observed for the amorphous PAR carbons. It would appear that the methylene carbons of the glycol residue are undergoing significant motion independent of whether they are included in the α and β crystallites or not.

In agreement with Perry et al.,[17] whose measurements were performed more than 80 °C below ours (105 °C), we do not find any significant differences between the spin–lattice relaxation times of the crystalline methylene carbons in α- and β-PBT. Similarly, the T_1's of the crystalline carbon nuclei belonging to the terephthaloyl residues in α- and β-PBT are also not markedly different. It does not appear that the α and β phases constrain the motions of their constituent PBT chains in any significantly different manner (also see Jelinski et al.[24] and Garbow and Schaefer[25] for further discussion of solid-state PBT motion).

High-resolution, solid-state ^{13}C NMR studies of α- and β-PBT have revealed several important features concerning the conformations and motions of PBT chains in both crystalline phases. We have found the glycol residues to be in the nearly extended (trans–trans–trans) conformations in both crystalline forms, while different orientations of the ester groups and phenyl rings probably account for the 10% difference in the fiber repeats of α- and β-PBT. In both crystals the methylene carbons are sampling rapid motions, which are significantly faster than the motions experienced by the carbons of the terephthaloyl residues.

These conclusions serve to recommend high-resolution, solid-state ^{13}C NMR spectroscopy as a powerful technique for studying the structure and dynamics of solid polymers.

Acknowledgment. We appreciate the help we received from T. H. Klein and J. T. Ryan during the preparation of our β-PBT sample in the Instron tensile tester.

Registry No. PBT (copolymer), 26062-94-2; PBT (SRU), 24968-12-5.

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Novel Polymer Electrolytes Based on ABA Block Copolymers

F. M. Gray,* J. R. MacCallum, and C. A. Vincent

Department of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, U.K.

J. R. M. Giles

Materials and Structures Department, Royal Aircraft Establishment, Farnborough,
Hants GU14 6TD, U.K. *Received May 25, 1987;*
Revised Manuscript Received August 13, 1987

ABSTRACT: Some properties of novel polymer electrolytes, based on a styrene–butadiene–styrene ABA block copolymer with pendant short-chain poly(ethylene oxide) (PEO), are described. The polymers were combined with lithium trifluoromethanesulfonate in different concentrations to form an ion conducting matrix. The concentration dependence of the conductivity was analyzed by fitting the data to a VTF type equation. Conductivities, typically 10^{-5} S cm^{-1} at ambient temperatures, were obtained by casting films from a selective solvent which favors microphase separation with PEO forming the continuous phase. The dimensional stability of the materials could be improved by adding quantities of polystyrene homopolymer. Providing the polystyrene molecular weight was low, the conductivity was not greatly affected. Ionic conductivity was enhanced by blending the polymeric material with low molecular weight PEO. These blends did not phase separate on a macroscale.

Introduction

The majority of polymer electrolyte systems reported in the literature to data have been largely based on high molecular weight poly(ethylene oxide), $-(CH_2CH_2O)_n-$ (PEO), incorporating an alkali-metal salt.[1–4] These systems exhibit poor ($<10^{-6}$ S cm^{-1}) ambient temperature conductivities as a consequence of their high degree of crystallinity. Much interest recently has been focused on

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producing polymer electrolytes with high ionic conductivity that are completely amorphous at ambient temperatures but have the dimensional stability of a solid electrolyte. Many systems are based on low molecular weight (<18 ethylene oxide (EO) repeat units) PEO grafted to a high T_g polymer backbone that imparts mechanical stability to the material.[5-7] Formation of networks by radiation or chemical cross-linking can greatly improve the the mechanical properties[8-10] or prevent recrystallization.[11,12] A loss of ionic conductivity, associated with loss of polymer chain flexibility, normally ensues, but its extent depends largely on the nature of the cross-linking groups.[13]

