Block copolymer ionomers: 1. Synthesis and physical properties of sulphonated poly(styrene–ethylene/butylene–styrene)

R. A. Weiss* and Ashish Sen†
Polymer Science Program and Department of Chemical Engineering, University of Connecticut, Storrs, CT 06269-3136, USA

C. L. Willis and L. A. Pottick
Shell Development Co., Westhollow Research Center, Houston, TX 77082, USA

(Received 10 April 1990; revised 23 April 1990; accepted 19 June 1990)

The styrene end-blocks of a poly(styrene–(ethylene-*co*-butylene)–styrene) (SEBS) triblock copolymer were sulphonated up to a concentration of 18 mol%. Sodium and zinc salts of the sulphonated polymers exhibited behaviour indicative of strong ionic interchain interactions, similar to what is observed with other ionomers. Dilute solution viscosities were enhanced upon sulphonation, the T_g of the styrene blocks was increased and the ionomers exhibited a rubbery plateau region above the styrene block T_g that was absent in the base resin. Whereas SEBS was insoluble in toluene and methanol mixed solvents, the sulphonated polymers were soluble. Moreover, the addition of the alcohol cosolvent significantly lowered the solution viscosity by solvating the interchain ionic interactions. The sulphonated polymers were thermal-oxidatively more stable and more hygroscopic than the unmodified polymers.

(Keywords: ionomers; block copolymers; synthesis; physical properties; sulphonation)

INTRODUCTION

Microphase separation has been exploited in a number of polymer systems to develop thermally reversible networks. Examples include block and segmented copolymers, ionomers and, in some instances, graft copolymers and polymer–polymer blends. The physical network that is responsible for the unique mechanical and viscoelastic properties of these materials forms as a consequence of thermodynamic immiscibility of the different chemical substituents. Macroscopic phase separation is prevented by the covalent attachment of the chemically dissimilar species, and, as a result, the phase size of the minority component is limited by steric and interfacial effects. For example, the characteristic sizes of the microphase-separated domains is of the order of 10 nm in block copolymers and 1 nm in ionomers. In block copolymers, the phase separation is driven by the immiscibility of the component blocks, while in ionomers, polar associations of the ionic groups provide sufficient driving force for phase separation.

One important application of thermally reversible networks is thermoplastic elastomers. Because of the physical crosslinks that result from microphase separation, these materials have the properties of cross-linked polymers at use temperatures. Yet at elevated temperatures, the network relaxes and the polymers can be processed as thermoplastics. Thermoplastic elastomers have been developed from styrene–diene block copolymers[1], segmented polyurethanes[1] and sulphonated ethylene–propylene–diene terpolymer ionomers (SEPDM)[2].

Weiss *et al.*[3] recently reported the synthesis of novel thermoplastic elastomers based on partially sulphonated styrene–(ethylene-*co*-butylene) triblock copolymers. These polymers exhibited two separate levels of phase separation: one characteristic of the block copolymer structure and one due to the ionomeric nature of the polymer. This paper describes in more detail the preparation and physical properties of these block copolymer ionomers. Subsequent papers will describe their rheological and mechanical behaviour.

EXPERIMENTAL

Materials

The starting polymer was a hydrogenated triblock copolymer of styrene and butadiene (rubber mid-block and styrene end-blocks), prepared by anionic polymerization. After hydrogenation the mid-block is essentially a random copolymer of ethylene and butylene; the ethylene segments arise from 1,4-additions of butadiene and the butylene groups from 1,2-additions. The polymer had a number-average molecular weight of 50 000 and was 29.8% (wt) styrene. The concentration of residual unsaturation was 0.08 meq/g.

The block copolymer was dried under vacuum at 70°C for 48 h prior to use. The sulphonating reagent was acetyl sulphate, which was prepared by the reaction of concentrated sulphuric acid with acetic anhydride. All reagents were used as received, and an excess of acetic anhydride was used to scavenge any water that might have been present.

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* To whom correspondence should be addressed
† Current address: Dow Chemical Co., Midland, MI 48640, USA

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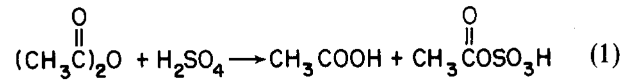
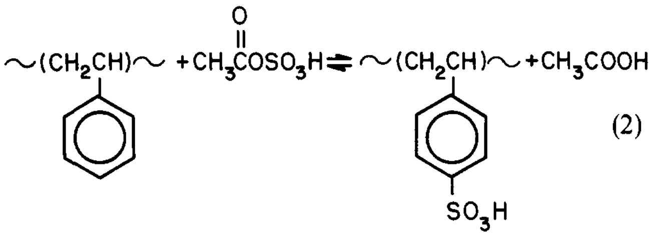
Sulphonations were carried out in 1,2-dichloroethane at 50°C following the procedure described by Makowski *et al.*[4]. The appropriate reactions are given by:



$$(CH_3\overset{O}{\overset{\|}{C}})_2O + H_2SO_4 \longrightarrow CH_3COOH + CH_3\overset{O}{\overset{\|}{C}}OSO_3H \quad (1)$$



(2)

Fresh acetyl sulphate was prepared prior to each sulphonation reaction. The reaction was terminated by the addition of 2-propanol and the sulphonated polymer was recovered as the free sulphonic acid derivative by steam stripping. In general, the polymer precipitated as a fine filterable crumb. At the highest sulphonation level studied, 18 mol% of the polystyrene blocks, an emulsion of the ionomer in water was formed, but this could be slowly filtered. The polymer was washed with boiling water, filtered, washed with ethanol and vacuum dried at 50°C. Sulphonic acid concentrations were determined by either elemental sulphur analysis or by titration with alcoholic sodium hydroxide. Na and Zn salts were prepared by dissolving the sulphonated polymer in a toluene and methanol (90/10 v/v) mixture and adding a stoichiometric amount of either sodium hydroxide or zinc acetate.

