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Comparison of the Physical Properties of Carboxylated and Sulfonated Model Polyurethane Ionomers

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ABSTRACT: A series of carboxylated and sulfonated model polyurethane ionomers based on tolylene diisocyanate and three polyols is investigated to determine the influence of pendant anion type on physical properties. Tensile testing results demonstrate that sulfonated ionomers give higher tensile strengths than carboxylated ionomers, as expected based on arguments of the higher acid strength of the sulfonate groups. DSC and DMTA results confirm the model ionomers based on 1000 molecular weight soft segments are more phase separated in the sulfonated than in the carboxylated ionomers. However, the surprisingly high Young's moduli for the carboxylated ionomers illustrates the dependence of ionomer properties on the morphology of the sample. DMTA results indicate a higher cross-linking efficiency in the carboxylated ionomers, corresponding to their larger ionic aggregate sizes, which counterbalances the lower acid strength of the carboxylate groups to give higher than expected moduli. The moduli of all ionomers investigated are significantly higher than predicted on the basis of ionic aggregates acting as cross-links and fillers. The modulus enhancement is attributed to entanglements formed in the process of ionic aggregation.

Introduction

The solid-state structure and properties of ionomers, polymers containing a small fraction of ionic repeat units, have been the subject of numerous papers and reviews.[1-6] As it has long been recognized that the aggregation of the ionic groups into microdomains, forming physical cross-links, gives rise to many of the unique properties of ionomers, extensive attention has been devoted to understanding the factors controlling the ionic association. The compatibility of the backbone and the ionic groups,[7] the placement of the ionic groups,[8] the degree of ionization,[9] the length of the spacer between the polymer backbone and the ionic groups,[10,11] and the choice of neutralizing cation[7,12-14] have all been shown to have important effects on the morphology and properties of ionomers. However, while the unusual qualities of ionomers are directly attributable to their ionic moieties, relatively little attention has been focused on the effect of pendant anion type on ionomer morphology and properties.

Two notable exceptions to this generalization are the studies of Hashimoto et al.[15] and MacKnight et al.[16-22] Hashimoto et al. completed a morphological comparison of carboxylated and sulfonated perfluorinated ionomer membranes.[15] It was observed that sulfonate groups exhibited larger dipole–dipole interactions than carboxylate groups, giving rise to larger ionic clusters and lower degrees of crystallinity in the sulfonated ionomer membranes. However, conclusions regarding ionic cluster morphology required deconvolution of the crystalline and ionic cluster reflections in the X-ray data, leading to possible ambiguities in the results. Also, crystallinity in the ionomers may have affected the morphology of the ionic aggregates, as well as the overall morphology, making extrapolation of the results to amorphous ionomers questionable.

MacKnight et al. published a series of papers on carboxylated, sulfonated, and phosphonated polypentenamers[16-22] that allowed some comparison between ionic group types. However, these studies were accompanied by a number of synthetic problems and mismatches between the different ionomers, including unexpected cross-linking reactions in some cases and unequal overall molecular weights and mole fractions of ionic groups. Thus, definitive conclusions regarding the influence of pendant anion type on ionomer properties could not be drawn.

To overcome problems associated with crystallinity, Lundberg and Makowski[23] compared sulfonated and carboxylated polystyrene ionomers. The sulfonated and the carboxylated ionomers gave evidence of ionic association in their increased solution and melt viscosities compared to the polystyrene parent polymer. In addition, data on the softening behavior, melt rheology, and dilute solution viscosity indicated that the physical cross-links formed in the sulfonated ionomer are significantly stronger than those formed in the comparable carboxylated ionomers. Like most ionomers, the polystyrene ionomers contained random placement of the ionic groups along the chain backbone that could account for the small morphological differences seen in small-angle X-ray scattering analyses of carboxylated and sulfonated polystyrene ionomers.[24] However, questions arise regarding the effects of ionic group placement.

Interest in studying nonrandom placement of ionic groups along the polymer backbone led to studies involving telechelic ionomers. While the behavior of sulfonated and carboxylated telechelic ionomers have been compared in identical systems,[25] the usefulness of telechelic ionomers as model systems for the random ionomers that are currently used in most ionomer applications has been called into question.[26] Thus, a model system more closely mimicking the nontelechelic ionomers is needed.