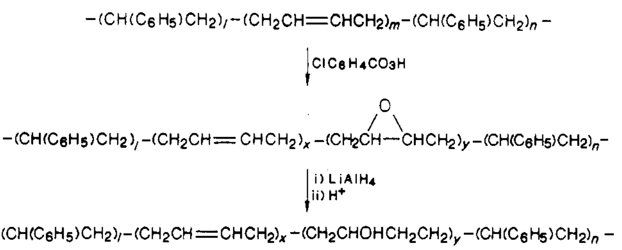
In this paper we describe some of the properties of a novel polymer electrolyte: a graft copolymer of short-chain methoxy poly(ethylene glycol) (MPEG) bonded to the B component of an ABA block copolymer. In conventional ABA block copolymers, for example, styrene–butadiene–styrene copolymers, the A and B constituents are incompatible. The phase separation that results is on a microscale only because the components are chemically bonded. Conventionally, the two-phase network comprises a minor, high T_g (or T_m) A block and a major, low T_g B fraction. They show similar behavior to cross-linked elastomeric networks, due to the "hard" A blocks aggregating into domains that act as glassy network junctions for the elastomeric chains. Unlike chemically cross-linked rubbers, however, they can become fluid and moldable at elevated temperatures and are usually soluble in simple solvents. As the components of block or graft copolymers undergo differential solvation, so choice of casting solvent can have a profound influence on the distribution and overall morphology of phases in the final material. Thus, dissolution in selective solvents can bring about systematic changes in domain morphology to form definite structures that are maintained into the solid state on removal of solvent.[14]

Grafting low molecular weight MPEG onto the elastomeric B blocks maintains the A and B block incompatibility, and, in addition, the B phase becomes ion solvating and conducting. It is thus feasible to microphase separate the ion-solvating polymer from the mechanically stabilizing domains to form a continuous, conducting phase in a situation where no gross phase separation can occur as is possible in polymer electrolytes based on macromolecular blends.[15] The unique properties of ABA block copolymers offer a versatile means of controlling independently the mechanical and conducting properties of polymer electrolytes through suitable A and B phase modifications, and, through careful selection of casting solvents, isotropic ion conduction may be achieved.

Experimental Section

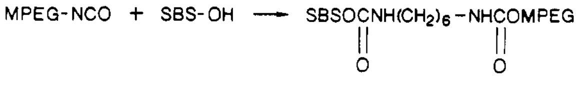
The basic triblock material used in this study was a styrene–butadiene–styrene (SBS) block copolymer with $M_n \sim 170\,000$ (GPC, polystyrene standards) and styrene content 28% (Aldrich Chemical Co. Ltd). Poly(ethylene glycol methyl ether) (MPEG) of average molecular weights 550 and 750 (Aldrich Chemical Co. Ltd) were dried by azeotropic distillation using toluene. Dicyclohexylcarbodiimide (DCC) (BDH), succinic anhydride, 4-(dimethylamino)pyridine (DMAP), 4-pyrrolidinopyridine (PP), hexamethylene diisocyanate (HDI), and dibutyltin dilaurate (Aldrich Chemical Co. Ltd) were used as supplied. Lithium trifluoromethanesulfonate, ($LiCF_3SO_3$) (3M UK Ltd) was dried under vacuum at 383 K for 6 h. Triethylamine was distilled before use. Tetrahydrofuran (THF) and diethyl ether were distilled after refluxing with lithium aluminum hydride. Nitromethane was distilled from calcium sulfate and dichloromethane (CH_2Cl_2) from phosphorus pentoxide.

The synthesis involves the initial modification of a selected number of butadiene repeat units on the ABA block copolymer to give a hydroxylated intermediate, SBS-OH:–



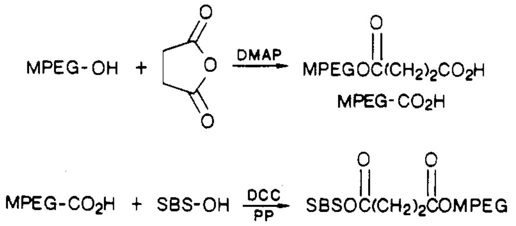
SBS-OH

A detailed account of this synthesis has been given elsewhere.[16] The formation of the desired SBS–PEO copolymer was carried out by two different routes: 1. MPEG was functionalised by reaction with hexamethylene diisocyanate (HDI) and subsequently grafted to the hydroxylated block copolymer,[16] giving



SBS–PEO (1)

2. A carboxylic acid derivative of MPEG was formed by reaction with succinic anhydride and a catalyzed esterification reaction gave the required copolymer.