There were two kinds of reactive sites in the starting polymer: (1) the phenyl rings (~150 sites/chain) in the polystyrene blocks and (2) the residual C=C (~4 sites/chain) in the hydrogenated rubber block. Although olefinic unsaturation is inherently more reactive to acetyl sulphate than the phenyl rings, the large excess of the latter preferentially favoured sulphonation of the styrene segments. Infra-red spectroscopy analyses confirmed that sulphonation occurred almost exclusively in the polystyrene blocks. The degree of sulphonation is expressed as mole per cent of the styrene repeat units sulphonated. (An alternative measure of the sulphonate concentration is meq phr = 2.86 × (mol% styrene sulphonation). This assumes that only the polystyrene block was sulphonated.)

Example sulphonation

Acetyl sulphate preparation. First 7.63 ml of acetic anhydride was added to 39.57 ml of 1,2-dichloroethane (DCE). The solution was cooled to below 10°C and 2.8 ml of 95% sulphuric acid was added, and a clear solution resulted. It was assumed that the reaction yield was quantitative, i.e. 50 meq acetyl sulphate.

Sulphonation reaction. First 10 g of block copolymer was dissolved in 100 ml of DCE. The solution was heated to 50–53°C and purged with nitrogen for 30 min. Then 6 ml of 0.996 N acetyl sulphate (based on product described above), corresponding to 6 meq, was added. The solution was stirred for 2 h at this temperature, after which 10 ml of 2-propanol was added to stop the reaction. The polymer was isolated by steam stripping, washed for 2 h in boiling water, filtered, washed with ethanol and vacuum dried at 50°C for 5 days. This particular product contained 1.04% sulphur (elemental analysis, Galbraith Laboratory), which corresponded to 11.7 mol% sulphonation or a sulphonation yield of 57% based on the amount of acetyl sulphate used.

Sulphonate analysis by titration. A standard sodium hydroxide solution, nominally 0.1 N, was prepared by dissolving 1 g NaOH in 250 ml absolute methanol. A minimum amount of distilled water was used to facilitate dissolution of the NaOH. The normality of the standard solution was determined by titrating with 0.1 N *p*-toluene sulphonic acid in methanol using a phenolphthalein indicator. Then 50 ml of a 0.2% solution of the sulphonated polymer in toluene/methanol (90/10 v/v) was prepared, and nitrogen was bubbled through the solution for 30 min in order to remove dissolved carbon dioxide. The standardized NaOH solution diluted five times with absolute methanol was used to titrate the polymer solution to a phenolphthalein endpoint. Titration of the polymer described in the example above indicated a sulphonation level of 11.9 mol%.

Sulphonation kinetics

A cursory investigation of the kinetics of the sulphonation reaction was carried out by sulphonating separate 10% solutions of the block copolymer and polystyrene with 50 meq phr acetyl sulphate. Aliquots (10 ml) were periodically removed from the reaction mixture and the polymer was recovered by steam stripping. The polymer was washed in boiling water followed by absolute ethanol and finally vacuum dried. The sulphonate concentrations were measured by titration with alcoholic sodium hydroxide.

Infra-red spectroscopy

Infra-red spectra were measured with a Nicolet 60SX Fourier transform infra-red (*FT*i.r.) spectrometer using compression-moulded films. One hundred scans were taken with a resolution of 2 cm^{-1}.

Thermal analyses

A Perkin–Elmer TGA-7 thermogravimetric analyser (t.g.a.) was used to measure the thermal-oxidative stability of the polymer. The specimens were heated in air at a rate of 10°C min^{-1}. A Perkin–Elmer TMS-7 thermomechanical analyser (t.m.a.) was used to measure the softening behaviour. The measurements were made under a helium atmosphere from −100 to 400°C at a heating rate of 10°C min^{-1}. A penetration probe with a flat tip of radius 0.5 mm and a force of 500 mN were used.

Dilute solution viscosity

Reduced solution viscosity measurements were made with an Ubbelohde No. 0B capillary viscometer. Measurements were made of solutions in tetrahydrofuran (THF) at 23°C and in toluene at 30°C. In addition, measurements were also made in various mixtures of toluene and methanol (0–10% v/v methanol) at 30°C.

Water sorption

Water sorption measurements were made for the starting copolymer and the acids, sodium salts and zinc salts of the 5.4 and 11.9 mol% sulphonated copolymers at 23 and 70°C. Discs 1.5 mm thick and 6.0 mm diameter were compression-moulded and thoroughly dried at 90°C

Table 1 Block copolymer ionomers

Designation[a]	Styrene sulphonated sample (mol%) S analysis	Titration
SEBS	0.01	
2.5M-SBC	2.5	3.1
2.9M-SBC	2.9	
4.2M-SBC	4.2	
5.2M-SBC	5.2	5.8
8.7M-SBC	8.7	9.2
11.9M-SBC	11.9	12.7
18.0M-SBC	18.0	19.5

[a] 'M' denotes the counterion; in this case H, Na or Zn. SBC denotes sulphonated block copolymer

under vacuum. These were immersed in jars of distilled water at the test temperature. The specimens were removed periodically, patted dry with a tissue and the mass was determined with an analytical balance. The average of five specimens was used to generate each experimental value.