The model polyurethane ionomer is such a system. The polyurethane ionomers are synthesized as 1:1 copolymers of a diisocyanate such as tolylene 2,4-diisocyanate (TDI) and a macroglycol soft segment, such as poly(tetramethylene oxide) (PTMO). This backbone is a single-phase viscous liquid, unlike most commercially available polyurethanes, which contain chain extenders. Upon abstraction of the urethane hydrogen with sodium hydride and derivatization with γ-propane sultone or β-propiolactone, a sulfonated or carboxylated ionomer is obtained, where the solid-state properties of the ionomer can be directly attributed to ionic aggregation.

The polyurethane ionomers combine the regular placement of the ionic groups and the well-characterized molecular architecture of the telechelic ionomers with the long-chain matrix properties of the commercial ionomers.

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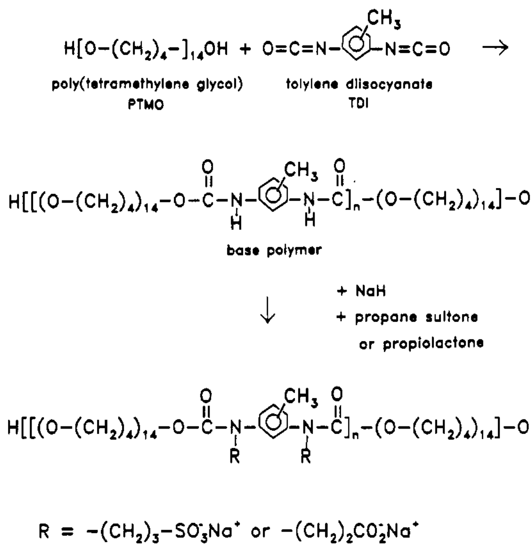

Figure 1. Synthesis scheme for model polyurethane ionomers, using a 1000 molecular weight PTMO soft segment as an example. n is the overall degree of polymerization.

The regular placement of ionic groups along the backbone chain results from ionic derivatization solely at the urethane linkages rather than randomly along the chain and from the lower polydispersities (1.4–1.5) of typical polyols. The regularity of the ionic group placement has already been shown by small-angle X-ray scattering studies to lead to an enhanced degree of phase separation and a more regular morphology than that seen in random ionomers.[27–29]

Like the telechelic ionomers, the ionic content of the polyurethane ionomers can be easily varied by changing the molecular weight of the spacer molecule, in this case the macroglycol unit. In addition, the backbone properties can be simply varied by changing the soft segment macroglycol type. To avoid the possibility of backbone crystallinity, a poly(propylene oxide) (PPO) macroglycol can be investigated.

Thus, polyurethane ionomers are excellent model systems, here chosen to study the influence of pendant anion type on the physical properties of ionomers. By variation of the backbone type and macroglycol molecular weight, the effect of ionic group concentration and interactions between the pendant anion and the polymer backbone are explored.

Experimental Section

Sample Preparation. The synthesis of sulfonated model polyurethane ionomers has been described previously[7] and has been slightly modified in this contribution. The synthesis scheme is diagrammed in Figure 1.

Tolylene diisocyanate (TDI, 80% 2,4 and 20% 2,6 isomers, Aldrich Chemical Co.), anhydrous *N,N*-dimethylacetamide (DMA, Aldrich), anhydrous toluene (Aldrich), sodium hydride (NaH, 60% dispersion in mineral oil, Aldrich), γ-propane sultone (Aldrich), β-propiolactone (Aldrich), and dibutyltin dilaurate (catalyst T-12, Air Products) were used as received. Poly(tetramethylene oxide) (PTMO, Quaker Oats Polymeg, $M_n = 990, 2070$), poly(propylene oxide) (PPO, Aldrich, average molecular weight 1000, 2000), and poly(ethylene oxide) (PEO, Aldrich, average molecular weight 1000) were purified by distillation as described below. The polydispersity (M_w/M_n) of the polyether polyols has been reported elsewhere to be <1.5 for PTMO[27] and <1.05 for PPO.[28]

The polyols were dissolved in DMA to form a 20% v/v solution. An azeotropic distillation was performed under argon atmosphere using 5% by volume of toluene to extract all water from the polyols. Heating reached no higher than 155 °C during distillation, and distillation was considered complete when no further distillate could be collected at the maximum temperature of distillation. The reaction was cooled to 70 °C, and a stoichiometric amount of TDI plus 0.5 wt % T-12 catalyst was added. The temperature was maintained at 70–80 °C for 2 h to complete the copolymerization reaction. All base copolymer molecular weights, as determined by gel permeation chromatography, were in excess of 50 000 g/mol based on comparison to narrow molecular weight polystyrene standards.

