Star-Branched Block Copolymer Ionomers. Synthesis, Characterization, and Properties

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ABSTRACT: A new kind of telechelic ionomer has been developed that incorporates multiple ionic groups, i.e., an ionic block, at the ends of each polymer chain. Each ionic block is envisioned to behave as a single ionic unit, analogous to a single ion pair in a random or conventional telechelic ionomer. The ionomers may be either linear or star-branched, and the average number of ionic groups per chain terminus can be strictly controlled. Thus, three-arm star-branched block copolymer ionomers composed of short ionic outer blocks and elastomeric inner blocks were synthesized as follows: oligostyrene blocks containing an average of four styrene units were initiated with *s*-BuLi; butadiene was added sequentially to produce block copolymer arms; the living arms were linked with trichloromethylsilane. The polybutadiene blocks, containing approximately 40% 1,2-enchainment, were exhaustively hydrogenated by using H_2 and Wilkinson's catalyst in 2-butanone/hexanes. Exhaustive sulfonation of the oligostyrene outer blocks was performed using acetyl sulfate in homogeneous CH_2Cl_2/hexanes solutions; neutralization was carried out in THF solutions using stoichiometric quantities of metal or quaternary ammonium hydroxides. Investigation of tensile properties revealed that low molecular weight samples, i.e., $10K < \bar{M}_n < 30K$, were weak, brittle, gellike materials; increasing the molecular weight to $\bar{M}_n = 120K$ yielded a tough elastomer with tensile strength of 7 MPa and elongation of 600% for K counterion. The value of the dynamic storage modulus (1 Hz) was constant from -10 to ~125 °C, forming a pronounced rubbery plateau, and gradually decreased over the range 125-225 °C for low molecular weight samples; the tan δ displayed a peak in the range 220-260 °C with the maximum shifting to higher temperature as the molecular weight decreased. SAXS performed on samples of molecular weight 10K and 18K revealed a large upturn near zero scattering angle for both samples; no other peaks were produced by the 18K sample, but the 10K sample displayed a weak shoulder consistent with a Bragg spacing of 2×10^2 Å. It is proposed that the properties of these ionomers are consistent with a morphology consisting of very large, widely spaced multiplets. In this model, particularly for low molecular weight samples, it is probable that a considerable proportion of the molecules incorporate more than one arm into a single multiplet, forming non-load-bearing loops, and for a molecule to span the intermultiplet distance, it would necessarily exist in a highly perturbed, chain-expanded state.

Introduction

Ionomers exhibit unique solid-state and solution properties as a result of strong associations among ionic groups attached to the polymer chains. An important potential application of ionomers is in the area of thermoplastic elastomers, where the associations constitute thermally reversible cross-links. Although the concept of a so-called "ionic cross-link" has been recognized for over 35 years,[1] the exact spatial arrangement of ions and attached chain segments within the domain structure of ionomers is still not understood. Many models have been put forth to describe the morphology of ionomers,[2] but unfortunately they are often system specific since the placement of the ions along the polymer chain can profoundly affect the nature of the aggregations.

Most of what is known about the morphology of ionomers has come from the study of random ionomers, e.g., lightly sulfonated polystyrene, in which the ionic groups are spaced more or less randomly along the polymer chain. Since in this type of ionomer an ionic group falls along the interior of the chain (usually not at the end), it trails two hydrocarbon chain segments, and these must be accommodated sterically within any domain structures into which the ionic group enters. These and other ideas were incorporated by Eisenberg into his now classical theory[3] describing the structuring of ionic aggregates in ionomers. The simplest ionic aggregate is the multiplet, which consists of tightly associated ion pairs within a region devoid of polymer chain segments. Many variables affect the average number of ion pairs that comprise a multiplet, and it is certain that this number increases with the overall ion pair concentration in the polymer; however, the maximum number of ion pairs that may be accommodated within a multiplet is determined largely by steric factors, i.e., the bulkiness of chain segments immediately adjacent to the ion pairs. For poly(ethylene-*co*-methacrylic acid)-derived ionomers the maximum was predicted to be about eight. Eisenberg[3] also introduced the concept of the cluster, which is a microphase-separated ion-rich domain resulting from higher order aggregation of primary multiplets. Recently, Eisenberg et al.[4] introduced a modified view of the relationship between multiplets and clusters. In this new model it is argued that the existence of the multiplet causes a local perturbation of the attached polymer chain segments characterized by a restriction in segmental mobility. Increases in the ion content bring about overlap of these regions of restricted mobility to form, ultimately, large, contiguous regions of restricted mobility that comprise phase-separated clusters. Whatever their true structure, the existence of clusters is now generally accepted, mostly on the strength of evidence from small-angle X-ray and neutron-scattering experiments.[5]

A promising, relatively new area of inquiry involves the synthesis of model ionomer systems composed of precisely tailored chain elements that lead to networks for which various physical property measurements yield direct inferences about the nature of aggregation. In the interest of space, we mention only two examples: the halato-telechelic polymers of Jérôme, Teyssié, and co-workers[6,7] and the sulfonated, telechelic, polyisobutylene- (PIB-) based

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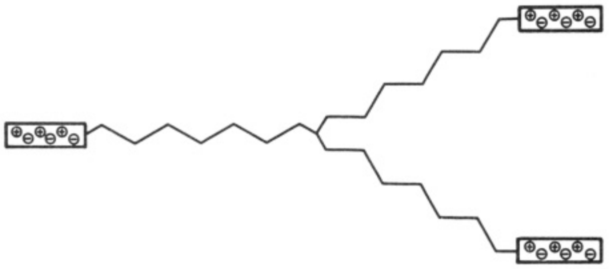

Figure 1. New telechelic star-branched ionomers composed of elastomeric inner blocks and short, sulfonated polystyrene outer blocks.

linear and star-branched ionomers first reported by Kennedy and Storey.[8] The latter materials, which contained one metal sulfonate group per chain end, and were in fact the only star-branched telechelic ionomers in existence at the time, were subjected to a number of mechanical properties investigations by Wilkes, Kennedy, and co-workers.[9-11] They found that samples containing chain segments sufficiently long to display elasticity were of relatively low ion contents, i.e., <3 mol %, and the mechanical properties data suggested that these materials contained only small multiplets, especially ion-pair dimers.[12] The most compelling evidence suggesting predominantly dimeric multiplets was the fact that linear samples were mechanically very weak compared to three-arm star samples. This is perfectly reasonable since ion-pair dimers produce only chain extension of linear ionomers, and the higher the incidence of dimeric multiplets, the lower the cross-link density. Additionally, linear ionomers contain no covalent cross-links. In comparison, star-branched ionomers form a relatively strong network containing covalent cross-links (the hubs of the star molecules), and dimeric multiplets yield network chain segments consisting of two "arms" joined together. An alternative way to view the difference is to appreciate that translational flow of a linear molecule requires detachment from only one ionic association whereas two detachments are required for star-branched ionomers.

It was also noted with the PIB ionomers that good elastomeric properties occurred only within a narrow range of molecular weights. The lowest molecular weight samples ($\bar{M}_n < 7500$) were stiff and brittle, and the highest molecular weight samples showed excessive flow.[10] These observations are understandable if one considers that ion content and molecular weight are inversely proportional in telechelic ionomers, and in fact, the limitation of telechelic ionomers both from the standpoint of experimental design and physical properties optimization is that it is impossible to change one without changing the other.

These thoughts led to our development of a new kind of telechelic ionomer system,[12] shown in an idealized fashion in Figure 1, which incorporates multiple ionic groups, i.e., an ionic block, at the ends of each polymer chain. The new ionomers are composed of elastomeric inner blocks and ionic outer blocks consisting of sulfonated styrene repeat units. The average number of ionic groups per chain terminus can be chosen at will, and independently of overall molecular weight. In other words, each ionic block is envisioned to behave as a single ionic unit, analogous to a single ion pair in a random or conventional telechelic ionomer. All the ion pairs within a single ionic block are bonded so closely together that they necessarily must participate in the same ionic multiplet; however, the high concentration of ionic matter within each block can produce very high interblock attractions, leading presumably to very large multiplets. In this paper we describe the synthesis and characterization of these ionomers in detail, and we report the effect of overall molecular weight and ionic block length on mechanical and X-ray scattering properties.