RESULTS AND DISCUSSION

Materials

Table 1 lists the block copolymer ionomers prepared for this study. The convention used to designate the samples in the table and in the following text is *X*.*Y*M-SBC, where *X*.*Y* is the degree of substitution of the styrene block (i.e. mol% styrene sulphonated) and M designates the counterion, either H, Na or Zn. The poly(styrene–(ethylene-*co*-butylene)–styrene) base block copolymer is designated as SEBS without a prefix.

The relationship between the extent of sulphonation and the amount of sulphonating reagent used is shown in *Figure 1* for SEBS and polystyrene (PS). For SEBS, the efficiency of the sulphonation reaction was about 55% based on the acetyl sulphate charge, which was somewhat lower than the 87% conversion attained for the sulphonation of polystyrene homopolymer. This may have been due to differences in the accessability of the styrene in the block copolymer in DCE compared to polystyrene. DCE is probably a better solvent for polystyrene than for SEBS owing to the presence of the EB mid-block for which DCE is not a good solvent. The calculated sulphonation yields were based on the assumption that the yield of acetyl sulphate in reaction (1) was quantitative. These yields would actually be higher if this were not the case, and, therefore, the conversions reported here for both SEBS and PS actually represent lower limits.

Sulphonation kinetics

A limited study of the reaction kinetics for the sulphonation of SEBS and PS was made and the data are summarized in *Figure 2*. In both cases, the degree of sulphonation increased rapidly for the first 2 h and then began to level off. The acetyl sulphate feed corresponded to a sulphonation target of about 17.5 mol% styrene sulphonate. Therefore, after 6 h of reaction, only about 52% conversion was achieved for SEBS and 86% for PS.

Infra-red analysis

The characteristic infra-red absorbances for styrene sulphonate have been identified by Fitzgerald and Weiss[5,6], who studied lightly sulphonated polystyrene (SPS). Thus, *FT*i.r. spectroscopy was used to confirm that styrene sulphonate was the product in the present study. *Figure 3* shows the spectra of the SEBS, 5.2Zn-SBC and 11.9Zn-SBC, and the difference spectra of (5.2Zn-SBC – SEBS) and (11.9Zn-SBC – SEBS). The difference spectra show the changes that result from the sulphonation reaction. The arrows denote the positions of the major sulphonate absorptions in the sulphonated polymers and these are clearly seen in the difference spectrum. The absorbance at 1010 cm^{-1} results from the in-plane bending vibrations of a phenyl ring substituted with a metal sulphonate group, and the 1127 cm^{-1} peak results from a sulphonate anion attached to a phenyl ring. The absorbance at 1042 cm^{-1} is due to the

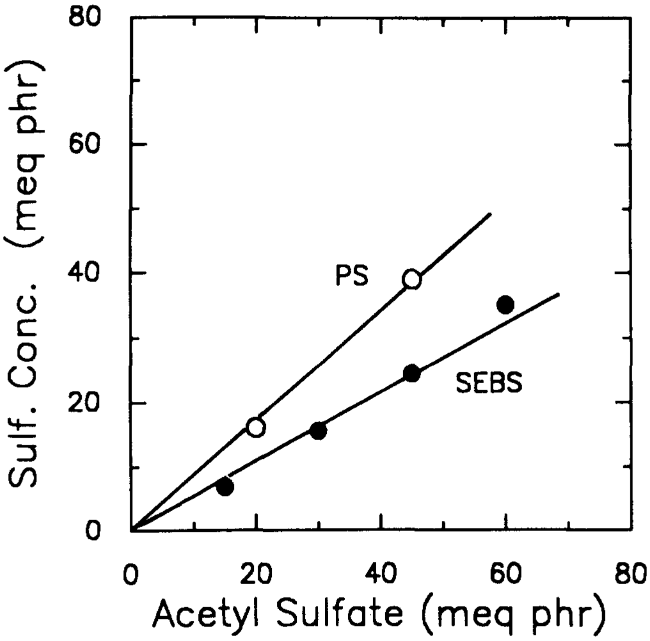


Figure 1 Sulphonation yield *versus* concentration of sulphonating reagent for sulphonation of SEBS block copolymer and polystyrene

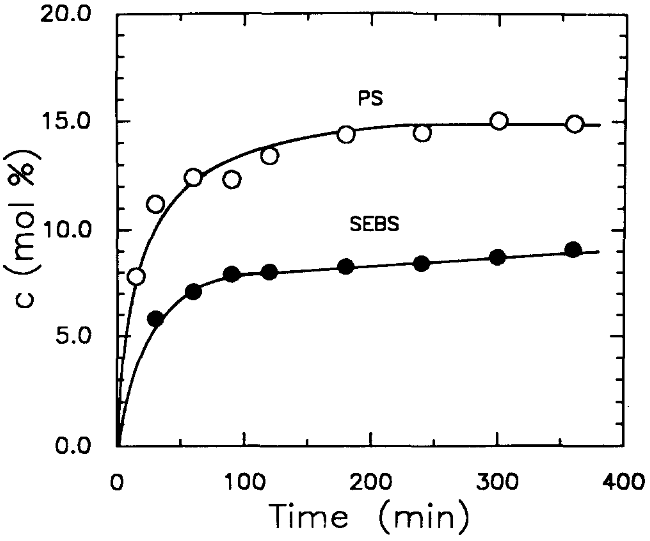


Figure 2 Extent of sulphonation *versus* time of reaction for sulphonation of block copolymer and polystyrene. The charge of acetyl sulphate corresponded to a sulphonation level of 17.4 mol% of the styrene repeat units (50 meq phr)

