Synthesis and characterization of ABA block copolymer-based polymer electrolytes

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The synthesis and some of the properties of a novel ion-conducting polymer are described. The polymer, based on a styrene–butadiene–styrene ABA triblock copolymer has pendant, short-chain poly(ethylene oxide) (PEO) grafted onto the B block. The concentration of PEO in the polymer can be controlled by varying either the number of pendant groups per molecule or the molecular weight of the PEO chain. The polymers were combined with $LiCF_3SO_3$ to form ion-conducting phases. The conductivities of films of these materials were found to be sensitive to preparation technique, and especially to casting solvent. The best conductivities, typically 10^{-5} S cm^{-1} at ambient temperatures, were obtained using solvents that were likely to induce microphase separation (with concomitant improvement in the mechanical properties of the system). The temperature dependence of the conductivity suggested that the materials were essentially amorphous over the range studied.

(Keywords: polymer electrolyte; ABA triblock; synthesis; conductivity; PEO)

INTRODUCTION

Over the last few years, numerous polymer electrolyte systems have been reported, largely based on high-molecular-weight poly(ethylene oxide) (PEO) with an incorporated alkali-metal salt[1-5]. Such systems show conductivity in the range 10^{-5} S cm^{-1} only at elevated temperatures (>343 K). At ambient temperatures, conductivity is greatly reduced by the crystallinity of PEO[4]. Kelly *et al.*[6] improved conductivity at lower temperatures by forming a polymer blend of low-molecular-weight, non-crystalline methoxy poly(ethylene glycol) (MPEG) and high-molecular-weight PEO. Many of the ambient-temperature ionically conducting polymers reported recently[7,8] have been comb-type copolymers of short PEO side chains grafted to a polymer backbone of high T_g. In addition, Blonsky *et al.*[9] have produced a highly conducting material based on a low T_g polyphosphazene backbone with very short (<10) ethylene oxide repeat unit side chains.

In this paper, we describe the synthesis and some of the properties of a polymer electrolyte that is a novel structural variation on the comb copolymer architecture. It is derived from a long-block ABA block copolymer with side-chain grafted PEO which provides the ion-conducting pathways. The two constituents of the block copolymer are incompatible and thus phase-separate, but only on a microscale, since they are chemically bonded at the two junctions. In conventional ABA copolymers, the two-phase physical network comprises a minor fraction of 'hard', high T_g or T_m block and a major 'soft', low T_g B fraction. The hard A block material associates to form small morphological domains which serve as physical crosslinking and reinforcement sites, and consequently determine the mechanical behaviour of the material. As a result of this morphology, the polymer exhibits novel features: it may be thermoplastic and soluble in conventional solvents yet display rubberlike elasticity while having no chemical crosslinks. Grafting of short PEO side chains onto the backbone of the amorphous B blocks creates an ion-solvating and conducting phase while leaving the basic structure unchanged. Owing to the differential solvation of the block copolymer components, solvents can alter the morphology of the domains quite substantially[10]. After casting films, definite structures are formed in the solid state and, depending on the choice of casting solvent, either the glassy or the elastomeric phase can become the continuous one. In principle, it is thus possible to control independently the mechanical properties and conductivity of the material by suitable choice of the A and modified B phase. Secondly, by control of polymer microstructure, isotropic ion conduction is feasible. In addition, it is possible to blend, for example, low-molar-mass polystyrene with the triblock copolymer and thereby add a further variable in the control of the microstructure of the final electrolyte[11].

EXPERIMENTAL

The basic triblock material used was a styrene–butadiene–styrene (SBS) block copolymer of average molecular weight ~170 000 (g.p.c., polystyrene standards) and a styrene content of 28% (Aldrich Chemical Co. Ltd). Poly(ethylene glycol methyl ethers) (MPEG) of $M_n = 550$ and 750 (Aldrich Chemical Co. Ltd) were dried by azeotropic distillation using toluene. Hexamethylene diisocyanate and dibutyltin dilaurate (Aldrich Chemical Co. Ltd) were used as supplied. Lithium trifluoromethane sulphonate, $LiCF_3SO_3$ (3M