The ionomers were synthesized by dissolving the base polyurethane copolymer in DMA (5 wt %) and mixing with a dispersion of NaH in toluene. The reaction mixture was kept at −5 to 0 °C with a dry ice bath under argon and vigorously stirred. After 45 min, a stoichiometric amount of γ-propane sultone or β-propiolactone was added, and the mixture was allowed to warm to room temperature. After reaction for 2 h, the ionomer was recovered by precipitation into an appropriate nonsolvent. Structures were verified by Fourier transform infrared spectroscopy, as described previously,[7] and by atomic absorption analysis (Galbraith Laboratories). Two of the carboxylated samples were derivatized significantly less than 100%. The percentages of derivatization are (in parentheses) M1CNa (57%) and M2CNa (59%).

All ionomers were examined as solution-cast films unless otherwise noted. The sulfonated ionomers were cast at 60 °C from DMA. The carboxylated ionomers were cast at 25 °C from 4:1 v/v toluene/methanol, except for the 98% carboxylated PTMO(1000)/TDI ionomers and the carboxylated PEO(1000)/TDI ionomers, because of solubility constraints. (The parenthetical 1000 indicates the approximate molecular weight of the polyol.) The 98% carboxylated PTMO(1000)/TDI ionomers were cast from 2:1 v/v toluene/methanol solutions. The carboxylated PEO(1000)/TDI ionomers were cast from methanol. Films were dried in a 50 °C vacuum oven for at least 1 week before testing to remove residual solvent and water.

Compression molded samples were molded at 160 °C for 5 min at 10 000 psi. Samples were tested within 2 days of molding so that aging effects were minimal.

Instrumental Conditions. Samples for uniaxial stress–strain testing were stamped out with a standard ASTM D1708 die and were tested by using an Instron Model TM at room temperature in air, with a crosshead speed of 0.5 in./min. Differential scanning calorimetry (DSC) thermograms were recorded by using a Perkin-Elmer DSC-7. Sample weights were 11 ± 2 mg. Thermograms were recorded from −130 to 150 °C at a heating rate of 20 °C/min. Dynamic mechanical thermal analysis (DMTA) data were obtained by using a Rheometrics RSA-II at a test frequency of 100 rad/s (15.9 Hz) under a dry nitrogen purge. Temperature steps of 3 °C/step were used, with a 0.1-min equilibration time at each step.

Sample Nomenclature. Samples are designated with the first letter indicating the soft-segment type (M = PTMO, poly(tetramethylene oxide); P = PPO, poly(propylene oxide); E = PEO, poly(ethylene oxide)), the number indicating the soft-segment molecular weight in thousands, the letter describing pendant ionic-group type (S = sulfonate; C = carboxylate), and the final two letters the chemical symbol for the neutralizing cation. Thus, M1SNa indicates the 1:1 copolymer of PTMO, molecular weight 1000, and TDI, sulfonated and neutralized with sodium.

Results and Discussion

Tensile Testing. The tensile testing results for the PTMO-based ionomers are shown in Figure 2 and Table I. As expected,[15–22] the weaker acid strength of the carboxylate groups led to formation of weaker physical cross-links in the carboxylated ionomers and decreased tensile properties in comparison to the sulfonated ionomers. As the soft-segment molecular weight is increased from 1000 to 2000, decreases in the initial modulus and increases in elongation at break are seen, as predicted since the lower ionic group concentration leads to lower physical cross-link densities and more rubbery polymers. Strain-

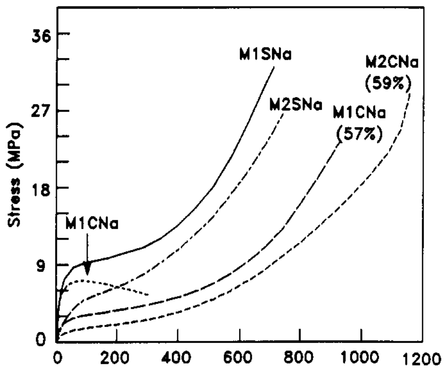

Figure 2. Uniaxial stress–strain results for PTMO-based ionomers cast from solution. Numbers in parentheses indicate the degree of pendant anion substitution at the urethane nitrogen. Where no degree of substitution is indicated, it can be assumed that substitution is essentially complete.

hardening behavior is observed for the sulfonated and for the partially carboxylated PTMO-based ionomers.