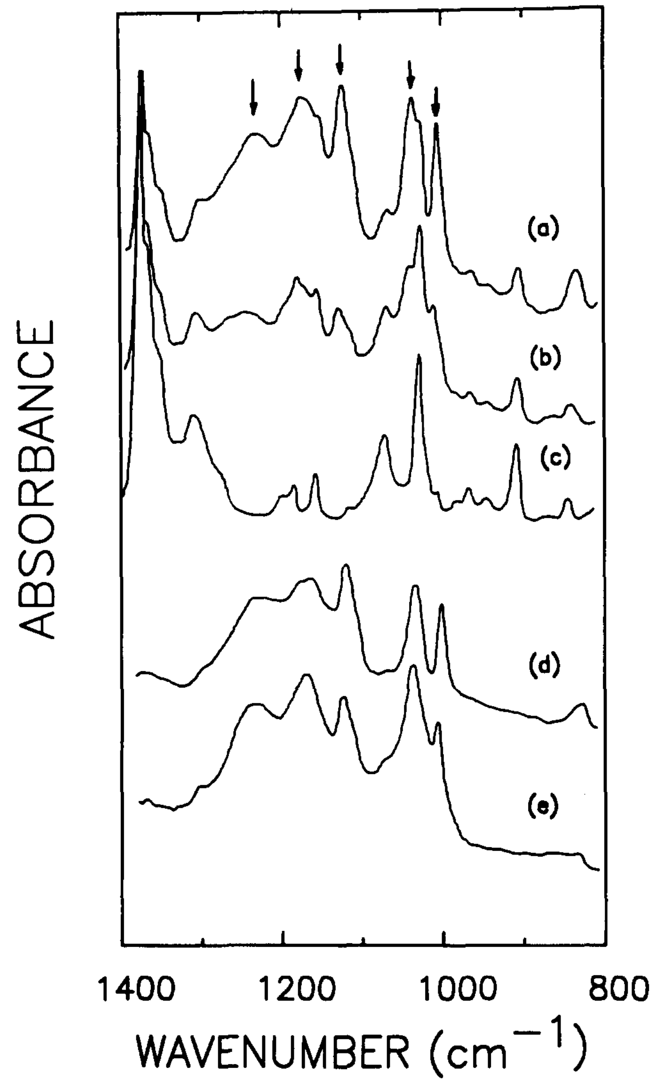


Figure 3 Infra-red spectra of (a) 11.9Zn-SBC, (b) 5.2Zn-SBC and (c) SEBS; difference spectra of (d) 11.9Zn-SBC–SEBS and (e) 5.2Zn-SBC–SEBS. The arrows designate the absorbances due to sulphonation

symmetric stretching vibration of the zinc sulphonate group, and the two peaks at 1172 and ~1235 cm^{-1} (1232 cm^{-1} for 5.2Zn-SBC and 1238 cm^{-1} for 11.9Zn-SBC) are consistent with the expected positions of the doublet due to the asymmetric stretching vibration of the sulphonate group.

Polymer stability

Thermal-oxidative stability of SEBS and the sulphonated polymers were measured in air by t.g.a. The data for the sulphonic acid derivatives are shown in *Figure 4*, and comparisons between the acid, Na salt and Zn salt derivatives of a 5.2M-SBC and 11.9M-SBC are shown in *Figure 5*. Similar results were found for other sulphonation levels. The onset of the major mass-loss process increased on the order of 100°C for the sulphonic acid and salt derivatives compared with the base resin. In general, the thermal-oxidative stability increased with increasing sulphonation level. The stabilities of the salts and the free acid derivatives were similar; no consistent trend was observed in their relative stabilities at a fixed sulphonation level. The differences in the t.g.a. thermograms between the acid and salts may be due in part to differences in the viscosity of polymers, which affects the diffusion rate of the volatile degradation products within the sample.

The stability of the sulphonated SEBS ionomers in air was qualitatively compared with two other ionomers, SPS and SEPDM, which by t.g.a. also exhibited thermal-oxidative stability to ~400°C for both the acid and metal salt derivatives. For both SPS and the SEBS

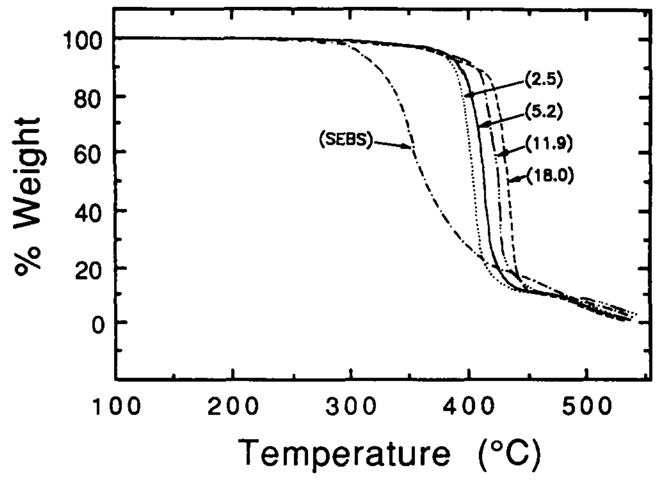


Figure 4 T.g.a. thermograms of SEBS and free acid derivatives of sulphonated SEBS. Numbers in parentheses correspond to the mol% styrene sulphonated