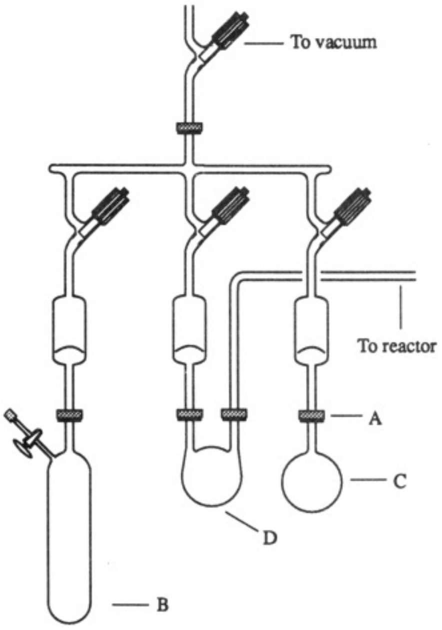

Figure 2. Butadiene purification and storage apparatus.

Experimental Section

Materials. Benzene (J. T. Baker, reagent grade) was stirred over concentrated sulfuric acid for 2 weeks, transferred onto a vacuum line, degassed, and stirred over calcium hydride for a minimum of 1 week. The solvent was then distilled onto sodium dispersion, degassed, and stirred for 3 days. A final distillation followed by stirring over a living styryllithium solution for a minimum of 48 h completed the purification sequence. Butadiene (Aldrich, 99+%) was purified by two different methods. In earlier work butadiene was condensed at −78 °C, transferred to the high-vacuum line, distilled onto calcium hydride, and stirred for 24 h at −20 °C. Distillation was then used to transfer the butadiene onto neat *n*-butyllithium, and the solution was stirred for 1–3 h at −20 °C, after which the purified monomer was distilled and sealed into ampules. To simplify this procedure, in later work a special apparatus, shown in Figure 2, was designed and constructed. Removable flasks and ampules were attached with 28/15 spherical o-ring ball joints, A, composed of Viton o-rings and union-type screw clamps. Butadiene was condensed at −78 °C directly into calibrated ampule B, via a ground-glass stopcock and threaded tubing connection. The butadiene was then transferred by vacuum distillation into flask C, which had been previously charged with a small amount of *n*-butyllithium, and the mixture was stirred for 8–12 h at −30 °C. The purified butadiene monomer was then distilled into storage flask D, which was sealed by closing the Rotoflo stopcock valves. The purified monomer was stored at −100 °C and used within 1 week. *sec*-Butyllithium in cyclohexane (Lithco, 12 wt % solution) was received in ampules and used as received. The concentration of active species, i.e., carbon to metal, was determined by the double-titration method.[13] Methyltrichlorosilane (Aldrich, 97%) was transferred to the vacuum line, degassed three times by freeze–pump–thaw cycles, distilled into a receiving vessel after a generous forecut was discarded, and distilled into calibrated all-glass microampules. Styrene (Aldrich, 99%) was stirred on the vacuum line over freshly ground calcium hydride for 3 days, degassed by freeze–pump–thaw, distilled onto neat dibutylmagnesium, degassed, stirred for 3 days, and placed in ampules. Triethylamine (Aldrich, 99%) was stirred on the vacuum line over finely powdered calcium hydride for 1 week, degassed by freeze–pump–thaw, distilled onto neat *n*-butyllithium, stirred for 1 day, and degassed one additional time before use. Triphenylphosphine (Aldrich, 99%) was recrystallized from diethyl ether and vacuum dried. Rhodium(III) chloride hydrate (Aldrich), hydrogen (Linde, 99.99%), acetic anhydride (J. T. Baker, 99+%), hexanes (Fisher), methyl ethyl ketone (J. T. Baker, 99.6%), methylene chloride (Burdick and Jackson, high purity), potassium hydroxide (Fisher, ACS reagent), sulfuric acid (Fisher, ACS reagent), and tetrahydrofuran (J. T. Baker, HPLC grade) were all used as received.

Polymer Synthesis. Polymerizations and reagent purifications were performed on a high-vacuum line in accordance with standard practices.[14] The general procedure employed for the synthesis of styrene-*b*-butadiene star-branched copolymers was to construct an all-glass reactor fitted with ampules and a magnetic stir bar. The rig was attached to the vacuum line, pumped down, and flamed with a hand torch several times during the course of a 4–6-h period to remove surface moisture. Approximately 500 mL of benzene was distilled into the reactor, followed by the contents of a styrene ampule. An ampule containing a cyclohexane solution of *sec*-butyllithium was added to initiate polymerization. Almost immediately a deep orange color appeared, and a time period of 36 h was allowed for complete formation of the styryl oligomers. At this point triethylamine (TEA), in a quantity equal to 44 times the molar amount of initiator, was distilled directly into the vessel containing the styryl oligomers, causing the solution to turn a very dark red. The reactor was flame-cut from the vacuum line, and an ampule of butadiene was sealed onto the now mobile rig. The butadiene was slowly distilled into the reactor after the breakseals were ruptured, and the temperature of the reactor was maintained at 10 °C to moderate the exotherm. The deep red color of the oligostyrene solution turned to a very pale yellow, and the solution became noticeably more viscous over the course of 24 h. An "arm" sample was taken after flame-cutting the butadiene ampule from the rig, and an ampule containing approximately 80 mol % of the methyltrichlorosilane was released into the reactor to form the three-arm star species. Smaller aliquots of coupling agent were added, if necessary, to maximize the yield of star polymer. In the presence of polar modifier (i.e., TEA), the coupling reactions were usually completed within a few hours at 0 °C.

In recent polymerizations, linking efficiency was improved, and setup time was greatly reduced by limiting the use of all-glass ampules equipped with breakseals in favor of reusable ampules equipped with Teflon Rotoflo stopcocks. The general synthetic procedure described above was modified as follows: A 3-L glass reactor (Figure 3) was constructed and attached to the high-vacuum line at A, via a 28/15 spherical o-ring ball joint, fastened with a union-type clamp, and dried in the usual manner. Approximately 1500 mL of benzene was distilled into the reactor, and an appropriate amount of *sec*-butyllithium was added via syringe through stopcock and septum assembly B. The stopcock was then closed, and the benzene was allowed to stir for 30 min. Styrene monomer was introduced into the reactor by attaching a styrene ampule at C via a 14/20 greased joint, closing valve D, and vacuum distilling the required monomer into calibrated region E. Once the required amount had been collected, the lower stopcock D was opened and the styrene was allowed to drain into the reactor. To ensure that all the styrene reached the reactor, an additional 250 mL of benzene were distilled into the reactor. At this point valve D was closed and the reaction was allowed to proceed for 24 h. Once the styryl oligomers had formed, triethylamine was added, and butadiene was slowly distilled into the reactor by opening valve F. Polymerization was allowed to proceed as previously described. Linking of the polymer arms to form a star-branched polymer was accomplished by titrating the living chain ends with methyltrichlorosilane. This was accomplished in greater than 97% linking efficiency through the use of a specialized ampule G (Figure 3). Once the glass breakseal had been shattered, the coupling agent was metered out by manipulating an internal magnetic valve H with an external magnet. Approximately half of the calculated coupling agent was added initially, with additional aliquots containing approximately 5% of the required coupling agent added every 20–30 min until completion.

Hydrogenation. Hydrogenation of the olefinic unsaturations, by in situ formation of diimide in refluxing toluene, was performed according to the method of Mango and Lenz.[15] A 3:1 molar ratio of *p*-toluenesulfonohydrazide to butadiene repeat units was employed. As a preferred alternative to the diimide method, a catalytic procedure[16] was also used for the hydrogenation of the ionomer precursors. Wilkinson's catalyst, tris(triphenylphosphine)rhodium(I) chloride, was prepared according to the literature procedure.[17] Catalytic hydrogenations were performed in a 316 SS 2-L pressure reactor (Parr Instrument Co.) equipped with a temperature controller and overhead stirrer. A typical procedure for low molecular weight polymers ($\bar{M}_n \leq 30$K) involved dissolving 50 g (<1 mol of butadiene repeat units) of star polymer in 900 mL of 2-butanone, transferring the solution to the pressure vessel, and adding 2 g of the rhodium catalyst. For higher molecular weight polymers, 20–40% of the 2-butanone volume was substituted with hexanes, with more hexanes required for higher molecular weight; for example, a sample with $\bar{M}_n = 120$K was hydrogenated by using 40 vol % hexanes. The reactor was purged with argon for 5 min, assembled, and pressurized to 700 psi with H_2, relieved, and repressurized to 700 psi. Stirring was commenced, and the reaction was conducted for 36 h at 48–50 °C. Workup was accomplished by precipitating the polymer solution into 1000 mL of methanol. When the red solution was decanted off, a gray-white polymer gum remained, occluding some of the spent catalyst. The hydrogenated polymer was dissolved in 500 mL of hexanes and passed through a 5-cm column of basic alumina to remove the residual catalyst.