The Young's modulus values shown in Table I are significantly higher than would be predicted from rubber elasticity theory, if the effective network elements are considered to be the PTMO chains bound to sulfonated or carboxylated urethane linkages. In this case the tensile modulus is given by[32–34]

$$E = 3[(f-2)/f]\nu RT \tag{1}$$

where f is the cross-link density, ν is the density of elastically effective chains, R is the gas constant, and T is the absolute temperature. If a density value of 0.98 g/cm^3 (for amorphous PTMO soft segments in segmented polyether–polyesters[35]) is used and if it is assumed that all sodium–anion pairs reside in ionic aggregates and that all elastically effective chains have ionic groups at both ends, the ν values given in Table I are calculated. If it is further assumed that the cross-link functionality is large so that $[(f-2)/f]$ approaches unity, an upper bound on E can be calculated. These values also appear in Table I, and a quick inspection of the calculated and experimental values reveals large differences.

The ability of ionic aggregates to act as filler could give rise to some of the observed modulus enhancement. The Guth–Einstein–Smallwood equation for modulus enhancement as a function of volume fraction filler can be used to quantify the filler effect:[36]

$$E_f/E_0 = 1 + 2.5v_f + 14.1v_f^2 \tag{2}$$

where E_f is the modulus of the filled elastomer, E_0 is the modulus of the unfilled elastomer, and v_f is the volume fraction of the filler. According to eq 2, a v_f value of 0.62 would be required to achieve the approximately 8-fold increase in the modulus of M1SNa from that calculated by rubber elasticity theory to that observed experimentally. The small-angle X-ray scattering analysis indicates the volume fraction of ionic aggregates in M1SNa is 0.29.[38] Similar clearly unreasonable values for v_f can be calculated for the other model polyurethane ionomers, indicating that although a filler effect may provide some contribution to modulus enhancement, it is not solely responsible for the increased tensile properties of these ionomers.

Trapped entanglements often contribute appreciably to the moduli of networks formed by chemically cross-linking in bulk.[37] Since the model polyurethane ionomers are of relatively high molecular weight, it is reasonable to assume that they are highly entangled. Furthermore, the ionic aggregation process would be expected to enhance the degree of entanglement in the polymer above that which would be caused by a chemical cross-linking reaction. Whereas chemical cross-linking in bulk simply freezes in the degree of entanglement present before cross-linking, ionic aggregation creates new entanglements as the ionic groups coalesce. This leads to a greater degree of entanglement and a large modulus enhancement. For example, interlocking chain loops, resulting from coalescence of two ionic groups on a single polymer chain into the same aggregate, could be formed.

The presence of trapped entanglements in the model ionomers explains the higher moduli values presented here for the sulfonated ionomers than had been seen in a previous study.[7] The higher molecular weight of the ionomers studied here (>50 000) compared to those of the previous study (>20 000) leads to a higher degree of entanglement and a higher tensile modulus.

The modulus enhancement resulting from trapped entanglements is clearly important in the model polyurethane ionomers; however, the reduced tensile toughness of the 98% carboxylated M1CNa ionomer compared to its sulfonated analogue is primarily caused by the absence of strain-hardening behavior in the carboxylated ionomer. Strain hardening generally results from either finite chain extensibility or from strain-induced crystallization. Since neither the P1- nor E1-based ionomers exhibit strain-hardening behavior, it seems likely that strain-induced crystallization in the M1-based ionomers is occurring. Supporting this conclusion, it has been shown that strain-induced crystallization occurs in PTMO-based polyurethanes by wide-angle X-ray scattering[39] and that sulfonate groups disturb the crystalline matrix less than carboxylate groups in polypentenamers.[16]

To study the strain-hardening behavior of the PTMO-based ionomers, the stress–strain data can be recast in the Mooney–Rivlin format:

$$[f] = \sigma/(\alpha - 1/\alpha^2) \tag{3}$$

where $[f]$ is termed the reduced stress, σ is the engineering stress, and α is the ratio of stressed to unstressed sample length.

Mooney[40] and Rivlin[41] noted that the data for many chemically cross-linked elastomers[37] lie on straight lines when plotted as $[f]$ versus $1/\alpha$. The Mooney–Rivlin plots for the PTMO-based ionomers are shown in Figure 3. The nonlinearity in the plots results from the time-dependent nature of the physical cross-links;[12] it should not interfere with the analysis of the strain-hardening behavior.