SBS-PEO (2)

The latter reaction sequence was carried out by using a similar method to that described by Zalipsky et al.[17] and Hassner and Alexanian.[18]

Formation of MPEG-COO(CH_2)$_2$COOH. Dry MPEG(750) (7 g) and 1 g of succinic anhydride was dissolved in tetrahydrofuran, allowed to react for 16 h at room temperature, and catalyzed by 1.3 mL of triethylamine and 1 g of (dimethylamino)pyridine (DMAP). Solvent was removed, the residue was taken up in carbon tetrachloride, filtered, and precipitated into cold ether. IR spectroscopy showed the presence of $C{=}N^+$ and COO^- groups, as reported by Zalipsky,[17] which indicated that a salt of DMAP and MPEG-succinate was also formed.

Formation of SBS–PEO Linked through a Succinate Group. SBS-OH (0.1 g) and 0.4 g of MPEG-COO(CH_2)$_2$COOH were dissolved in dichloromethane. To this was added 0.1 g of dicyclohexylcarbodiimide (DCC) and a catalytic quantity of 4-pyrrolidinopyridine. The solution was refluxed for 2 h. Precipitated dicyclohexylurea (DCU) was filtered, and the residue was dried and taken up in acetone. Further DCU residues were separated from the solution. The polymer was purified further by precipitating from THF/cold methanol.

Four polymer systems were synthesized by route 1: (30)SBS–PEO(550), (30)SBS–PEO(750), (52)SBS–PEO(550) and (52)-SBS–PEO(750). (30)SBS–PEO(550) was synthesized by route 2. The first number refers to the percentage of modified butadiene units and the second to the average molecular weight of MPEG side chains.[16]

Preparation of Thin Films. Films of polymer and lithium trifluoromethane sulfonate ($LiCF_3SO_3$) were prepared with O:Li ratios of 7:1, 16:1, 30:1, and 50:1.

Method A. Appropriate quantities of polymer and electrolyte were dissolved in THF; solvent was removed under vacuum, initially at room temperature and then at 323 K. The material was pressed between two stainless-steel plates and heated to 373 K under slight pressure to form an even thickness and film between the plates.

Method B. Polymer and electrolyte were dissolved in THF or nitromethane/THF (10:1) 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.

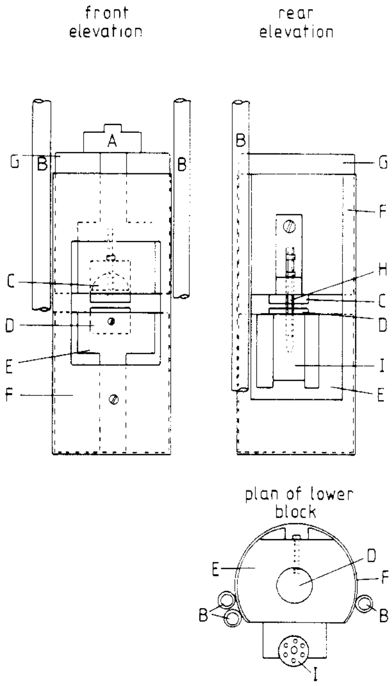


Figure 1. Design of cell holder: A, variable weight; B, stainless-steel screen for electrical connections; C, self-leveling stainless-steel electrode; D, fixed stainless-steel electrode; F, brass casing; G, vertically free-moving ceramic mount; H, transducer core; I, transducer.

Conductivity Measurements. Films of the order of 200 μm in thickness were mounted between stainless-steel ion-blocking electrodes within a cell holder which has been described previously.[12] Conductivity measurements were carried out by using a frequency response analyzer (Solartron, Model 1174) controlled by a microcomputer (Tektronix 4052), which enabled complex impedance to be measured as a function of frequency from 1 Hz to 100 kHz. The zero frequency conductivity was found from the intersection of the low-frequency spike, associated with electrode impedance and the high-frequency semicircle associated with bulk relaxation.[19]

Dimensional Stability. The mechanical stability of the polymer systems was investigated by penetrometry at specific temperatures and, in general, a pressure of 60 kPa. Pellets of polymer material were prepared with a diameter of approximately 8 mm and thickness of the order of 1.5–2 mm.

Samples were mounted between the stainless-steel plates of the vertical cell holder shown in Figure 1 and a 5-mm diameter stainless-steel probe placed on the sample surface. The lower plate is static and is mounted on a block of ceramic which also incorporates a displacement transducer (S&P Aldridge Electronics Ltd, type D201-01). The upper plate is self-leveling and mounted in a ceramic block which is free to move vertically. This could be lowered onto the probe and sample via an external lever. The moveable core of the transducer is also mounted here. Movement causing a change in spacing between the plates causes the core to move, and this is recorded on a transducer indicator (S & P Aldridge Electronics Ltd, 8C 35-100) giving the spacing directly in millimeters. The pressure acting on the sample can be varied by altering the weighting on the upper block. The cell holder is enclosed in an oven under an argon flow and the internal temperature monitored via a thermocouple.

