in the complex impedance plot[3]. The ionic conductivity of a polymer electrolyte is due to the salt complexation and the segmental mobility[12]. However, the segmental mobility due to the lithium salt complexation in the EO units may differ from that of the ester group in MMA. The respective resistive component may increase with respect to the ratio of MMA. Hence the RC time constant of the ester complexation in the MMA units with the salt may have different (larger) time constant than the pendant side chains of EO units. This may result in two semicircles in the impedance spectra. As MMA percentage increases the respective resistance component may increase and can give high impedance of the corresponding semicircle and hence the total impedance, which is observed in our series of copolymer

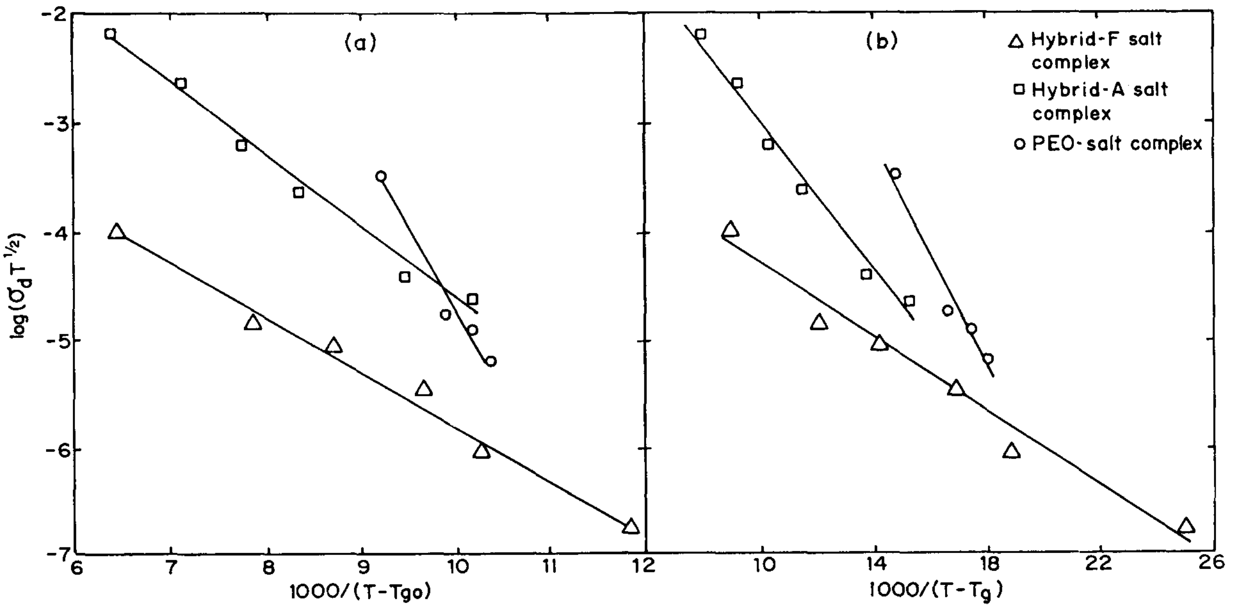

Figure 2 (a) The log($\sigma T^{1/2}$) vs. $(T - T_{g0})^{-1}$ (where T_{g0} is the glass transition temperature of the undoped (co)polymer) plotted for the PEO, hybrid A and hybrid F–salt complexes. (b) The log($\sigma T^{1/2}$) vs. $(T - T_g)^{-1}$ (where T_g is taken as that of the actual/salt complex under study) plotted for the PEO, hybrid A and hybrid F–salt complexes

hybrid systems. The results show that the high frequency response (switching) is not affected by the MMA ratio in the system. However, more critical experimentation would be required for confirmation.