Strain hardening appears as a strong positive deviation from linearity in the Mooney–Rivlin plots as $1/\alpha$ becomes small. The point at which the deviation begins, the elongation at which the onset of strain hardening occurs, is designated α_c in Table I. Before direct comparisons are made between the carboxylated and sulfonated ionomers, it should be noted that the degrees of substitution at the urethane nitrogens of two of the carboxylated ionomers which strain harden are approximately equal to each other but not to their sulfonated analogues. For the M1CNa ionomers, it appears that a critical degree of carboxylation, which must be greater than 57%, is necessary to prevent strain hardening in these ionomers. Comparing the M1CNa (57% carboxylated) sample to the M1SNa sample, it is seen that the type of anionic group has no effect on the elongation at which the onset of strain hardening occurs. The same is seen for the M2CNa and M2SNa samples. Pendant-anion type apparently has no influence on strain-hardening behavior in those ionomers

Table I
Tensile Properties of Model Polyurethane Ionomers

sample	% substitution[a]	E_0,[b] MPa	stress at break, MPa	elongation at break, %	Mooney–Rivlin results α_c	rubber elasticity $10^4\nu$, mol/cm^3	rubber elasticity E, MPa
M1SNa	93	53.7	32.0	710	5.0	6.69	4.97
M1SNa[c]	93	40.8	33.9	650	4.1	6.69	4.97
M1CNa	98	55.7	5.4	310		7.18	5.34
M1CNa[c]	98	35.6	5.3	46		7.18	5.34
M1CNa	57	17.9	19.2	930	5.0		
M2SNa	94	13.5	25.3	740	5.3	3.98	2.96
M2CNa	59	5.6	26.7	1160	5.3	4.14	3.08
P1SNa	95	24.0	0.50	430		7.47	5.56
P1CNa	89	4.81	0.60	15		8.06	5.99
P2SNa	93	6.07	*d*	*d*		3.74	2.78
P2CNa	96	8.15	0.97	31		4.54	3.38
E1SNa	100	21.1	1.4	340		7.42	5.51
E1CNa	96	*e*	*e*	*e*	*e*	8.00	5.95

[a] From elemental analysis for sulfur, in the case of sulfonated ionomers, or for sodium, for carboxylated ionomers. [b] Zero-strain Young's modulus from extrapolation of the Mooney–Rivlin plots to $\alpha = 1$ (zero strain) and multiplication by 3. [c] Compression-molded sample. [d] P2SNa did not break within the extension limits of the instrument. [e] E1CNa was too weak to test with this method.

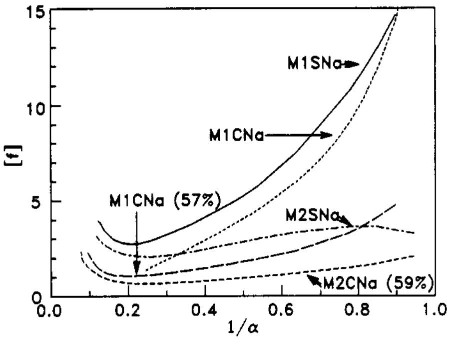

Figure 3. Mooney–Rivlin plots of data shown in Figure 2.

that exhibit strain hardening.

The degree of carboxylation has a strong effect on tensile properties for the carboxylated ionomers. Large differences in physical properties were seen for similar model sulfonated polyurethane ionomers based on 1000 molecular weight PTMO and MDI previously; a 2-fold decrease in modulus was found when the sulfonation level was decreased from 81% to 49%.[29] The 98% carboxylated M1CNa ionomer has a Young's modulus approximately 3 times greater than that of the 57% carboxylated M1CNa ionomer. A critical concentration of ionic groups is apparently necessary before the full effects of carboxylation, such as increased Young's modulus and inhibition of stress crystallization, are observed in the bulk polymer properties. Below the critical degree of ionization, stress crystallization is observed, as well as lower tensile properties and, possibly, a minimal degree of ionic group aggregation. The stress crystallization of M2CNa, which is only 59% carboxylated, supports this conclusion.

It could be argued that the different solvents used to produce the cast specimens discussed above gave rise to the differences observed between the sulfonated and carboxylated ionomers. To address this issue, M1SNa and M1CNa were compression molded under identical conditions and tested. Results are shown in Figure 4. While compression molding lowers the initial modulus of both M1SNa and M1CNa and significantly decreases the overall tensile strength of M1CNa, it does not change the trends observed in the solution-cast samples. The M1CNa sample remains significantly weaker than the M1SNa ionomer in tensile strength while nearly matching its initial modulus. Moreover, the moduli of M1SNa and M1CNa still greatly exceeded those predicted by rubber elasticity theory, emphasizing the importance of trapped entanglements in these systems.