Results and Discussion

The temperature variation of the conductivities is shown in Figure 2 for (30)SBS–PEO(750) complexed with $LiCF_3SO_3$, with an O:Li ratio of 7:1, 16:1, 30:1, or 50:1. All films were prepared by method A. Hysteresis in the conductivities between the heating and cooling cycles was observed only for an O:Li ratio of 50:1. The rate of crystallization for this system is much faster than for complexes with higher salt concentration.

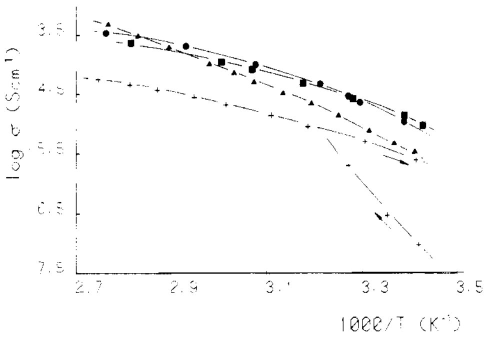


Figure 2. Temperature dependence of the conductivity of (30)SBS–EO(750) with O:Li = 50:1 (+), 30:1 (●), 16:1 (■), and 7:1 (▲).

Table I
Calculated VTF Parameters

polymer	O:Li ratio	RB/kJ mol^{-1}	σ_0/S cm^{-1}
(30)SBS-PEO(550)	7:1	8.9 ± 0.2	0.04 ± 0.005
	16:1	6.3 ± 0.1	0.005 ± 0.001
	30:1	6.1 ± 0.1	0.002 ± 0.0001
(30)SBS-PEO(750)	7:1	9.0 ± 0.4	0.13 ± 0.03
	16:1	6.5 ± 0.2	0.02 ± 0.002
	30:1	6.5 ± 0.3	0.03 ± 0.007
	50:1	5.7 ± 0.2	0.002 ± 0.0002
(52)SBS-PEO(550)	7:1	10.8 ± 0.3	0.30 ± 0.04
	16:1	8.0 ± 0.2	0.03 ± 0.004
(52)SBS-PEO(750)	7:1	10.6 ± 0.2	0.15 ± 0.03
	16:1	8.9 ± 0.3	0.11 ± 0.02
blend 1	7:1	11.3 ± 0.5	0.15 ± 0.05
blend 2	7:1	11.4 ± 0.5	0.05 ± 0.01
blend 3	7:1	8.7 ± 0.2	0.09 ± 0.01
blend 4	7:1	9.6 ± 0.1	0.05 ± 0.004

The temperature variation of the conductivity changes as the O:Li ratio decreases, particularly between 16:1 and 7:1. These data do not follow an Arrhenius dependence but rather, as in many amorphous polymer electrolyte systems,[5,12] data can be fitted to an equation of the form proposed by Vogel, Tamman, and Fulcher:[20]

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

where σ_0, B, and T_0 are empirical constants.[13,21] A recent review by Ratner[22] discusses these constants in relation to the polymer chain motion and ion transport. T_0 is closely related to the glass transition temperature, and B can be related to such parameters as a free energy barrier, expansivity, etc.: these terms relate to the dynamic behaviour of the polymer chains. Variations in σ_0, on the other hand, relate to changes in charge carrier density and percolation conditions. Conductivity data for all the polymer electrolyte systems can be linearized by taking a value of T_0 = 210 K, an optimum value reported previously for a fully amorphous high molecular weight PEO-based electrolyte,[12] the glass transition for the modified B phase of the parent polymers not being detectable.[16] Correlation factors were better than 0.990. Values of RB, where R is the gas constant, the σ_0 are given in Table I, and examples of linearized conductivity data, for $(30)SBS–PEO(550)_7LiCF_3SO_3$, are shown in Figure 3. Although there is some spread in values, a consistent increase in B and σ_0 accompanies an increase in salt content. Change in dynamic behavior may be expected through loss of segmental motion brought about by increasing the salt concentration in the polymer matrix while an increase in σ_0 might be anticipated for increases in salt concentration.