The Arrhenius plot of the ionic conductivity of amorphous polymer-electrolyte is not a simple straight line. These are not describable by the Arrhenius equation, as the data lie on a positively curved line[21]. Such curves are well represented by the Vogel–Tamman–Fulcher (VTF)[22–24] and Williams–Landel–Ferry (WLF) type equations[25]. The log($\sigma T^{1/2}$) data were plotted against different reciprocal temperature functions[26]. In method (i) it was plotted against $(T - T_{g0})^{-1}$ as shown in *Figure 2a*, where T_{g0} is the glass transition temperature of the undoped (co)polymer. The T_{g0} for the polymers of PEO = −66°C, PEGEEP = −67.5°C and $[(\mathrm{PEGEEM})_{25}(\mathrm{MMA})_{75}] = -64.3$°C. In method (ii), the plot is against $(T - T_g)^{-1}$ (see *Figure 2b*), where T_g is taken as that of the actual polymer electrolytes under study. The T_g for salt complex of PEO = −25°C, hybrid A = −34.7°C and hybrid F = −20°C. The straight line nature of both the plots indicate that the temperature dependent conductivity of the synthesized polymer electrolyte obeys VTF/WLF type equations[26]. From *Figure 2*, it is clear that the apparent activation energy is highest for the PEO–salt complex and lowest for the hybrid F–salt complex.

The conductivities of all the polymer electrolytes were normalized with respect to that of hybrid-F–salt. These are plotted against the PEGEEM percentage in *Figure 3*. In all cases the normalized conductivity increases with increase in the mol% of PEGEEM. For EO/Li = 8 the increase is slower, but for EO/Li = 12 and 20 the increase is approximately at the same rate and higher than that for EO/Li = 8. This conductivity (σ_d) increase with increase in mol% of PEGEEM is related to increase in EO units in the side chain which facilitates the lithium ion conduction. For EO/Li = 8, the concentration of Li is higher which decreases the segmental mobility (available sites), whereas for EO/Li = 12 and 20 the complexes have apparently crossed the critical limit for good conductivity and show saturation.

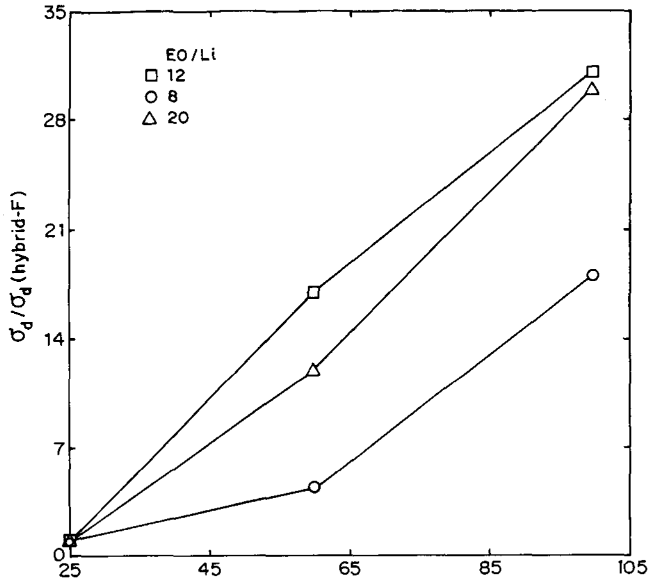

Figure 3 The normalized conductivity $[\sigma_d/\sigma_{d(\text{hybrid-F--salt complex})}]$ vs. PEGEEM mol% for the hybrid A, hybrid D and Hybrid F–salt complexes with respect to EO/Li [units] = 20, 12 and 8

Conclusion

New (co)polymers were synthesized and characterized by n.m.r. and d.s.c. (Co)polymers were blended with PEO and $LiClO_4$ to form PEO + (co)polymer–$LiClO_4$ complexes. The a.c. electrical conductivity for the comb-like hybrid A–$LiClO_4$ salt complex is higher than for the linear PEO–$LiClO_4$ salt complex. The total bulk (σ_d) conductivity is higher than the PEO salt complex up to 20–30% of the MMA concentration.

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