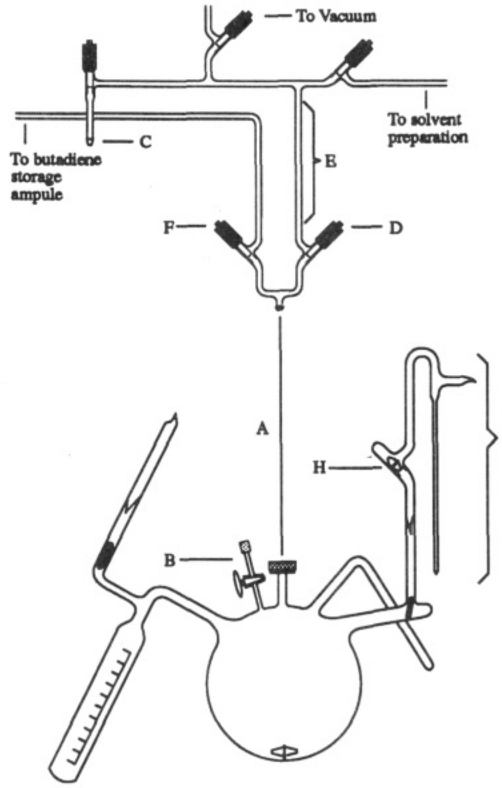

Figure 3. Anionic polymerization reactor and high-vacuum line.

Sulfonation. A modification of the method of Thaler[18] was used for the sulfonation of the outer oligostyrene blocks. The procedure for sulfonation of a polymer with $\bar{M}_n = 15$K (0.78 mmol of styrene units/g of sample) was as follows: To a clean, dry 1000-mL round-bottomed flask equipped with a reflux condenser, nitrogen inlet, and magnetic stir bar were added 8.4 g (82 mmol) of acetic anhydride, 300 mL of CH_2Cl_2, and 8.0 g (81 mmole) of concentrated sulfuric acid. This resulted in a 3-fold molar excess of acetyl sulfate based on moles of styrene repeat units. A solution containing 35 g of polymer in 500 mL of CH_2Cl_2, was slowly added to the flask containing the acetyl sulfate and allowed to react for 12 h at ambient temperature, during which time the solution would sometimes darken. For sulfonation of higher molecular weight polymers, 20–40% of the CH_2Cl_2 volume was substituted with hexanes, with more hexanes used for higher molecular weight; for example, a sample with $\bar{M}_n = 120$K was sulfonated by using 40 vol % hexanes. The sulfonated polymer was recovered by pouring the reaction mixture into boiling water, thus flashing off the solvents and yielding light-yellow to white crumbs. The moist crumbs were freed of residual

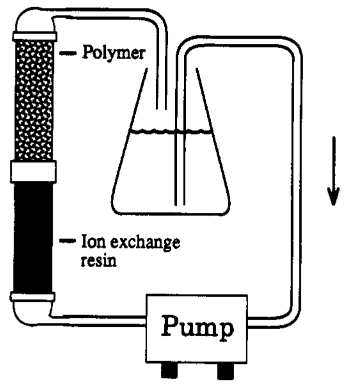

Figure 4. Cold-water extraction apparatus for purification of sulfonated polymers.

acids by extracting with warm water for 36 h in a Soxhlet apparatus; extraction was facilitated by adding one small pellet of KOH and 1–2 vol % absolute ethanol to the distilling flask. In later work, cold-water extraction was carried out using the apparatus shown in Figure 4. It consisted of two 50 mm × 2 ft chromatography columns (Ace Glass) stacked vertically in series with a small pump, forming a closed loop through which was circulated deionized water. The lower column was packed with a weakly basic ion-exchange resin (Rohm and Haas, Amberlyst A-21), and the upper column was charged with the sulfonated polymer crumbs. By circulating water continuously through the columns, excess acids were removed from the polymer and retained by the basic column. The purified crumbs were observed to be somewhat thermally and/or oxidatively unstable in the free-acid form (discoloration would often occur upon exposure to elevated temperatures or upon standing in air for prolonged periods at room temperature) and were thus stored in a sealed container at −10 °C until neutralization.

Neutralization. Determination of the extent of sulfonation was accomplished by titrating a small quantity of polymer with ethanolic KOH. A typical procedure was as follows: To a tared 250-mL Erlenmeyer flask containing a magnetic stir bar were charged 2 g of wet, sulfonated polymer crumbs, 150 mL of THF, and several drops of 0.25% (w/v in methanol) Phloxine B indicator solution. The mixture was purged with nitrogen for several minutes and titrated with 0.05 N KOH in ethanol to the characteristic orange-pink end point. Standardization of the KOH solution was performed with a 0.1 N solution of potassium biphthalate. The equivalents of sulfonic acid per gram of polymer was then determined by evaporating off most of the THF/ethanol and vacuum-drying the flask at 50 °C until constant mass was reached. Large-scale neutralizations of the sulfonic acid precursors were performed in the following manner: To a 2000-mL Erlenmeyer flask fitted with a magnetic stir bar were charged 50 g of wet crumbs, 1000 mL of THF, and 1 mL of the Phloxine B indicator solution. About 90–95% of the required amount of titrant, estimated from the results of the analytical titration, was rapidly added, and the resulting mixture was titrated to the end point. With this procedure, either alkali metal or quaternary ammonium counterions could be obtained by the addition of an ethanolic solution of the appropriate hydroxide. Removal of the solvent was accomplished by gentle heating under bubbling nitrogen, followed by drying in vacuo for 24 h at 50 °C. The above procedure can also be performed using phenolphthalein indicator, but the accuracy is less since the color change is less apparent than that obtained with Phloxine B.

Molecular Weight and Structural Characterization. Number-average molecular weights, $\bar{M}_n$, were determined for poly(styrene-*b*-butadiene) arm samples with a Knauer No. 11.00 vapor pressure osmometer using toluene at 40 °C. Calibration solutions of benzil or biphenyl were prepared over a concentration range of 2–8 g/kg in HPLC grade (99.9+%) toluene, and polymer solutions were prepared over a concentration range of 20–140 g/kg. All readings were taken after a 4-min equilibration period.

Gel permeation chromatography (GPC) data were obtained with use of a Waters Associates system equipped with a Rheodyne injector, Model 6000A solvent delivery module, four Ultrastyragel columns of nominal pore sizes 100, 500, 10^3, and 10^4 Å connected in series, and a Model 410 differential refractometer detector. THF, freshly distilled from calcium hydride, served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. The sample concentrations were approximately 0.25% (w/w) in THF, with an injection volume of 50 μL. Polystyrene standards (Polysciences Corp.) were used for calibration.

Room-temperature ^1H and ^{13}C NMR spectra were recorded with a Bruker AC-300 spectrometer. The spectra of polymers were obtained by using 5–10% (w/w) $CDCl_3$ solutions and are reported with respect to an internal reference (0 ppm) of TMS.

Small-Angle X-ray Scattering. Small-angle X-ray scattering (SAXS) was carried out with an Anton-Parr Kratky camera equipped with a Braun position-sensitive detector (PSD) from Innovative Technology Inc. A Philips 1729 table-top X-ray generator with a copper-target fine-focus tube was used to provide the incident X-ray radiation. The operating conditions were fixed at 40 kV and 20 mA. A lupolen standard sample was used to facilitate the calculation of absolute scattering intensity. SAXS profiles were obtained by use of compression molded films of 250–750-μm thickness.

Film Preparation. Ionomer films were compression molded between Teflon sheets in a Dake press for 20 min at 120 °C and 20 000 psi. For ion contents above 8 mol %, a temperature of 150 °C was employed.

Samples with ionic contents of <3 mol % were solvent castable by filling a polyethylene mold with a 20% solution of the ionomer in toluene/methanol (90/10, w/w). The solvents were allowed to slowly evaporate over the course of several days, followed by careful vacuum-drying, first at ambient temperature and 380 Torr for 24 h, and then at 70 °C and 380 Torr for 36 h.

Mechanical Characterization. Dynamical mechanical analysis (DMA) studies were performed with a Rheometrics RMS-800 dynamic mechanical spectrometer fitted with a 25-mm parallel plate fixture, 2000 g·cm transducer, and cryogenic capability. The rheometer was interfaced to a Recap II data station. Compression-molded sample disks (1 mm × 25 mm diameter) were softened to ensure proper mounting and relieve residual stresses. Temperature scans were performed at a frequency of 1 Hz and data points were taken in 10 °C increments.