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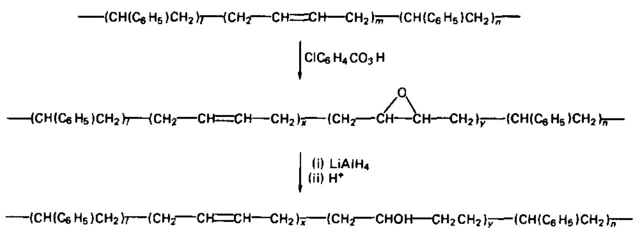
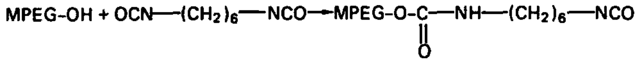
UK Ltd) was dried under vacuum at 383 K for 6 h. Tetrahydrofuran (THF) and diethyl ether were distilled after refluxing with lithium aluminium hydride. Nitromethane was distilled from calcium sulphate, and dichloromethane was distilled from phosphorus pentoxide.

The first step of the synthetic procedure involved epoxidation of a fraction of the polybutadiene double bonds, followed by reductive ring opening to give the hydroxylated intermediate, SBS–OH:



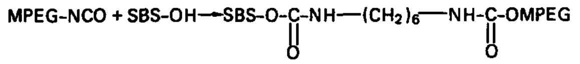
SBS-OH

MPEG was functionalized by reaction with a diisocyanate and subsequently grafted to the hydroxylated block copolymer, SBS–OH:



$$\text{MPEG-OH} + \text{OCN}\!-\!(\text{CH}_2)_6\!-\!\text{NCO} \rightarrow \text{MPEG-O-}\underset{\underset{\text{O}}{\|}}{\text{C}}\!-\!\text{NH}\!-\!(\text{CH}_2)_6\!-\!\text{NCO}$$

MPEG-NCO



$$\text{MPEG-NCO} + \text{SBS-OH} \rightarrow \text{SBS-O-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-NH}\!-\!(\text{CH}_2)_6\!-\!\text{NH-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-OMPEG}$$

SBS-PEO

An alternative route to achieving the grafted structure, through a simpler linkage, has also been studied[11]. Four polymer systems were investigated: (30)SBS–PEO(550), (30)SBS–PEO(750), (52)SBS–PEO(550) and (52)SBS–PEO(750) where the first number refers to the percentage of butadiene repeat units per chain reacted and the second refers to the number-average molar mass of the MPEG side chain.

Epoxidation of SBS triblock

To 5 g (69 mmol) of SBS copolymer in 75 cm^3 CH_2Cl_2 was added an appropriate quantity of 3-chloroperbenzoic acid (8 g, 46 mmol, for 52% substitution; and 4 g, 23 mmol, for 30% substitution) in 80 cm^3 CH_2Cl_2. After 4–5 h refluxing, the solution was stirred at room temperature for 16 h. A precipitate of 3-chlorobenzoic acid was removed by filtration and the polymer precipitated twice into excess methanol. Yields were 85–90%. The presence of epoxide groups was confirmed by ^{1}H n.m.r. and i.r., and the level of epoxidation confirmed by n.m.r. proton integral ratios.

N.m.r. ($CDCl_3$): δ 2.6–2.9 ppm (CHOCH), δ 5.4 ppm (CH=CH), δ 6.5–7.2 ppm (C_6H_5), δ 1.5–2.1 ppm (CH–CH_2, CH_2).

I.r. (film): 1250 cm^{-1} (CHOCH).

N.m.r. integral ratios, CHOCH:C_6H_5—30%, 1.65:1 (found), 1.56:1 (calc.); 52%, 1.08:1 (found), 1:1 (calc.).

Reduction of epoxide to the alcohol (SBS–OH)

One gram of epoxide in 90 cm^3 THF was refluxed with a molar excess of lithium aluminium hydride ($LiAlH_4$) for 3 h. Excess hydride and inorganic complex intermediates were decomposed by addition of hydrochloric acid. Water (60 cm^3) was added and the resultant polymer, SBS–OH, was extracted into CH_2Cl_2 (three 100 cm^3 portions) with vigorous stirring. The organic extract was separated and washed several times with water. The polymer was extracted twice from dichloromethane/methanol and dried under vacuum at 60°C. Yields were 80–85%. The peaks at δ 2.6–2.9 ppm (CHOCH) in the n.m.r. spectrum were replaced by a broad peak centred at δ 3.7 ppm (CH–OH) and the presence of hydroxyl groups confirmed by the absorption centred at 3400 cm^{-1} in the i.r. spectra.