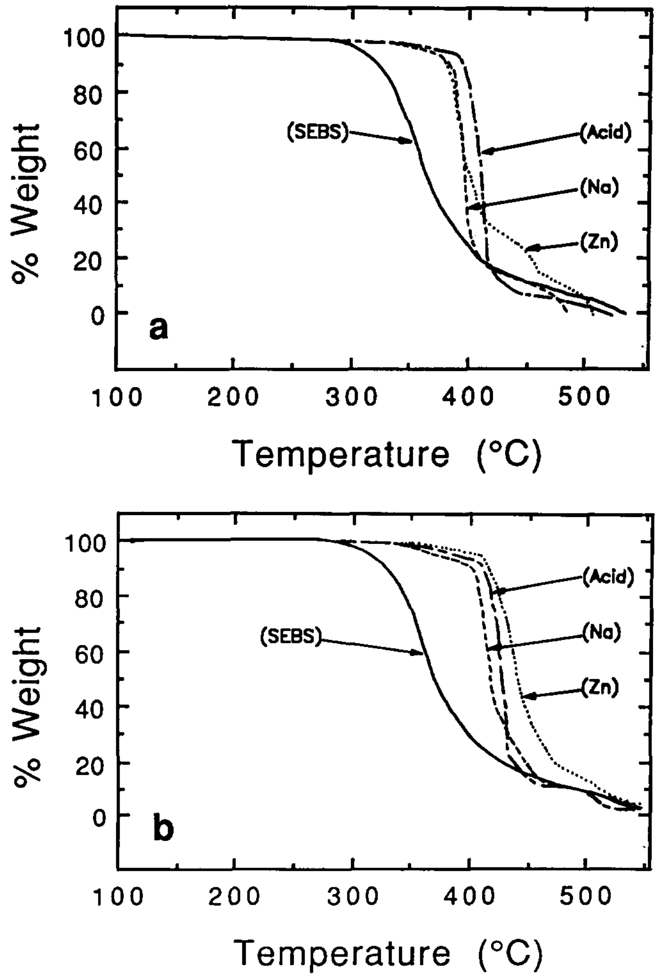


Figure 5 T.g.a. thermograms of SEBS and free acid, sodium salt and zinc salt of (a) 5.2M-SBC and (b) 11.9M-SBC

Table 2 Solubility of polymers

	Polymer						
Solvents	SEBS	5.2H-SBC	5.2Na-SBC	5.22n-SBC	11.9H-SBC	11.9Na-SBC	11.9Zn-SBC
Toluene	Yes	Gel	Gel	Gel	Gel	Gel	Gel
Toluene/MeOH (10/1)	Yes	Yes	Yes	Yes	Gel	Yes	Yes
THF	Yes	Gel	Yes	Yes	Gel	Yes	Yes
THF/water (10/1)	Yes	Gel	Yes	Yes	Gel	Yes	Yes
Dichloroethane	Yes	No	No	No	No	No	No
Chloroform	Yes	Gel	Yes	Yes	Gel	Yes	Yes
Dimethyl sulphoxide	No	No	No	No	No	No	No
Glycerol	No	No	No	No	No	No	No
Methanol	No	No	No	No	No	No	No
Heptane	Yes	No	No	No	No	No	No
Acetone	No	No	No	No	No	No	No

ionomers, no detrimental effects on the appearance of the polymer or the mechanical and rheological properties were observed upon extended storage of the acid or salt derivatives. This was in marked contrast to the acid derivative of SEPDM, which is unstable in air even at ambient temperatures[7]. The poor stability of the H-SEPDM was attributed to the instability of the sulphonic acid group attached to ethylidene norborane. This was manifested by discoloration of the polymer and a reduction in its viscosity. The stability of the sulphonated SEBS ionomers, however, was comparable to that of SPS, which was most likely due to the greater stability of the aromatic sulphonic acid compared with sulphonated ethylidene norborane.

Pyrolysis gas chromatography–mass spectroscopy (g.c.-m.s.) analysis of several of the SEBS ionomers at 350°C found acetic acid in all the sulphonated polymers, in addition to degradation products attributable to the SEBS and the sulphonate groups (e.g. styrene, 1,3-diphenylpropane, various SO_2 compounds and oligomers). This indicates that the procedure used to recover the ionomer following sulphonation, i.e. steam stripping followed by separate washes with water and alcohol, was not sufficient for removing all traces of the acetic acid by-product of the reaction. Similar trace amounts of acetic acid were also found by pyrolysis g.c.-m.s. of SPS and SEPDM ionomers, and it was assumed that the amounts of residual acetic acid probably remaining in the ionomers would have a negligible effect on their properties.

Solution behaviour

Sulphonation of the SEBS markedly altered its solubility as shown in *Table 2* for the 5.2M-SBC and 11.9M-SBC ionomers. 'Gel' denotes that the polymer swelled substantially, but did not dissolve.