Tensile properties were obtained with an Instron Model 1122 tensile tester fitted with a 5 kg load cell. Film thicknesses were in the 1.2–1.8-mm range, and all measurements were conducted at room temperature. The cross-head speed was 5 cm/min, which corresponded to a constant elongation rate of approximately 225%/min with a gauge length of 22 mm. The chart speed was 5 cm/min and the full-scale maximum loading was 2000 g.

Results and Discussion

Synthesis and Structural Characterization. The basic synthetic strategy used to prepare the block copolymer ionomers was to first prepare, using living anionic polymerization, an ionomer precursor molecule that incorporated the desired star-branching geometry and was composed of arms consisting of butadiene-based elastomeric inner blocks and short oligostyryl outer blocks. Then, appropriate postpolymerization reactions were conducted, i.e., hydrogenation of the inner blocks followed by sulfonation of the outer blocks, leading to the desired regiospecific placement of the sulfonic acid functional groups. The synthesis scheme leading to the formation of the three-arm star, block copolymer precursor is shown in Figure 5. The star-branched molecules were assembled from the outside inward by use of a central linking moiety. The first step of the synthesis was the formation of a short oligostyrene outer block, which ultimately becomes the ionic block after sulfonation. For initial studies the outer block was arbitrarily chosen to be, on average, a tetramer, both to maintain compactness of the outer ionic block and to ensure that every chain end would contain multiple sites for sulfonation. The outer block oligomerization was generally conducted at room temperature for convenience; however, we were concerned about the distribution of the

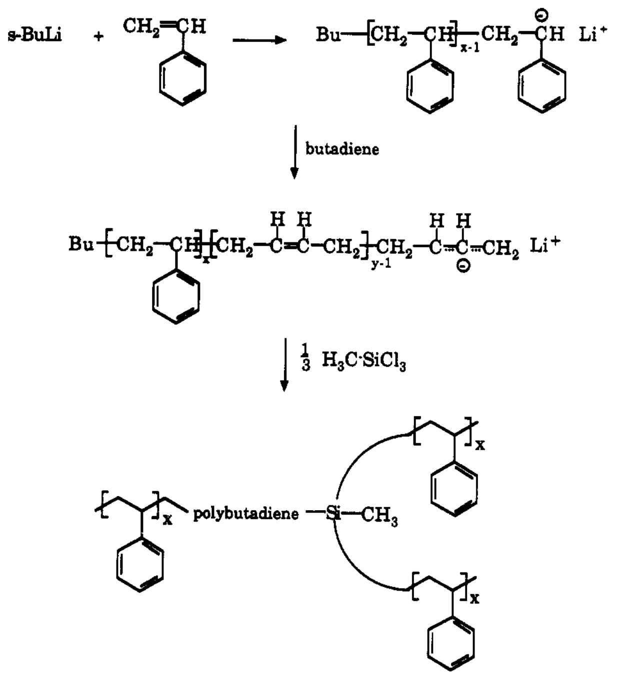

Figure 5. Synthesis scheme for three-arm star block copolymer ionomer precursor.

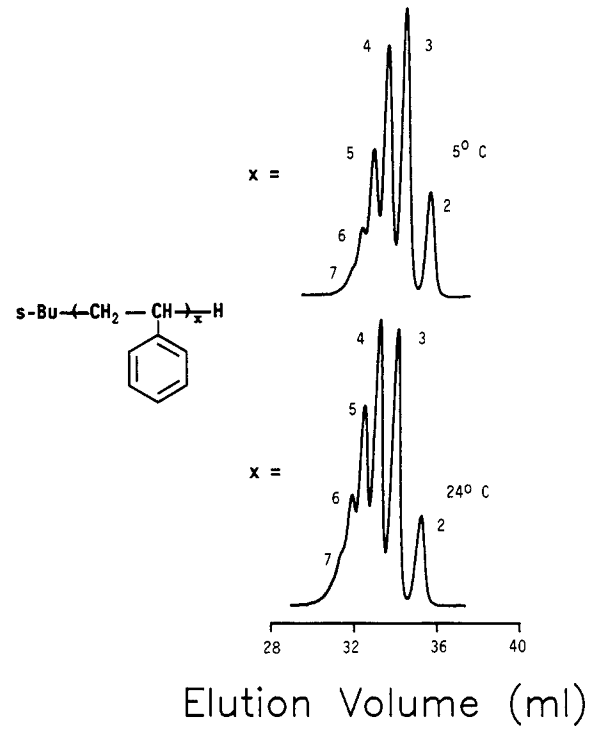

Figure 6. GPC chromatograms of oligostyrene outer blocks synthesized at two temperatures.

degree of polymerization in this short block, and thus on one occasion the oligomerization was conducted both at room temperature and at 5 °C, and the oligomers were terminated and analyzed by GPC. The results are shown in Figure 6. The identities of the peaks were assigned by running an authentic sample of phenylhexane, representing the monomer–butyllithium adduct, and a commercial standard of styryl hexamer (Polysciences, Inc.). In both cases a distribution of species ranging from dimers to heptamers was formed, and the temperature appeared to have very little effect on the distribution of species. Estimation of the number ($\bar{X}_n$) and weight-average degrees of polymerization ($\bar{X}_w$) using peak heights revealed that in both cases the polydispersity index was 1.1, although $\bar{X}_n$ for the 5 °C oligomerization was slightly lower (3.5 compared to 3.7 for the 24 °C oligomerization), indicating that the conversion of monomer was lower at the lower temperature in spite of a purposefully longer reaction time. In neither case was phenylhexane, i.e., the species representing degree of polymerization equal to 1, observed in any significant amount; therefore it is reasonable to assume that all of the *sec*-butyllithium reacted with monomer to form at least dimeric species and that all of the block copolymer arms would have at least two styrene repeat units.

A series of three-arm star polymers of various molecular weights were synthesized, and molecular weight data are listed in Table I. Actual molecular weights were determined for many of the polymers by performing vapor pressure osmometry (VPO) measurements on arm samples isolated prior to linking; however, the values reported in Table I have been multiplied by 3 to reflect the expected molecular weight after linking. It can be seen in the table that measured molecular weights are in quite excellent agreement with molecular weights calculated from the stoichiometry of the polymerizations. Within this first series of polymers, the outer block length for all samples was held nominally to an average of four styryl units. The one exception was sample 16.4-8, which possessed an average of eight units per outer block.

Table I
Molecular Weight and Inner Block Microstructure of Three-Arm Star Block Copolymers

sample	$\bar{M}_n$ stoichiometry	$\bar{M}_n$ VPO[a]	microstructure, mol % 1,2	microstructure, mol % 1,4	theor ion content, mol %
18.2-4	18 200		8	92	
10.0-4	10 000	9 300	38	62	4.4
15.0-4	15 000		42	58	2.9
15.1-4	15 100	16 000	41	59	2.9
18.0-4	18 000		43	57	2.4
23.7-4	23 700	21 400	42	58	1.8
29.9-4	29 900	33 500	43	57	1.4
30.3-4	30 300	32 800	41	59	1.4
16.4-8	16 400	16 700	40	60	5.5
120-4	120 000		43	57	0.35

[a] VPO was performed on arm samples; values in Table I have been multiplied by 3 to reflect expected molecular weight.

The sample identification scheme used in Table I and throughout the remainder of the paper is best described by example: 15.1-4 refers to an ionomer precursor sample (a sample at any stage prior to sulfonation) with a stoichiometric molecular weight of 15 100 and styryl outer blocks that are on average four units long. Once a sample has been sulfonated, a suffix is attached to the above designation to indicate the identity of the counterion; for example, 15.1-4-H and 15.1-4-K would be the free sulfonic acid and potassium-neutralized versions of the above sample. In all cases, sulfonations were carried out exhaustively, i.e., with the intent of sulfonating every available phenyl ring in the outer blocks, and neutralizations were carried out with an exact stoichiometric quantity of base. To obtain the theoretical mole fraction of ionic groups contained in the samples after sulfonation and neutralization, i.e., the fraction of total monomer units that carry an ionic group, it was necessary to calculate the mole ratios of ethylene and butylene residues that would be obtained in the polymers after hydrogenation. All of the polymers listed in Table I, except for the control sample 18.2-4, contained ~40 mol % 1,2-addition units. Thus, for every 10 units of butadiene incorporated, 6 were enchained as 1,4-additions and 4 as 1,2-additions; after hydrogenation this yielded a total of 2 × 6 = 12 ethylene

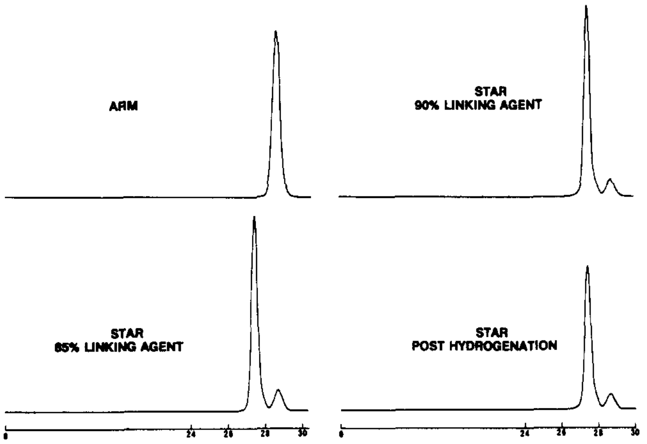

Figure 7. GPC chromatograms that monitor the course of silane linking reaction.