MPEG–NCO

MPEG(550)–NCO and MPEG(750)–NCO were prepared by a similar method to that used by Zalipsky *et al.*[12] A solution of MPEG in THF was added dropwise over 5 h to a stirred solution of hexamethylene diisocyanate (HDI) (five times molar excess over OH groups) and dibutyltin dilaurate (three drops) in a dry nitrogen atmosphere. The solution was stirred for 18 h and the polymer precipitated into dry diethyl ether at 268–271 K. Two further precipitations were carried out. Yields were generally low: 25–35% for MPEG(550) and 40–50% for MPEG(750).

N.m.r. ($CDCl_3$): δ 1.3–1.6 ppm ($CH_2CH_2CH_2$), δ 3.7 ppm (OCH_2).

I.r. (film): 2250 (NCO), 1110 (CH_2), 1715, 1535 (HN-COO), 3300 cm^{-1} (NH).

SBS–PEO

A slight molar excess of MPEG–NCO dissolved in THF was added to a solution containing SBS–OH and three drops of dibutyltin dilaurate. After 16 h refluxing, solvent was removed leaving a clear, gel-like solid. This was purified by washing with cold methanol and precipitating from dichloromethane/cold methanol. The material was dried under vacuum at 333 K.

Ratio of ^{1}H n.m.r. peak integrals, C_6H_5:CH_2CH_2O—(52)SBS–PEO(550), 1:25.2 (calc.), 1:26.7 (found); (52)SBS–PEO(750), 1:34.5 (calc.), 1:36.3 (found); (30)SBS–PEO(550), 1:14.7 (calc.), 1:16.2 (found); (30)SBS–PEO(750), 1:20.1 (calc.), 1:22.2 (found).

Film preparation

Films of the modified block copolymer complexed with lithium trifluoromethane sulphonate ($LiCF_3SO_3$) with an O:Li ratio of 7:1 were prepared the following methods.

Method A. Appropriate quantities of polymer and salt were dissolved in THF and the solvent removed under vacuum at room temperature and subsequently by heating at 323 K for 3 h. The material was pressed between two stainless-steel plates and heated to 373 K under slight pressure to form an even thickness of film between the plates.

Method B. Polymer and salt were ground together as previously reported[13]. Films were pressed as described in method A.

Method C. Polymer and salt were dissolved in THF and cast onto a stainless-steel plate by allowing slow evaporation of solvent under a nitrogen flow. Residual solvent was removed by heating under vacuum at 373 K.

Method D. Films were prepared as in method C but with a 10:1 mixture of nitromethane and THF as solvent. Residual solvent was removed by heating to 403 K for 24 h.

Conductivity measurements

A.c. conductivity measurements were carried out using stainless-steel ion-blocking electrodes contained in a cell holder that has been described elsewhere[4,14]. Measurements were carried out using a frequency response analyser (Solartron model 1174), controlled by a microcomputer (Tektronix 4052) and the complex impedance measured as a function of frequency over the range 1 Hz to 100 kHz. Films ($\sim 200\,\mu m$ thick) were held at room temperature for at least 5 h before measurements were made.

Calorimetry

Differential scanning calorimetry (d.s.c.) experiments were performed using a Du Pont 1090 Thermal Analyser, where samples were hermetically sealed in aluminium pans and quenched (cooling rate $\sim 30\,K\,min^{-1}$) from 298 to 148 K and heated to 473 K at 10 or $20\,K\,min^{-1}$.

RESULTS AND DISCUSSION

Grafting MPEG to SBS–OH through a urethane linkage[14,15] represents a convenient route to this class of polymer for initial characterization of its use as a component of a solid electrolyte. One disadvantage, however, is that the hexamethylene diurethane group constitutes approximately 15% of the polymer's total mass and is essentially non-functional. In addition, it proved difficult to find a suitable method for the purification of MPEG–OCO·NH$(CH_2)_6$NCO when the molecular weight for the MPEG was lower than 550. Apart from this, the synthetic procedure allows easy variation of the PEO content of the polymer by choice of extent of grafting and the MPEG chain length used. We hope to present details of the synthesis of other similar ABA block copolymers with B block grafted PEO where a simpler linkage is employed and consequently the bulk of the non-conducting material in the side chain is reduced[11].