The ionomeric nature of the sulphonated polymers was clearly shown by their solubility in toluene, which is a good solvent for SEBS. Although the metal sulphonates were insoluble in toluene, the addition of a small amount of a polar cosolvent such as methanol resulted in dissolution. This behaviour is similar to the solubility characteristics of other ionomers, such as SEPDM and SPS[8]. The insolubility of the ionomer in toluene is due to the formation in the polymer of a physically crosslinked network from intermolecular associations of the ionic dipoles. The polar cosolvent preferentially interacts with the sulphonate group[9], thereby weakening the dipolar interactions. It is also worth noting that the solubilities of the free acid derivatives were qualitatively similar to those of the salts, which indicates that an effective physical network also arose from intermolecular hydrogen bonding of the sulphonic acid groups. An unexpected result was the insolubility of the free acid derivatives in any of the solvents except aromatic hydrocarbon and alcohol mixed solvents. This suggests that the physical associations resulting from hydrogen bonding are more resistant to solvation than the metal sulphonate associations. Alternatively, the insolubility may simply reflect a change in the overall polarity, or solubility parameter, of the polymer, though it is not clear why the metal salts should be different. This behaviour was also in marked contrast to the behaviour of SPS ionomers, for which the acid derivatives are much more soluble than the salts.

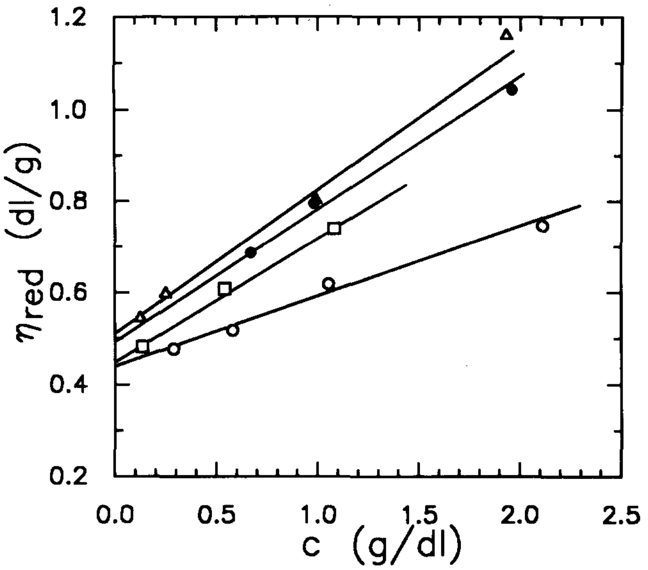


Figure 6 Reduced viscosities *versus* concentration for sulphonated polymers and SEBS in toluene at 30°C: (○) SEBS, (□) 2.9Na-SBC, (●) 4.2Zn-SBC, (△) 4.2Na-SBC

The reduced solution viscosities of SEBS and several of the metal sulphonates measured in toluene at 30°C and in tetrahydrofuran (THF) at 23°C are shown in *Figures 6* and *7*. At a given solution concentration, the viscosity increased with increasing sulphonation level and solutions of the sodium salts were more viscous than for zinc salts. The increase of the viscosity compared with

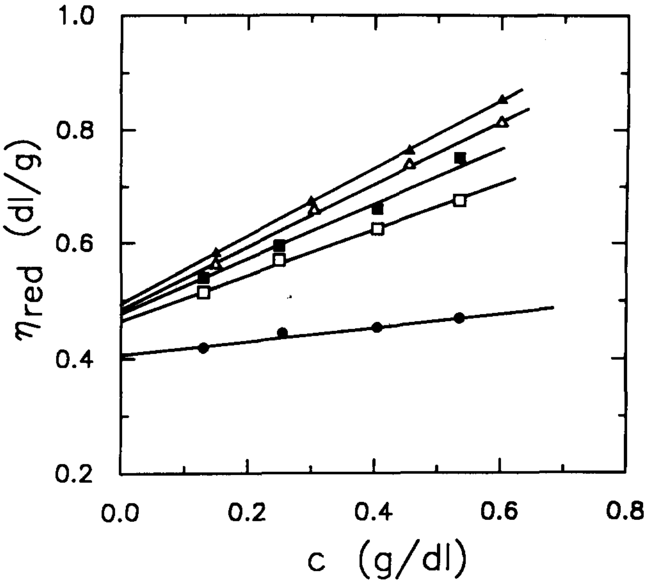


Figure 7 Reduced viscosities *versus* concentration for sulphonated polymers and SEBS in tetrahydrofuran at 23°C: (●) SEBS, (□) 5.2Zn-SBC, (■) 5.2Na-SBC, (△) 11.9Zn-SBC, (▲) 11.9Na-SBC

that of a solution of the unmodified polymer, which has also been reported for other ionomers[8], is due to the strong intermolecular ionic associations that occur even in dilute solution. The enhancement of the viscosity is due to an increase of the hydrodynamic volume of the basic flow unit, which is now an aggregate of multiple chains.

A noticeable difference between the viscosity–concentration curves for the sulphonated SEBS solutions and SEPDM and SPS solutions is that, in the latter cases, the curves cross over that for the base resin as the solution is diluted[8]. That is, SPS and SEPDM solutions in relatively non-polar solvents have lower viscosities at very low concentrations than a comparable solution of the base resin, but higher viscosities at higher concentrations. This has been attributed to a transition from inter- to intramolecular associations as the concentration was lowered, thus giving rise to a collapse of the polymer coils[8]. More recent experimental results by Pedley *et al.*[10] using small-angle neutron scattering (SANS) indicated that the reduction of the viscosity at low polymer concentrations was not due to chain collapse, but rather to the formation of small aggregates of several chains. Whether the differences in the viscosity behaviour of the block copolymer ionomers and the 'random copolymer' ionomers is due to differences in the chain conformations or different aggregate microstructures cannot be inferred from these viscosity results. A similar absence of cross-over behaviour was also observed for solutions of emulsion copolymers of styrene and sodium styrene sulphonate[11]. Although those ionomers were chemically equivalent to SPS, the authors believed that the sulphonated monomer incorporated in a blocky, rather than random, fashion. These results suggest that there may be a fundamental difference in the conformations or aggregation of the block copolymer ionomers and the random copolymer ionomers in dilute solution. Certainly SANS experiments on the SEBS ionomers similar to those performed by Pedley *et al.*[10] would be instructive.