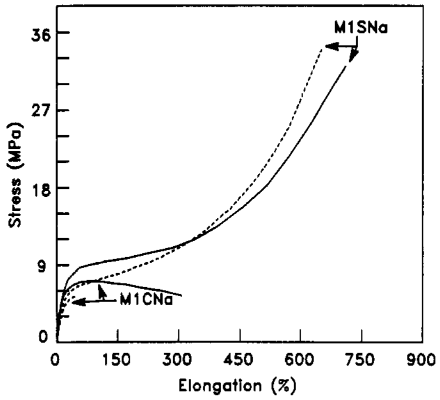

Figure 4. Uniaxial stress–strain results for solution-cast and compression-molded ionomers based on 1000 molecular weight PTMO. Solution cast samples are represented with solid lines, and compression molded samples are shown as the dashed curves.

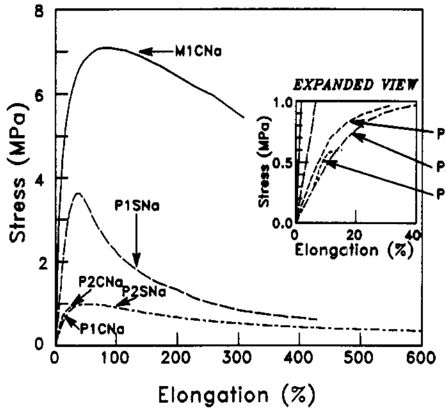

Figure 5. Uniaxial stress–strain results for the PPO-based ionomers. The solid curve, for M1CNa, is shown for comparison.

The tensile testing results for the PPO-based ionomers are shown in Figure 5, and the tensile parameters for the PPO- and PEO-based ionomers are summarized in Table I. As Figure 5 and Table I show, the PPO- and PEO-based ionomers are significantly weaker than their PTMO-based counterparts. Also, a marked yield point is visible in the P1SNa ionomer data, which is attributable to yielding of the ionic aggregates. The weaker properties of the PPO-based ionomers result from the inability of the PPO soft segments to stress crystallize and from the

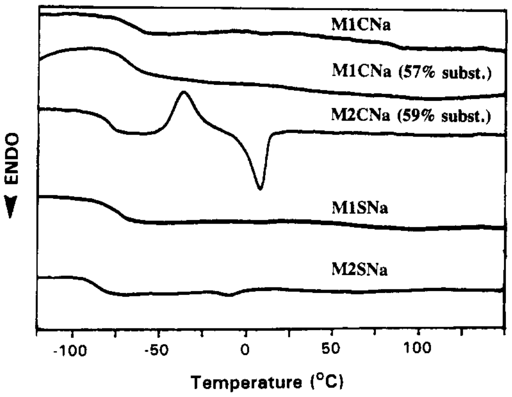

Figure 6. Representative DSC traces for PTMO-based ionomers.

Table II
Differential Scanning Calorimetry Results for Polyurethane Ionomers

sample	glass transition temp T_g, °C	crystallization peak, °C	crystalline melting peak, °C
M1SNa	−76		
M1CNa (57% carboxy.)	−70		
M1CNa (98% carboxy.)	−67		
M2SNa	−80		
M2CNa	−79	−36	14
P1SNa	−52		
P1CNa	−43		
P2SNa	−62		
P2CNa	−63		
E1SNa	−45		
E1CNa	−35		

smaller size of the ionic aggregates, as shown by SAXS analysis.[38] Smaller aggregates contain fewer ionic groups and therefore fewer load-bearing points that can impart strength and stiffness to the ionomer. The PEO-based ionomers also have smaller ionic aggregates,[38] resulting from the increased compatibility of the ionic groups with the more highly polar polymer matrix.

Using density values of 1.1 g/cm^3 for PPO and 1.13 g/cm^3 for PEO,[39] the moduli from rubber elasticity theory were calculated and are presented in Table I. On the basis of arguments of the greater acid strength of the sulfonate group,[15] the higher tensile modulus of P1SNa than P1CNa is expected. Similarly, the higher ionic concentrations in the P1-based ionomers explain their higher tensile properties compared to the P2-based ionomers. The anomalously high modulus of the P2CNa ionomer cannot be explained by either of these arguments.