D.s.c. measurements show the occurrence of low-energy history-dependent endothermic processes. For example, (30)SBS–PEO(550), solvent cast from THF, showed three endotherms, with onset 280 K, peaks at 293, 315 and 329 K. On rescanning, a single endotherm, with onset at 285 K and a peak ($\Delta H \sim 40\,J\,g^{-1}$) at 303 K, was detected using a heating rate of $20\,K\,min^{-1}$. This behaviour might be due to melting of regions containing crystalline PEO side chains. The glass transition of the B block phase was not detected. Small melting endotherms ($\sim 15\,J\,g^{-1}$) were noted for the electrolytes studied, but none of these thermal events was reflected as a discontinuity in the conductivity–temperature behaviour over the salt concentration range studied here. The conductivities of films prepared by method A, over the temperature range 293–373 K, are shown in *Figure 1*. The PEO contents of the modified block copolymers, (30)SBS–PEO(750), (30)SBS–PEO(550), (52)SBS–PEO(550) and (52)SBS–PEO(750) are 64, 52, 63 and 71 wt% respectively. Conductivities recorded at a particular temperature are comparable for all four materials, varying at most hy half a decade. However, materials with the higher PEO content show slightly greater values over the amjority of the temperature range.

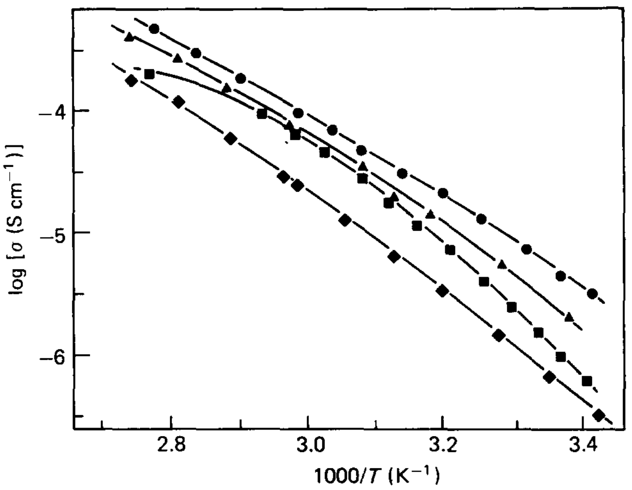


Figure 1 Temperature variation of the conductivity of (30)SBS–PEO(750) (●), (30(SBS–PEO(550) (◆), (52)SBS–PEO(550) (■) and (52)SBS–PEO(750) (▲). O:Li = 7:1

As in many simple fully amorphous polymer electrolytes above the glass transition temperature[4,7–9,16–19], the conductivities of these triblock-based materials did not show Arrhenius dependence. This has been discussed elsewhere by one of us[20,21]. Rather, the conductivity data could be fitted to an equation of the form proposed by Vogel, Tamman and Fulcher[22], expressed as:

$$\sigma = \sigma_0 \exp[-B/(T - T_0)]$$

where σ_0, B and T_0 are empirical constants. Interpretation of these constants in terms of polymer chain motion and ion transport has recently been comprehensively reviewed by Ratner[23]. The B and T_0 terms relate to those properties of the polymer host that affect its dynamic behaviour, with T_0 being closely related to the glass transition temperature. The constant σ_0 includes factors such as the charge carrier density in the system, percolation condition, etc. *Figures 2* and *3* demonstrate the importance of the method of preparation on the measured conductivity. *Figure 2* shows the conductivities for (30)SBS–PEO$(550)_7$LiCF$_3$SO$_3$ films prepared by methods A and B. *Figure 3* shows the temperature variation of the conductivity of (30)SBS–PEO$(550)_7$LiCF$_3$SO$_3$ films prepared by methods A, C and D and demonstrates how the film casting solvent can markedly alter the conductivity attained for these materials. The full curves in *Figure 3* represent the fitted Vogel–Tamman–Fulcher (VTF) equation, taking $T_0 = 210$ K, the optimum value reported previously for a fully amorphous high-molecular-weight PEO-based electrolyte[4]. The fitting routine was rather insensitive to the value of B and some random spread in this value was found. The principal cause of the variation in the conductivity resulting from the different film preparation methods is clearly a consequence of changes in the pre-exponential factor σ_0. We suggest that variations in this term reflect changes in the tortuosity of the material, due to microstructural rearrangements that are taking place. To a lesser extent, there may be some variation in the number of charge carriers contributing to the