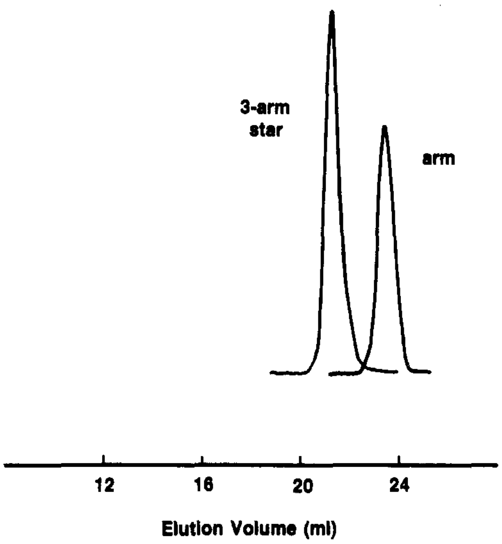

Figure 8. GPC chromatograms of arm and star polymer samples after fractionation of star polymer to remove unlinked arm.

units and 4 butylene units. Theoretically, then, one obtained a combined total of 16 hydrogenated monomer units, from every 10 butadiene units, and this was taken into account during calculation of the mole fraction of ionic groups in each sample, listed in Table I.

Typical GPC results, which monitor the course of the linking reaction, are shown in Figure 7. Consistent with living anionic polymerization, molecular weight distributions for arm samples were always very narrow (≤1.05), and the linked polymer had an elution volume corresponding to a molecular weight approximately 3 times that of the arm. Our goal for the linking reaction was to achieve linking of no less than 90% of the arms. In the event that more than 10% of the arms remained unlinked, fractionation to remove the arms was in some cases performed using a toluene/methanol solvent system. As shown in Figure 8, this could in fact be used to produce virtually pure three-arm star polymers. However, we found that use of this solvent/nonsolvent system resulted in significant losses of product, and thus to achieve the target and avoid fractionation, we found that a successful approach was to initially add an ampule containing ~85% of the theoretical amount of linking agent and then analyze the progress of linking by GPC (Figure 7), thereby arriving at a more accurate estimate of the remaining amount of linker required. To facilitate the procedure, the glass reactor was preequipped with a selection of linker ampules of varying size, e.g., 5, 10, and 15% of the theoretically required linking agent, so that whatever the required amount of linker, an appropriate ampule was available.

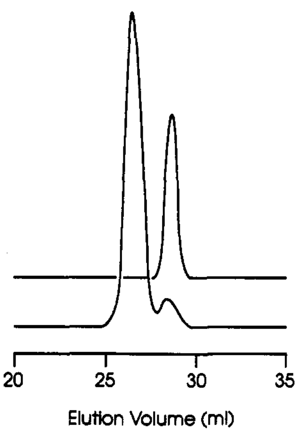

Figure 9. GPC chromatograms of arm (background) and three-arm star (foreground) block copolymers synthesized by using metered addition of linking agent.

To further refine our linking procedure and improve linking efficiency, we designed a new type of ampule, G (Figure 3), for addition of the linking agent. The linking reaction was initiated by breaking the glass breakseal, and the rate of addition and amount of linking agent added was controlled by manipulating the internal, magnetic valve H with a handheld magnet. In practice, approximately 50% of the theoretically required linking agent was distilled into the reactor and allowed to react for ~1 h. At this point small aliquots, usually ~5% of the required linking agent, were allowed to distill into the reactor every 15–20 min and the progress of the reaction was occasionally checked by removing a sample for GPC analysis. This procedure was designed to achieve, in effect, a titration of the living arms with linking agent, leading to a high yield of three-arm star, with only minimal amounts of unreacted arm left at completion. Greater than 97% linking efficiency has been achieved with this procedure, as demonstrated by the GPC trace of sample 120-4 after linking, shown in Figure 9.

To complete the ionomer synthesis, a postpolymerization reaction sequence was applied to the precursor molecules, as outlined in Figure 10. Before the actual sulfonation reaction, the polymers were hydrogenated to render the inner block inert toward sulfonation. It was recognized early that control of the polybutadiene microstructure was essential to obtain desired properties. When polybutadiene containing low amounts of side vinyl (<10 mol %) units is hydrogenated, a partially crystalline material resembling high-density polyethylene (HDPE) is obtained. Although an interesting and potentially useful class of materials could be generated, it was nevertheless the intent of this work to synthesize ionomers that were essentially amorphous materials of low T_g; therefore, the amount of 1,2-addition was a parameter to be optimized. The effect of 1,2-addition content on the crystallinity and T_g of hydrogenated polybutadiene has been reported by Gergen,[19] and from this reference an optimum value of 40 mol % 1,2-addition units was selected. At this level of 1,2-addition, predicted crystallinity would be less than 10% and the T_g would remain below −50 °C.

Temperature and incorporation of polar modifiers have been demonstrated to have a profound effect upon the side-vinyl content of polybutadiene.[20,21] Numerous bases can be employed to vary the 1,2-content from approximately 10 to 99+ mol %. We have found that incorporating triethylamine at a molar ratio to initiator of 44:1, and conducting the reaction at 10 °C yields approximately

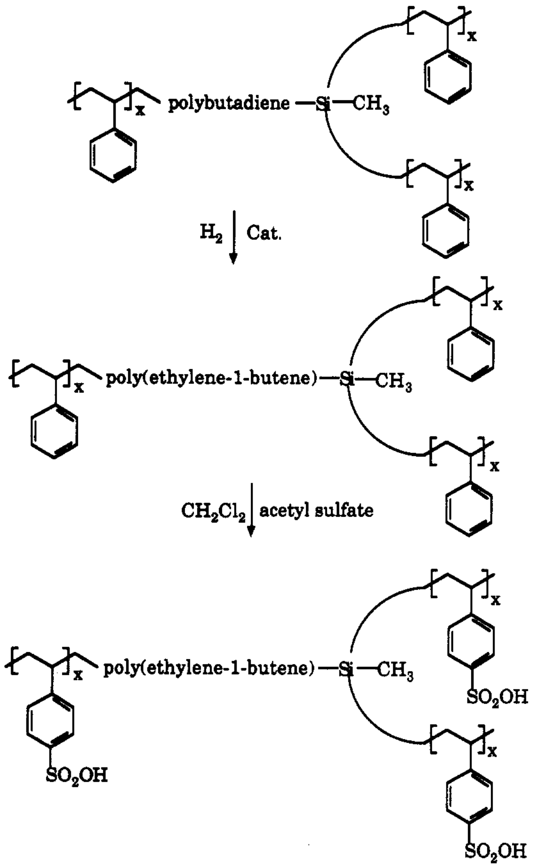

Figure 10. Postpolymerization reaction sequence used to complete the synthesis of block copolymer ionomers.

40% 1,2 addition. Analysis of 1,2- vs 1,4-addition content was accomplished using ^{13}C NMR and a recently described procedure,[22] and the data are listed in Table I. A control sample, 18.2-4, was made at 24 °C without using the polar modifier.

Hydrogenation of the unsaturated inner blocks was performed on some early samples using diimide,[15] but all later samples have been hydrogenated catalytically by using Wilkinson's catalyst.[16] The catalytic method using tris(triphenylphosphine)rhodium(I) chloride is clearly the superior method; the workup is much simpler, and it does not produce the low level of cross-linking that is a persistent problem with the diimide method.

To obtain elastomeric inner blocks free of sulfonate groups, it was necessary to have essentially 100% hydrogenation. Effectiveness of the hydrogenation reaction was judged by comparison of the ^{1}H NMR spectra of the unsaturated and hydrogenated species, shown in Figure 11. The resonances between 4.8 and 5.7 ppm due to the olefinic hydrogens have been completely eliminated from the spectrum of the hydrogenated polymer. Confirming evidence comes from the ^{13}C NMR spectra compared in Figure 12. Virtually all of the peaks between 110 and 150 ppm have disappeared with the exception of the aromatic resonances centered around 130 ppm, which are due to the oligostyryl outer blocks. On the strength of this evidence it was concluded that the desired level of hydrogenation had been achieved.