The effects of a polar cosolvent, methanol, on the dilute solution viscosity of 4.2Na-SBC and the base SEBS are shown in *Figure 8*. These data were measured at a polymer concentration of about 1% (wt), and the viscosities were normalized by the viscosity of the polymer in toluene. The SEBS precipitated from solution if more than 1% (v/v) methanol was used, but the addition of 1% methanol had a negligible effect on the viscosity of the SEBS solution. The addition of methanol to the sulphonated SEBS solutions significantly lowered the viscosity; the effect was already clear at methanol concentrations as low as 1%. This is similar to the effect of a polar cosolvent on SEPDM and SPS solutions in which the polar solvent solvates the ionic associations that persist in solutions with non-polar solvents. This effect was recently verified spectroscopically for SPS solutions by Fitzgerald and Weiss[12].

Although the SEBS precipitated if more than 1% methanol was used, the sulphonated polymers remained soluble even at cosolvent concentrations of 10%. The solubility of the sulphonated block copolymers in the mixed solvent was most likely due to the affinity of the methanol for the sulphonate group, which keeps the local concentration of methanol low in the vicinity of the hydrophobic polymer backbone.

Thermomechanical analysis

T.m.a. thermograms of SEBS and the sodium and zinc salts of 5.2M-SBC and 11.9M-SBC are given in *Figure 9*. Two features of these curves are noteworthy. First, the softening point, i.e. T_g, of the styrene end-blocks increased as the sulphonate concentration increased, which is a consequence of the restrictions on the segmental motion in the styrene blocks due to the ionic crosslinks. Secondly, a pseudo-rubbery plateau above the T_g of the styrene block was observed for the sulphonated polymers, but not for the SEBS. This resulted from the physical network formed from ionic interactions in the styrene block. The plateau persisted to nearly 300°C for the more highly sulphonated polymers, at which point the melt began to exhibit viscous flow. This network was thermally reversible in that it was re-established when the temperature was lowered below the T_g of the styrene blocks.

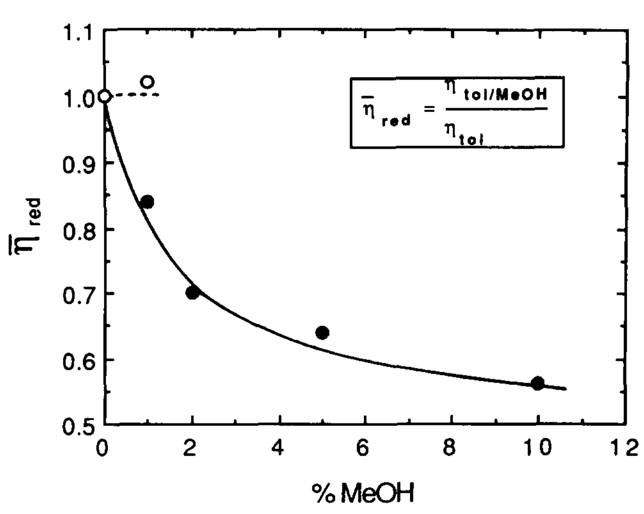


Figure 8 Normalized reduced viscosities of (○) SEBS and (●) 4.2Na-SBC in toluene and methanol mixed solvents as a function of methanol concentration in toluene at 30°C. All polymer concentrations are 1% (wt), and the data are normalized by the reduced viscosity of the polymers in toluene without alcohol

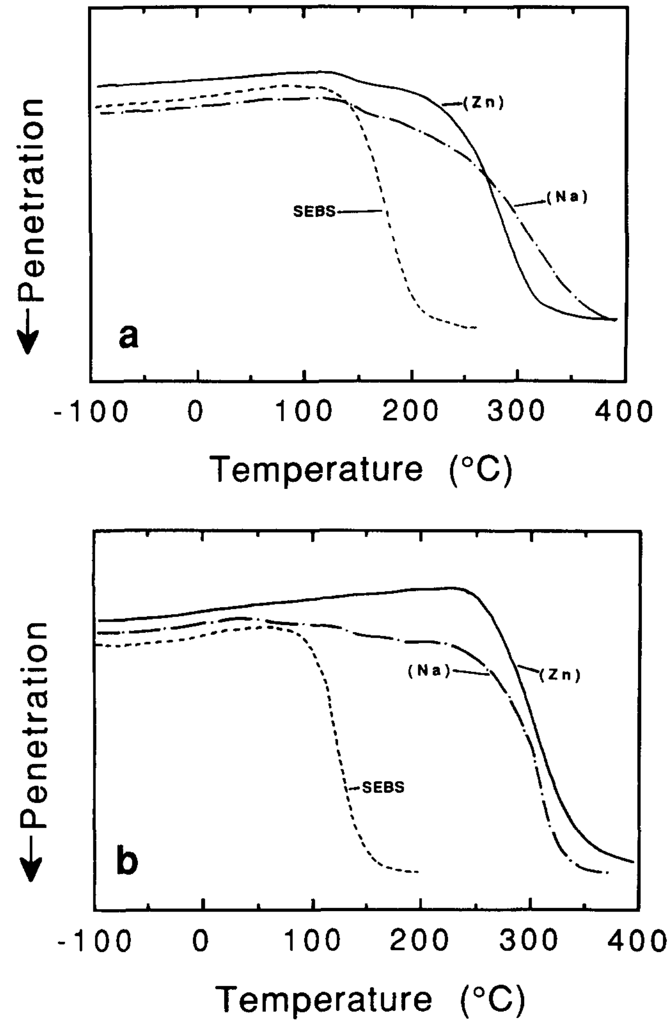


Figure 9 T.m.a. thermograms of SEBS and sulphonated SEBS for (a) 5.2M-SBC and (b) 11.9M-SBC