It is well-recognized that the nature of the casting solvent and its interaction with the polymer segments can play a major role in determining the morphology of block and graft copolymer systems.[14] Selective solvents, which

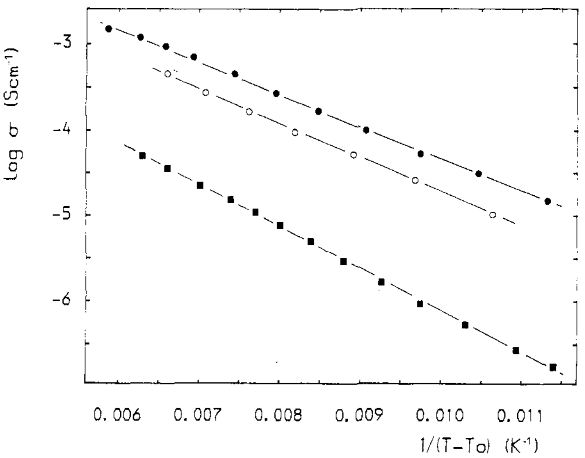


Figure 3. Linearized conductivity plots for (30)SBS–PEO-(550)$_7$LiCF$_3$SO$_3$ prepared by casting from nitromethane (●) and from THF (■) and (30)SBS-PEO(550)$_7$LiCF$_3$SO$_3$ prepared by route 2 and cast from nitromethane (○).

are "good" for one block but "poor" (or non-solvent) for the other, can determine which phase will be the last to come out of solution and, provided the block size is large enough,[23] form the continuous phase. In this study, nitromethane and THF were compared as casting solvents. THF is a good solvent for polystyrene, polybutadiene, and PEO, so one would expect a very different distribution of the components in the solid state in comparison to a nitromethane cast system, where polystyrene and polybutadiene are poorly solvated, leaving PEO as the last phase to come out of solution. Figure 3 compares the conductivity of (30)SBS–PEO(550) with incorporated LiCF$_3$SO$_3$ (O:Li = 7:1), cast from THF and from a 10:1 mixture of nitromethane and THF. The latter electrolyte has the better conductivity by a factor of 100 at all temperatures studied. We have interpreted this previously[16] as being due to differences in the preexponential factor, which reflects changes in the tortuosity of the material as well as variations in the charge density, which may be brought about under certain conditions of microphase separation by the formation of isolated areas of conducting material. Such changes are consistent with the improved phase separation expected to nitromethane cast films. The possibility that the enhanced conductance was due to the presence of residual nitromethane was investigated. First, identical films were heated under vacuum for 24 and 48 h at 413 K. The variation in log σ was less than 0.25 at all temperatures, so that the B and σ_0 parameters, before and after extended heat treatment, were within the calculated limits of uncertainty. In addition, the mass spectra of these samples were recorded for probe temperatures between 325 and 473 K. At higher temperatures, serious polymer degradation was found which masked peaks arising from the solvent and, consequently, the probe temperature was generally maintained at 345 K. Prior to heating, samples of cast film showed peaks in their mass spectrum at m/e of 61, which corresponds to the nitromethane molecular ion. After 24 h of heating under vacuum at 413 K, this peak could not be detected and it was concluded that such treatment was sufficient to remove all significant traces of casting solvent.

The main disadvantage of using a hexamethylene diurethane linking group between MPEG and the block copolymer is the bulk, as this constitutes approximately 15% of the total mass. A succinate linkage, however, contributes only about 8% of the total; i.e., considerably less "nonfunctional" material. Films of this latter polymeric system were rubberlike and free standing while the former materials resembled waxes and were difficult to form into films. The conductivities of (30)SBS–PEO-(550)$_7$LiCF$_3$SO$_3$ are compared in Figure 3 and show there is only slight difference across the temperature spectrum between the two forms of the polymer. Despite the small loss in ionic conductivity the succinate group imparts more desirable characteristics to the physical properties of the polymer.

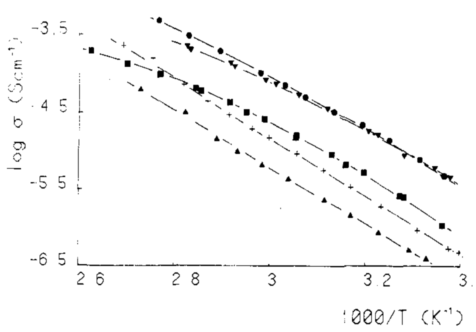


Figure 4. Temperature variation of the conductivity of (30)-SBS–PEO(550)$_7$LiCF$_3$SO$_3$ blended with PS homopolymer: unblended, PEO content 64 wt % (0); with PS(100 000), PEO content 58 wt % (+) and 50 wt % (▲); with PS(20 200), PEO content 50 wt % (▼) and 42 wt % (■).