Upon hydrogenation, the clear liquid polymers did not exhibit any pronounced physical changes except for a slight darkening of color and an increase in viscosity. However, sample 18.2-4, containing only 8 mol % side-vinyl units, exhibited a distinct change in morphology upon hydrogenation, from a clear liquid to a waxy solid. As reported in an earlier paper,[12] DSC analysis of this particular sample revealed a sharp melting transition at 95 °C, with a peak area consistent with ~63% crystallinity compared to 100% crystalline HDPE.

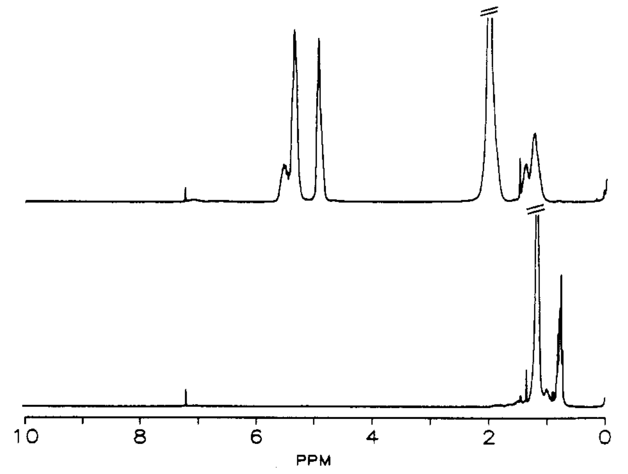

Figure 11. ^{1}H NMR spectra of (upper) unsaturated and (lower) hydrogenated ionomer precursors.

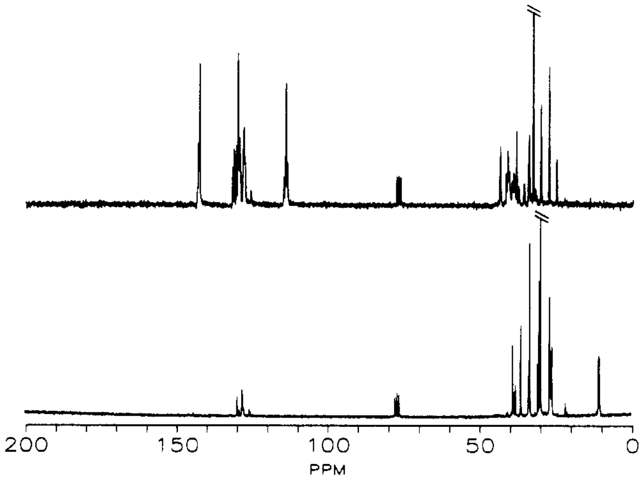

Figure 12. ^{13}C NMR spectra of (upper) unsaturated and (lower) hydrogenated ionomer precursors.

Sulfonation of styrene-*b*-(ethylene-*co*-1-butene) copolymers was performed using homogeneous methylene chloride/hexanes solutions at room temperature, and using 3 mol of acetyl sulfate/mol of styrene repeat units. During sulfonation, the solution would often darken, and this seems to be a function of the effectiveness of removal of the catalyst after hydrogenation, since highly purified polymers did not darken. Routine acid–base titration of the recovered sulfonated polymers revealed that the white, crumblike materials were generally contaminated with unbound acidic impurities, i.e., acetic and sulfuric acids. It was necessary to remove these contaminants since they interfere with determination of percent sulfonation, may decrease the thermal stability of the unneutralized product, and may weaken properties by having a disruptive effect on the associating chain ends. Purification of the sulfonated polymer was accomplished by continuous warm-water extraction in a Soxhlet apparatus or preferably by cold-water extraction using the apparatus pictured in Figure 4. During extraction, samples were taken periodically for titration. The results, shown in Table II, reveal that a sample containing a four-unit outer block requires ~24-h extraction time to yield a constant titration value, while a sample with an eight-unit outer block takes nearly 48 h to be purified. Although the eight-unit outer block sample occluded nearly twice as much unbound acid as the four-unit outer block sample, both samples settled to

Table II
Acid Contents of Sulfonated Three-Arm Star Block Copolymers as a Function of Continuous Warm-Water Extraction Time

sample	*extractn* time, h	mequiv H^+/g	% styrene units sulfonated (theor)
18.0-4	0	0.726	113
	24	0.585	91
	48	0.596	93
	72	0.559	87
16.4-8	0	2.871	207
	24	1.563	112
	48	1.217	88
	72	1.215	88

a constant value of ~90% of the styrene units sulfonated, based upon polymerization stoichiometry. It may in fact be the case that sulfonation did occur at every aromatic ring, but that the number of styryl units was slightly less than theoretical due to incomplete oligomerization of the styrene. It will be recalled that under the conditions typically employed for the oligomerization, GPC analysis of the product in one case showed an average degree of polymerization of 3.7 compared to a value of 4 expected theoretically from the stoichiometry. In any event, we may be reasonably certain that the sulfonation is nearly quantitative, and that the ionic groups are blocked tightly at the ends of the chains.

Mechanical Characterization. Of the various samples listed in Table I, the earliest synthesized samples were those in the molecular weight range $10K \leq \bar{M}_n \leq 18K$. In a strictly subjective, qualitative sense, the lower molecular weight samples appear weak and brittle with marginal elastomeric extensibility. In fact, they are reminiscent of highly swollen gellike polymers, suggesting that the ionic associations may impose severe conformational demands on the chain; i.e., they cause chain expansion, which for low molecular weight materials such as these might produce chains so perturbed that their capacity for further rubberlike uncoiling is strictly limited. Such a scenario would be expected to lead to weak, brittle networks, much like those actually observed. However, as will be seen, increasing the molecular weight to 120K substantially increases the strength and elongation of the ionomer, and materials in this range exhibit quite respectable elastomeric properties.

Engineering stress vs strain data were obtained in a series of experiments examining the effects of molecular weight, counterion, and partial crystallinity. The profound effect of a crystalline vs an amorphous backbone, i.e., amount of 1,2-addition, is illustrated in Figure 13. The two samples are of essentially the same molecular weight and ion content; however, the crystalline sample behaves like a rigid plastic, displaying a high modulus and strength and low elongation, while the amorphous sample displays a low modulus and an elongation of over 200%.

The effect of increasing the length of the ionic outer block at similar inner block molecular weight is shown in Figure 14. It may be seen that the four-unit sample yields a stress–strain curve that is reasonably characteristic of an elastomer, consisting of an initial elastic response followed by a region of viscoelastic response, and then finally rupture when, apparently, the network chains reach their full extent of uncoiling. It should be noted that the strain at break for this sample, i.e., slightly less than 2, is not particularly large, implying that the network chains were already expanded somewhat at zero strain. It is unclear whether the aforementioned viscoelastic response consists of relaxation of entanglements within the rubbery chains of the inner blocks, or whether it consists of migration of individual ionic blocks from one ionic domain to another, i.e., so-called "ion hopping."

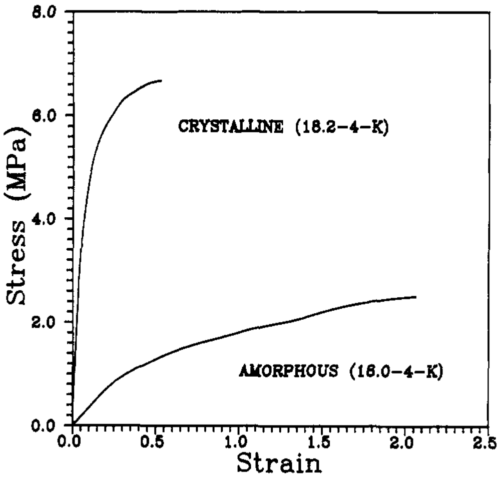

Figure 13. Stress vs strain curves of star-branched block copolymer ionomers comparing amorphous and semicrystalline inner blocks.