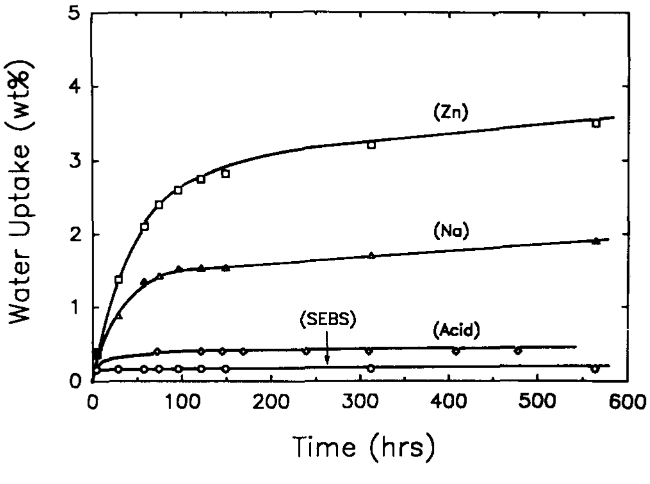


Figure 10 Water uptake *versus* time at 23°C for SEBS (○) and the free acid (◇), sodium salt (△) and zinc salt (□) of 5.2M-SBC. Water concentration (wt%) is based on dry mass of the polymer

Water sorption

Water sorption isotherms at 23 and 70°C for SEBS and the 5.2M-SBC ionomers are shown in *Figures 10* and *11*. The amounts of water sorbed for the 5.2M-SBC and 11.9M-SBC materials are summarized in *Table 3*. Except where noted, the results in *Table 3* are either equilibrium values (i.e. constant mass was reached) or are within 10% of the equilibrium value estimated by extrapolating the data past 24 days immersion.

The sulphonated polymers were considerably more hygroscopic than the SEBS, and the amount of water uptake increased with increasing sulphonation. This was expected since the polar nature of the sulphonate group provides a more favourable environment for water than the hydrophobic hydrocarbon polymer backbone. The amount of water sorbed at 23°C increased in the order of free acid < sodium salt < zinc salt. This order was consistent with the ability of the cation to form a hydrogen bridge with water, which is related to its polarization potential[13]. At 70°C, however, the sodium salts were the most hygroscopic, and equilibrium was not achieved even after 24 days for either the 5.2Na-SBC or 11.9Na-SBC samples. In fact, discs of these materials began to break apart, which suggests that these ionomers may have been partially soluble or at least on the verge of water solubility.

CONCLUSIONS

Block copolymer ionomers were prepared by partially sulphonating the styrene end-blocks of a poly(styrene–(ethylene-*co*-butylene)–styrene) triblock copolymer. The sulphonated polymers exhibited better thermal-oxidative stability than the parent block copolymer and were more hydrophilic. Strong intermolecular associations occurred in the bulk and in non-polar solutions. The interactions

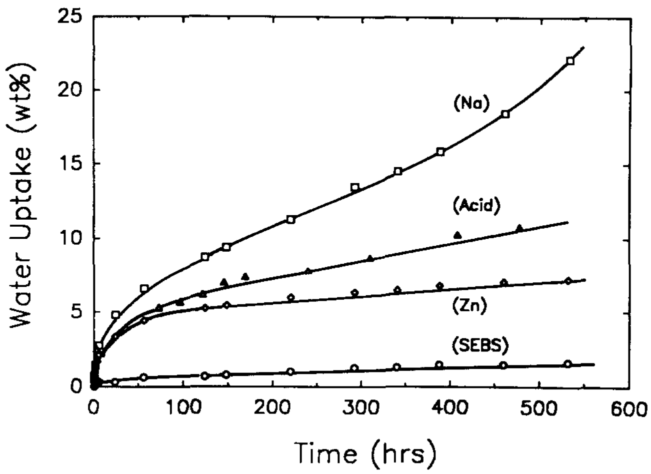


Figure 11 Water uptake *versus* time at 70°C for SEBS (○) and the free acid (△), sodium salt (□) and zinc salt (◇) of 5.2M-SBC. Water concentration (wt%) is based on dry mass of the polymer

Table 3 Water sorption data for SEBS and sulphonated polymers

	Water sorbed (%)	
Material	23°C	70°C
SEBS	0.15	1.6
5.2H-SBC	0.40	10.70
5.2Na-SBC	1.85	22.2
5.2Zn-SBC	3.52	7.2
11.9H-SBC	2.35	11.07
11.9Na-SBC	2.65	25.86
11.9Zn-SBC	5.33	9.36

gave rise to a physical network within the styrene phase that increased the softening temperature of the styrene end-blocks and introduced a pseudo-rubbery plateau region above the styrene T_g. This persisted in the more highly sulphonated polymers to 300°C. As a result of the formation of a physical, ionic network, these materials may have application as elastomers with superior high-temperature properties than SEBS. The mechanical properties of these block copolymer ionomers will be discussed further in a subsequent paper.

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