Table II
Dimensional Stability Measurements

T/K	casting solv	penetration rate × 10^3/mm s^{-1}	sample
298		50	MPEG(750)
		10	MPEG(750)$_7$LiCF$_3$SO$_3$
	THF	1.3	(30)SBS–PEO(750)$_7$LiCF$_3$SO$_3$
	nitromethane	1.3	(30)SBS–PEO(750)$_7$LiCF$_3$SO$_3$
	nitromethane	0.5	blend 4
313	THF	1.8	(30)SBS–PEO(750)$_7$LiCF$_3$SO$_3$
	nitromethane	1.3	(30)SBS–PEO(750)$_7$LiCF$_3$SO$_3$
	nitromethane	0.3	blend 4
333	THF	4.5	(30)SBS–PEO(750)$_7$LiCF$_3$SO$_3$
	nitromethane	1.7	(30)SBS–PEO(750)$_7$LiCF$_3$SO$_3$
	nitromethane	0.5	blend 4

Blending the copolymer with the homopolymer of either component is feasible without macroscopic phase separation, as the homopolymer aggregates in domains with its block copolymer counterpart.[23] Thus, the fraction of glassy or elastomeric component in the material can be readily modified.

Quantities of polystyrene (PS) homopolymer (M_n ~ 100 000 and 20 200) were blended with (30)SBS–PEO-(750)$_7$LiCF$_3$SO$_3$ by method A to improve the mechanical stability of the materials. The overall PEO content was reduced from 64 wt % to 58, 50, and 42 wt %. Figure 4 shows that, on adding PS(100 000) to the copolymer (blends 1 and 2), the conductivity falls progressively as the polystyrene content increases. In contrast, by reducing the PEO content to 50 wt % by mixing with PS(20 200) (blend 3), there is little effect on the conductivity. Reducing the PEO content further to 42 wt % (blend 4) brings about a fall in conductivity, but this is less significant than for a system containing PS(100 000) and having a PEO content of 50 wt %. The higher molecular weight homopolymer is unlikely to aggregate entirely into discrete domains, and a bridged system is probable, increasing the tortuosity and hence reducing the ionic conductivity. On the other hand, the shorter PS chains are more capable of aggregating in specific areas, allowing greater dimensional stability of the material without unduly affecting the conductivity.

Table II shows the dimensional stability measurements,

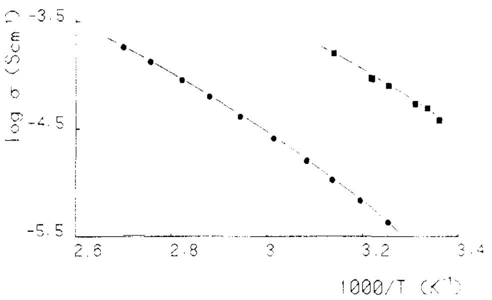


Figure 5. Temperature variation of the conductivity of (30)-SBS–PEO(550)$_7$LiCF$_3$SO$_3$ (●) and blended with MPEG(350), PEO content 75 wt % (■).

given as the initial rate of penetration in mm s^{-1}. The mechanical strength of these materials is greatly superior to that of MPEG(750) itself or of its complexes with LiCF$_3$SO$_3$. Addition of polystyrene homopolymer (20 200) further increases the mechanical stability of the material, but the consequent reduction in overall PEO content from 64 to 42 wt % brings about a conductivity decrease of only half a decade. This implies that the mechanical properties of such systems may be controlled, within limits, independently of the conductivity. By comparison, the conductivites are far superior at all temperatures to a high molecular weight PEO system blended with polystyrene with an overall PEO content of approximately 40%.[15] In addition, it should be feasible to improve tensile strength of ABA block copolymer based systems, by optimizing the microphase separation in the copolymer.[14] Comparison has been made in Table II between samples cast from THF and nitromethane. Although these values just fall within the experimental uncertainty of the measuring system at low temperature, at higher temperatures, nitromethane systems consistently show the better mechanical stability.