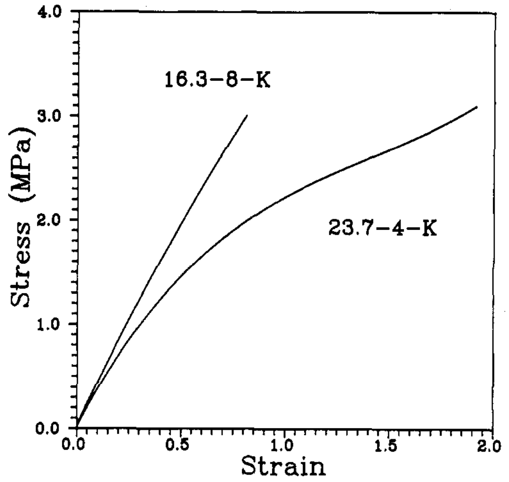

Figure 14. Effect on static mechanical properties of increasing the length of the ionic outer block at similar inner block molecular weight.

Now, in contrast, the stress–strain behavior of sample 16.3-8-K in Figure 14 is almost completely elastic up to the point of rupture at a strain of ~0.8. There is virtually no viscoelastic response in this sample, implying that the network chains at zero strain already existed in quite extended conformations, and that only a small amount of additional strain was necessary to bring the chains to their fully extended, elastic limit. As well, it is also reasonable to assume that an ionic block consisting of eight ion pairs would experience a much stronger energy barrier than a four-unit block, when, in the process of ion hopping, it must detach itself from its ionic domain and enter the hydrocarbon environment between domains.

As shown in Figure 15, increasing the length of the inner block while holding the outer block length constant at four units causes a transformation from an almost totally elastic, brittle, gellike material (10.0-4-K) to a comparatively strong elastomer with an ultimate elongation of nearly 600% (120-4-K). This latter sample, with strength at break of nearly 7 MPa, is clearly in a different class from the other materials. It is in fact remarkable that such a sample, containing only 0.35 mol % ionic groups, can exhibit such toughness and strength.

It should also be mentioned here that sample 120-4-K, in spite of its much higher molecular weight, was observed

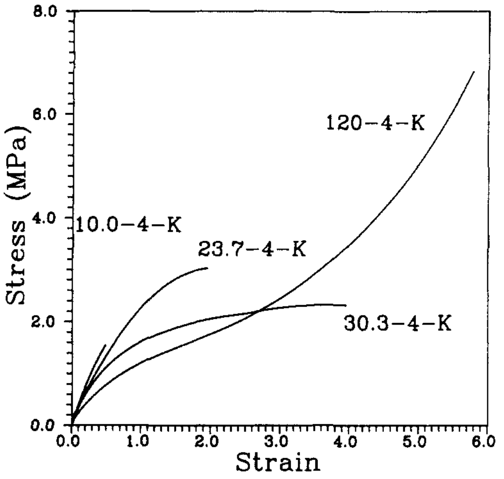

Figure 15. Effect on static mechanical properties of increasing the length of the inner, elastomeric block at constant outer block length of four ionic groups.

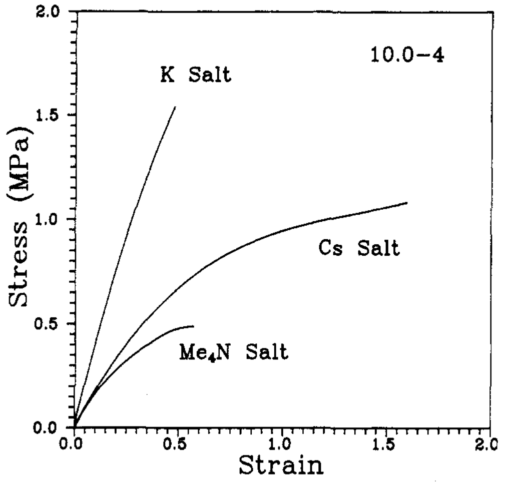

Figure 16. Effect on static mechanical properties of different counterions.

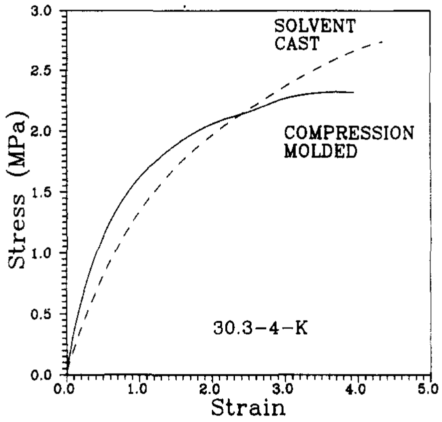

Figure 17. Effect on static mechanical properties of mode of film preparation. Solvent cast (dotted line); compression molded (solid line).

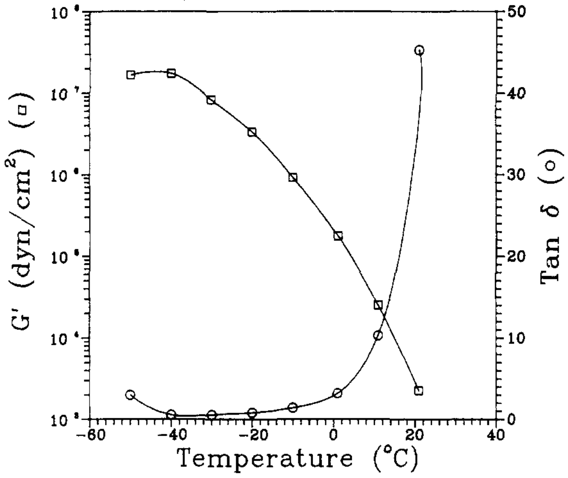

Figure 18. DMA of hydrogenated star-branched block copolymer ionomer precursor, sample 15.1-4.

to be much more easily melt processed and much more soluble than ionomers of lower molecular weight. The lower molecular weight samples in the series are highly ionic, and apparently the aggregational forces are so high that a large amount of energy is needed to disrupt them. Yet, because the hydrocarbon chains between aggregates are so short, and probably highly perturbed, the materials are brittle rather than strong and tough. It remains to be seen what the optimum combination is, with regard to properties and processibility, of outer ionic block length and inner elastic block length for ionomers within this family.

Counterion effects are also marked in these systems, as shown in Figure 16. A large, i.e., soft, counterion such as cesium forms weaker attractions, resulting in materials having higher elongations and lower strengths. Smaller, harder counterions like potassium, due to their greater charge density, form stronger associations, leading to higher strengths and lower elongations.

Since the morphology, and hence the mechanical properties, of ionomers can be greatly affected by the mode of sample preparation, the static mechanical properties of a compression-molded sample of number-average molecular weight 33K are compared, in Figure 17, to the same ionomer that was solution cast. It may be seen that the solution-cast sample displays a lower modulus and slightly higher tensile strength; however, the difference is less dramatic than that observed upon changing the conditions under which the sample is compression molded. In general, properties are improved by higher temperatures and longer molding times so long as thermal and/or oxidative degradation of the sample are avoided.

Dynamic mechanical analysis was performed on selected ionomer samples. First to be examined, however, was an unsulfonated, hydrogenated precursor, 15.1-4. The DMA temperature scan at 1 Hz, illustrated in Figure 18, shows behavior typical of a viscous liquid. A T_g is observed near -50 °C and the storage modulus falls essentially to zero beyond room temperature. The high tan δ is also indicative of the dominance of the viscous (loss) component.

The ionomer spectra are shown in Figures 19 and 20 for samples 10.0-4-K and 18.0-4-K, respectively. The data were taken at 1 Hz over the temperature range starting just after the primary transition (T_g) of the hydrocarbon inner blocks, up to $\sim$250 °C, at which temperature the sample had begun to flow out from between the parallel plates. Comparison of the storage moduli, G', shows a divergence in behavior between the two samples within the rubbery plateau region. Sample 10.0-4-K, with the higher ion content and shorter network chains, displays a slight, gradual increase in modulus from 0 to 100 °C and thereafter a broad decrease in the modulus associated with a gradual decrease in the strength of the ionic aggregations. The increase in modulus with temperature suggests that this sample was in a nonequilibrium state, and apparently a reorganization of the ionic aggregates occurs as the temperature is raised. It also suggests that our compression-molding procedure failed, at least for this lowest molecular

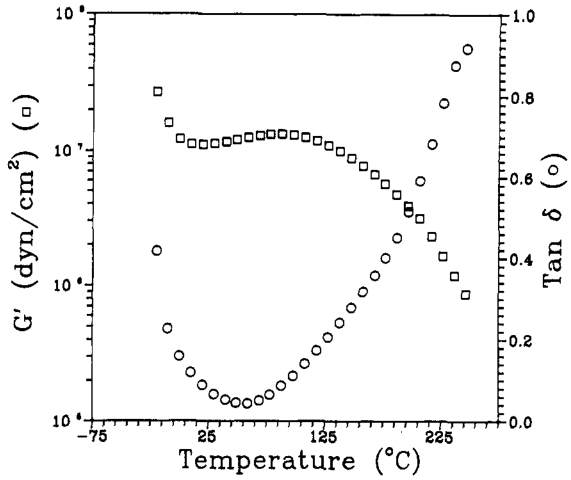

Figure 19. DMA of star-block copolymer ionomer, sample 10.0-4-K.