The higher modulus of P2CNa compared to P1CNa can be interpreted with reference to SAXS data on this material.[38] SAXS analysis for P2CNa shows clear evidence of ionic aggregation, whereas the absence of an "ionomer peak" for P1CNa indicates only multiplet interactions or low levels of clustering. Thus, P2CNa has a higher modulus than P1CNa because of a higher degree of ionic aggregation. P2CNa also has larger ionic aggregates than P2SNa, resulting in more cross-links and a higher Young's modulus.

The surprisingly high modulus values of all the carboxylated ionomers can be explained by the larger sizes of their ionic aggregates.[38] The greater functionality of the physical cross-links gives rise to a higher initial modulus than in the sulfonated ionomers. However, as the strain increases, the strength of each individual cross-link element becomes more important. The carboxylate groups pull out of the ionic aggregates at lower strains than the sulfonate groups, failing as physical cross-links and resulting in lower tensile strengths. The higher degree of cross-linking in the M1CNa ionomer also explains why the 98% carboxylated ionomer does not stress crystallize. The high degree of crosslinking causes stress crystallization to begin at lower elongations so that the fraction of chains favorably oriented for crystallization is small; a large fraction of chains remain ineligible for crystallization. Lower degrees of cross-linking favor delays in the onset of stress crystallization until higher elongations are reached, as the α_c values show, allowing development of a higher overall degree of crystallinity and higher tensile properties.

Differential Scanning Calorimetry. DSC thermograms for PTMO-based ionomers are shown in Figure 6, and the DSC data for all the ionomers are summarized in Table II. All ionomers examined except the M2-based ionomers exhibited only a well-defined glass transition. M2CNa also showed a crystallization exotherm and a melting endotherm, and M2SNa showed evidence of a small melting endotherm at ~−5 °C.

A noticeable difference in glass transition behavior was seen between the carboxylated and sulfonated ionomers. Two factors may be responsible for the differences between the carboxylated and the sulfonated ionomers: the length of the hydrocarbon chain attaching the ionic group to the polymer backbone and the type of pendant ionic group. Flexible pendant side chains on many aliphatic polymers have been shown to lower the glass transition temperature by acting as internal diluents, lowering the frictional interaction between neighboring chains in the bulk. Longer side chains, up to a certain length, lower the glass transition to a greater degree. The influence of side-chain length on T_g in ionomers has been demonstrated.[11] Because the sulfonated ionomers contain side chains with three methylene groups whereas the carboxylated ionomer side chains contain only two methylene groups, the dilution effect could explain at most 3–4 °C of the differences in the T_g's between the carboxylated and the sulfonated ionomers.

It seems that the primary cause of the differing T_g's must be attributed to ionic group type. For the 1000 molecular weight soft-segment ionomers, whether based on PPO, PEO, or PTMO, a difference of 9–10 °C in the T_g's can be seen for the fully ionized polymers, with the T_g's of the carboxylates always greater. As was described above for the tensile testing results, the sulfonate groups form stronger physical cross-links in the material and result in more phase-separated structures. Because the soft-segment phase contains fewer ionic "contaminants", the T_g in the sulfonated ionomers more closely approaches the T_g of the pure soft-segment material, −84 °C for PTMO, −73 °C for PPO, and −41 °C for PEO.[43] Similar thermal behavior has been observed for sulfonated and carboxylated polystyrene ionomers.[23] Apparently, the ionic group type exerts an equivalent influence on the glass transition properties of the ionomers regardless of the polarity of the polymer backbone, based on the 9–10 °C difference in T_g of the carboxylated and sulfonated analogues seen in the 1000 molecular weight soft segment PTMO-, PPO-, and PEO-based ionomers.

In contrast, the glass transition temperatures of the carboxylated and sulfonated ionomers based on 2000 molecular weight soft segments are approximately the same for identical soft-segment types. These ionomers exhibit higher degrees of phase separation than the 1000 molecular weight polyol-based ionomers because the higher molecular weight polyol-based ionomers possess a higher thermodynamic driving force for phase separation, which

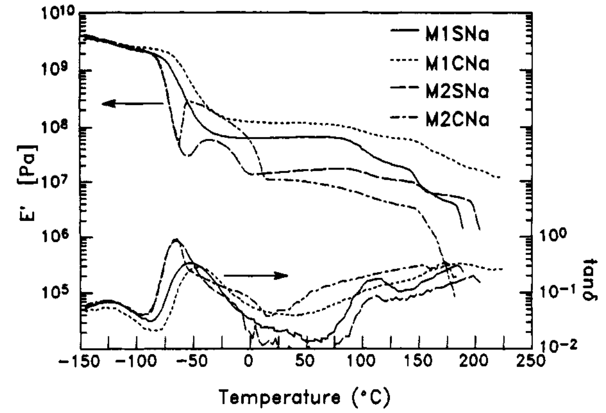

Figure 7. DMTA results, E' and tan δ, for solution-cast PTMO-based ionomers.