Just as the SBS–PEO polymers blended with short-chain polystyrene homopolymer, so a blend with short-chain MPEG can form a microphase separated blend. In the former blends, dimensional stability is enhanced whereas the latter materials would be expected to show increased conductivity. Sufficient MPEG(350) was mixed with (30)SBS–PEO(750) in THF to increase the PEO content to 75 wt % (blend 5). LiCF$_3$SO$_3$ was added to give an overall O:Li ratio of 7:1. The material was translucent and gel-like. Conductivity measurements were carried out in the cell holder shown in Figure 1. The thickness and hence changes in cell constant could be monitored as the temperature was varied. Figure 5 shows the conductivity variation in the temperature range 293–318 K and is compared with values for a (30)SBS–PEO(750) film. Cell constant changes were negligible in this temperature region, but at higher temperatures, creep prevented accurate measurement of the cell constant. The ambient temperature conductivity for this blend was 4×10^{-5} S cm^{-1}. Enhancement of the conductivity by blending with low molecular weight MPEG has been previously reported.[24-26] This decreases the mechanical strength of the materials, resulting in creep, which is a serious disadvantage. However, in the novel systems studied here, there exists the potential to offset this mechanical stability loss by also blending with polystyrene as such a blend has been shown to have minimal effect on the conductivity. These conductivity values and the best data for nonblended systems (nitromethane cast) are shown in Figure 6 along with data for a high T_g backbone graft copolymer system,[5] a high molecular weight PEO system,[15] and a polyphosphazene-based material, all complexed with LiCF$_3$SO$_3$ at similar O:Li ratios. These materials exhibit some of the best conductivities for their "class". Ionic conductivity in our materials compare well with the amorphous systems. However, by exploiting the novel properties of ABA block copolymer based polymer electrolytes, there exists the potential to tailor the mechanical and conducting properties independently to optimum requirements.

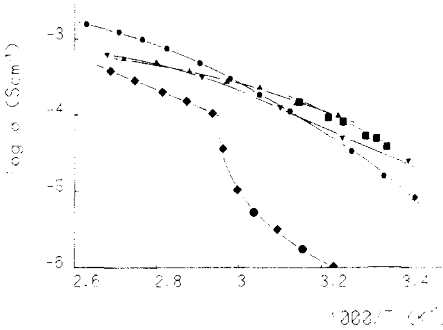


Figure 6. Temperature variation of the conductivity of (30)-SBS–PEO(550)$_7$LiCF$_3$SO$_3$ cast from nitromethane (●), blended with MPEG(350) (■) compared with data reported by Blonsky et al.[7] (▲), Bannister et al.[5] (▼) and Gray et al.[15] (♦).

Conclusions

Electrolytes have been formed by incorporating a salt in B-block, side-chain MPEG grafted ABA block copolymers. The film casting solvent can influence the conductivity of the resultant film depending on its relative block solvating properties. Significant side-chain crystallization was detected only at very low salt concentration. Blending with polystyrene homopolymer can improve the dimensional stability without unduly affecting the conductivity, provided the molecular weight of the homopolymer is low. Conductivity can be enhanced by blending with low molecular weight MPEG which is compatible with the "B" phase and does not phase separate on a macroscale, although some loss in mechanical stability results.

Acknowledgment. Financial support from the Ministry of Defence is gratefully acknowledged.

Registry No. (MPEG-NCO)(B)(S) (copolymer), 111379-82-9; (MPEG-CO$_2$H)(B)(S) (copolymer), 111379-84-1; PS, 9003-53-6; MPEG, 9004-74-4; F$_3$CSO$_3$Li, 33454-82-9; (B)(S)(oxirane) (copolymer), 31292-96-3.

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Light-Scattering Characterization of Poly(tetrafluoroethylene)

Benjamin Chu,[*,†,‡] **Chi Wu,**[‡] **and Warren Buck**[§]

Chemistry Department and Department of Materials Science and Engineering, State University of New York at Stony Brook, Long Island, New York 11794-3400, and Polymer Products Department, Experimental Station, E.I. du Pont de Nemours & Co., Inc., Wilmington, Delaware 19898. *Received June 25, 1987*