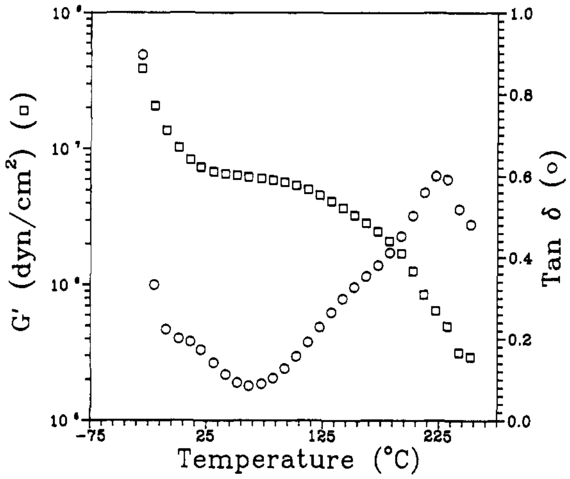

Figure 20. DMA of star-block copolymer ionomer, sample 18.0-4-K.

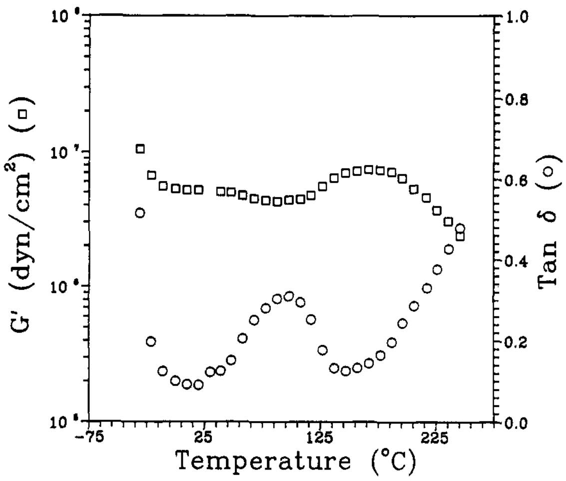

Figure 21. DMA of star-block copolymer ionomer, sample 16.3-8-K.

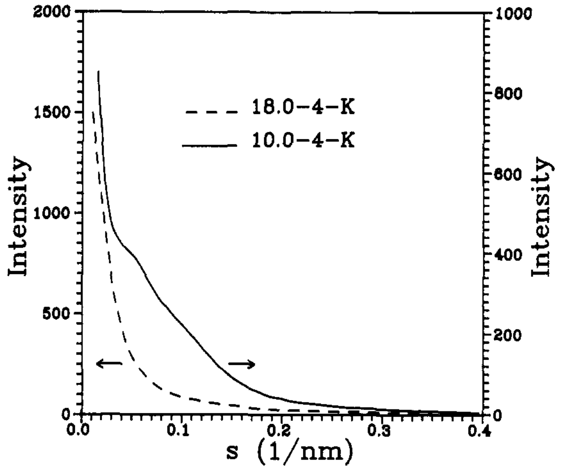

Figure 22. SAXS spectra of star-block copolymer ionomers. Sample 10.0-4-K (dotted line); sample 18.0-4-K (solid line).

weight sample, to bring about complete flow and organization of the network. In comparison, the higher molecular weight sample, 18.0-4-K, does not show an increase in modulus in the plateau region and displays a significantly lower modulus over the entire temperature range to 250 °C. Comparison of the dynamic loss, as tan δ, shows a peak for either sample in the region of disruption of the ionic aggregates. For sample 10.0-4-K the tan δ is near 1.0 and still increasing at 250 °C, but it appears to be nearly at its maximum at this temperature. In comparison, sample 18.0-4-K displays a peak maximum at ~225 °C with a value of 0.6. The lower tan δ for the higher molecular weight sample may indicate greater retention of elastic behavior at high temperatures due to chain entanglements.

The DMA results for sample 16.4-8-K, which possesses ionic blocks carrying an average of eight ion pairs, are presented in Figure 21. The storage modulus, G′, shows the usual rubbery plateau extending to ~100 °C. However, for this sample it is followed by a second, higher plateau region from 120 to 200 °C, and then a gradual decrease. A prominent peak located in the tan δ curve, centered at 100 °C, corresponds to the onset of the second plateau and indicates that a major reforming or rearrangement of the ionic aggregates must have occurred.

Small-Angle X-ray Scattering (SAXS). SAXS was performed on samples 10.0-4-K and 18.0-4-K to yield information about the preferred spacing between ionic aggregates. As shown in Figure 22, sample 18.0-4-K shows no discernible peak other than a strong upturn as the zero angle is approached. This implies that the ionic aggregates are in the form of widely spaced multiplets with intermultiplet spacings much larger than those typically associated with clustering. The zero-angle upturn, seen for most ionomers, has been proposed recently[23,24] to be due to inhomogeneities in the distribution of multiplets and/or isolated ion pairs within the sample. Sample 10.0-4-K shows a weak scattering peak at approximately 0.05 nm^{-1}, which appears as a shoulder to the zero-angle upturn. This yields an estimate of 2×10^2 Å as a preferred spacing between multiplets, which is a considerably larger value than is normally observed for linear, telechelic (two-arm star) ionomers with approximately the same arm molecular weight.[25] Such a large spacing predicts that the multiplets must be very large and composed of a very large number of chain ends per multiplet.

Conclusions

This paper outlines the development of a new family of ionomers of well-defined structure, which incorporates multiple ionic groups (i.e. an ionic block) at the ends of each polymer chain and which is unique in terms of the number of structural parameters that can be varied systematically. The basic synthetic strategy consists of creating block copolymer arms by sequential comonomer addition, which comprise first a short ionic precursor block and then a longer elastomeric block. These living arms are then reacted with a linker compound at the elastomeric ends to produce the desired ionomer precursor molecule. Subsequent postpolymerization reactions, including exhaustive sulfonation and neutralization of the short, outer blocks, completes the synthesis. By use of the basic synthetic scheme described, star-branched ionomers of near-monodisperse molecular weight distribution, consisting of any desired number of arms including one, two (linear telechelic), or three, can be synthesized with any desired molecular weight. In addition, the overall ion content can be chosen independently of all other parameters.

Subjectively, two general properties of the ionomers, manifest at lower molecular weights, their general insolubility and intractability and their poor mechanical properties, taken together with the quantitative measure of intermultiplet spacing obtained from SAXS, suggest a bulk morphology dominated by very large multiplets, spaced widely apart. Clearly, if the two SAXS spectra presented are considered to constitute a trend, i.e., the position of the scattering park (the shoulder in the spectrum of sample 10.0-4-K) moves to lower scattering angle with increasing molecular weight, and is quickly lost in the zero-angle upturn, then the results are qualitatively in harmony with results obtained for carboxy-terminated linear, telechelic ionomers.[25] However, the absolute magnitude of the intermultiplet spacing is much larger for the present ionomers, to the degree that one is lead to speculate how the molecules can possibly span the distances between multiplets. A random walk calculation performed on the sum of two arms of sample 10.0-4-K, which considers fixed tetrahedral bond angles but for simplicity assumes completely free rotation, yields a root mean square end-to-end distance of 4 nm, which is significantly smaller than the SAXS-derived spacing of 20 nm. In view of this, one suspects that there might be a high incidence of looping, i.e., the situation in which two or three arms of the same molecule incorporate into the same multiplet, and this would be expected to detract materially from network strength. If a molecule must span the distance between domains, this may require considerable chain expansion to the point that the capacity for further rubberlike uncoiling is strictly limited. Such a scenario would be expected to lead to a weak, brittle network, much like what is actually observed. Since we strongly suspect that multiplets are composed of a very large number of chain ends, perhaps on the order of 10^3, it may prove that the central core of the multiplet contains a greater proportion of looped chains (implying that these "multiplets" contain hydrocarbon) and that the ionic blocks of spanning chains pack into the outer radius of the large multiplet, thereby decreasing the effective span distance.

Clearly, more data must be gathered to begin to understand the apparently complex morphology of these ionomers. An obvious need is to examine the mechanical and SAXS properties of the linear (two-arm star) analogues of the star ionomers. In addition, the effect of altering the length of the ionic outer block, from one ion pair to many, should be examined. These matters will be the subject of our future investigations.

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