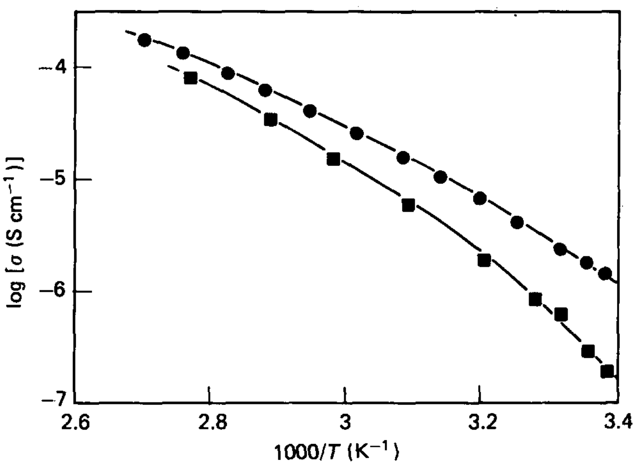


Figure 2 Temperature dependence of the conductivity of (30)SBS–PEO(550) Films prepared by methods A (■) and B (●)

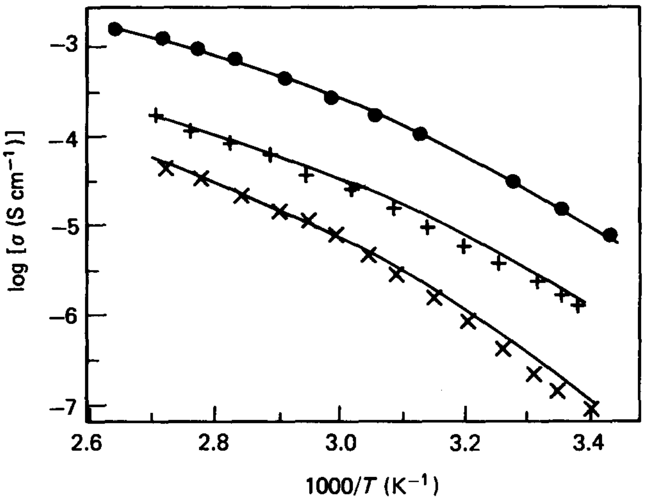


Figure 3 Temperature dependence of the conductivity of (30)SBS–PEO(550) prepared by solvent casting from nitromethane/THF (●), from THF (×) and by pressing (method B) (+). The full curves give the fitted VTF equation, with $T_0 = 210$ K

conductivity as, under certain conditions of microphase formation, isolated areas of conducting material may be formed. Thus it is proposed that for a film cast from THF, the tortuosity is relatively high, whereas for a film cast from nitromethane it is low. This suggestion is consistent with morphological changes which are known to take place in ABA triblock copolymers when different casting solvents are used[10,24]. THF is a good solvent for both the polystyrene A blocks and polybutadiene/PEO B blocks. The solubility parameters are too similar to favour microphase separation and, consequently, casting films from this solvent is likely to result in poor microphase separation of the two phases. Nitromethane, on the other hand, is a poor solvent for the A blocks but a good solvent towards the PEO phase. Thus, use of nitromethane is expected to improve microphase separation and lead to better defined boundary regions with the ion-conducting PEO forming the continuous phase.

The possibility that residual solvent was responsible for the greatly enhanced conductivity of the nitromethane-cast films was investigated by heating the latter under vacuum at 413 K for periods of 24 and 48 H. The change in conductivity on extended heating was very small and could easily be accommodated by variation of the *B* parameter within the previously found range. In comparison with the values determined for films formed by other methods, the change in σ_0 was marginal. We conclude that the superior conductivities of the nitromethane-cast films could not be attributed to plasticizing effects of trapped solvent. It is therefore suggested that morphological effects are responsible for the increase in conductivity of approximately two decades. Experimentally, a 10:1 nitromethane/THF mixture was utilized in order to bring about the full dissolution of polymer and salt. Conductivity values of the best triblock materials we have produced to date are comparable to those reported by Bannister *et al.*[7] for monomethoxy poly(ethylene glycol methacrylate) systems incorporating $LiCF_3SO_3$ and are considerably superior to the ambient-temperature values of 10^{-7}–10^{-8} S cm^{-1} reported[14,25] for high-molecular-weight PEO–$LiCF_3SO_3$.

CONCLUSIONS

Styrene–butadiene–styrene block copolymers may be modified by graft addition of low-molar-mass monomethoxy poly(ethylene glycols) to form materials of high ionic conductivity when complexed with lithium trifluoromethane sulphonate. Microphase-separated triblock materials have the potential of combining high ionic conductivity with acceptable mechanical properties.

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