ABSTRACT: Laser light scattering including angular dependence of absolute integrated scattered intensity and of the spectral distribution has been used successfully, for the first time, to characterize a tetrafluoroethylene polymer [$-(CF_2CF_2)-]_x$; PTFE] in oligomers of poly(chlorotrifluoroethylene) at 340 °C. In order to carry out the experiments at high temperatures, i.e., at 340 °C instead of 240 °C which was the temperature needed for the light scattering characterization of an alternating copolymer of ethylene and tetrafluoroethylene $-(C_2F_4C_2H_4)-_y$, we modified a high-temperature light-scattering spectrometer and developed a new all-glass dissolution/filtration apparatus, capable of dissolving, transferring, and clarifying the polymer solution at elevated temperatures under an inert gas without moving components except for the stopcock. For the PTFE polymer sample, we determined the weight-average molecular weight M_w [$= 2.8 \times 10^5 \pm 10\%$ g/mol], the *z*-average radius of gyration R_g [$= 18.0 \pm 10\%$ nm], the second virial coefficient A_2 [$= 6.5 \times 10^{-5} \pm 20\%$ mol cm^3 g^{-2}], the *z*-average translational diffusion coefficient at infinite dilution $\bar{D}_0$ [$= 3.26 \times 10^{-7} \pm 2\%$ cm^2/s], and the variance $\mu_2/\bar{\Gamma}^2$ [$= 0.2 \pm 10\%$]. Precise measurements of the intensity-intensity time correlation function permit us to make a Laplace inversion using a variety of techniques including a multiexponential singular value decomposition (MSVD), regularized inversion of Laplace integral equation (RILIE), and the CONTIN algorithm developed by Provencher. We were able to obtain an estimate of the normalized characteristic line-width distribution which could be reduced to a distribution of translation diffusion coefficient at infinite dilution, independent of the method used in the Laplace inversion. By assuming a scaling exponent of ~0.5 between $\bar{D}_0{}^\circ$ and M_w, i.e., $\bar{D}_0{}^\circ \sim M_w{}^{-0.5}$, we could estimate the molecular weight distribution (MWD) of the PTFE polymer with $M_z/M_n{:}M_w/M_n \sim 2.9{:}1.9$.

1. Introduction

Laser light scattering (LLS) has been used successfully to characterize a range of relatively intractable polymers, such as polyethylene (denoted as PE) in 1,2,4-trichlorobenzene,[1,2] poly(ethylene terephthalate) (denoted as PET) in hexafluoro-2-propanol,[3] poly(1,4-phenylene terephthalamide) (denoted as PPTA) in concentrated sulfuric acid,[4-8] and an alternating copolymer of ethylene and tetrafluoroethylene (denoted as PETFE) in diisobutyl adipate.[9-11] An absolute determination of the molecular weight of polytetrafluoroethylene (denoted as PTFE), $-(CF_2CF_2)-_x$, commercially known as "Teflon" TFE fluorocarbon resin (a registered trademark of Du Pont) by means of laser light scattering represents another advance in the development of LLS as an analytical technique for polymer characterizations.[12] In this paper, we present details of our light scattering studies on PTFE solution properties above the melting point of PTFE (~330 °C). Although "Teflon" was invented more than 40 years ago, an absolute determination of the molecular weight represents an interesting challenge by any analytical techniques. To date, no solvents that are suitable for Teflon have been found. Thus, in our approach to create a Teflon solution, we used oligomers of Teflon-like polymers, e.g., oligomers of poly(chlorotrifluoroethylene), with the following criteria: (a) a boiling point sufficiently high so that the oligomer melt forms a liquid at temperatures greater than 330 °C, (b) a refractive index sufficiently different from that of the Teflon polymer so that a reasonable refractive index increment exists, and (c) the oligomer molecular weights sufficiently low so that the characteristic decay times are distinctly different from those of Teflon. The same approach could be applicable to other difficult to dissolve polymers.

Oligomers of poly(chlorotrifluoroethylene) appear to be poor solvents for Teflon. We were able to study only a low molecular weight Teflon polymer in detail. As a delicate balance exists among the three criteria above, higher molecular weight Teflon polymers can be expected to dissolve in higher molecular weight fractions of polyperfluorocarbons. Nevertheless, the present study demonstrates our new approach to light-scattering characteriza-

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[*] To whom correspondence should be addressed at Chemistry Department, State University of New York at Stony Brook.

[†] Department of Materials Science and Engineering, State University of New York at Stony Brook.

[‡] Chemistry Department, State University of New York at Stony Brook.

[§] E.I. du Pont de Nemours & Co., Inc.

0024-9297/88/2221-0397$01.50/0