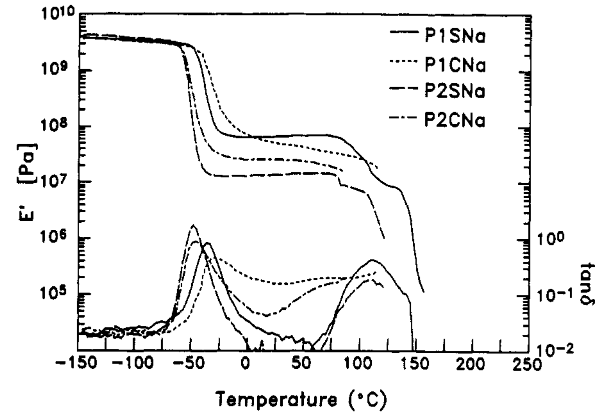

Figure 8. E' and tan δ data for solution-cast PPO-based ionomers.

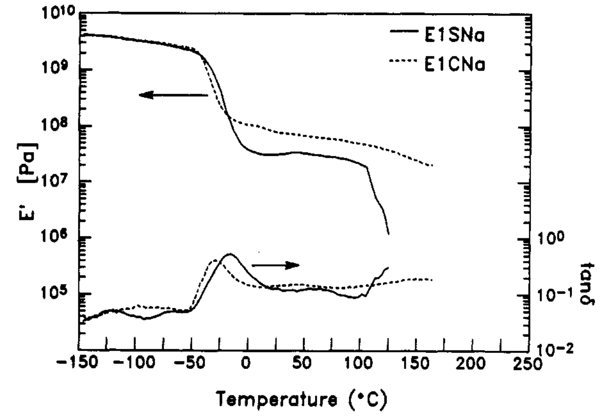

Figure 9. E' and tan δ data for solution-cast PEO-based ionomers.

can apparently outweigh differences due to pendant anion type.

Dynamic Mechanical Thermal Analysis. To fully explore the mechanical and thermal properties of the model ionomers, DMTA was performed. The storage moduli and loss tangents are plotted as a function of temperature for the model ionomers in Figures 7–9, and the DMTA results are summarized in Table III. The glass transition temperatures are taken as the maxima in the loss moduli (data not shown).

The general features of the systems correspond to those previously seen for other model polyurethane ionomers.[7] A well-defined glass transition is followed by a broad rubbery plateau, resulting from ionic aggregation, with a final downturn in the E' versus temperature curve, which indicates the onset of flow. In addition, peaks in the tan δ curves of the sulfonated PTMO-based and PPO-based ionomers at ~105 °C and small decreases in the E' curves of the carboxylated PTMO-based ionomers at temperatures in excess of 100 °C indicate transitions associated with ionic aggregate dissociation or rearrangement. Ionic transitions have been observed in a number of ionomer systems by DMTA[44] and dielectric measurements[45] and may indicate a higher degree of ordering within the ionic aggregates. In addition to these characteristic ionomer features, the M2-based ionomers also show peaks in the storage moduli curves at temperatures slightly above the glass transitions which correspond to the presence of crystallinity in the ionomers. This agrees with the evidence of crystallinity seen in the DSC results. Scans of M1CNa, P1CNa, P2CNa, and E1CNa could not be run to higher temperatures to ascertain the onset of flow because of mechanical failure of the samples.

Table III
Dynamic Mechanical Analysis Results for Polyurethane Ionomers

sample	T_g, °C	onset of flow, °C	T_{in}, °C	E'_{in}, MPa	$M_{c,exp}$, g/mol	$M_{c,calc}/M_{c,exp}$
M1SNa	-66	189	-37.7	91.2	63.3	15.6
M1CNa	-58	*a*	-29.2	170.0	35.1	28.2
M2SNa	-75	197	-0.4	14.0	477.0	4.17
M2CNa	-75	144	14.5	11.4	617.0	3.22
P1SNa	-43	140	-25.4	79.1	86.1	11.6
P1CNa	-37	*a*	-15.9	116.0	55.5	18.0
P2SNa	-57	103	-40.8	18.0	354.0	5.65
P2CNa	-54	*a*	-33.6	42.0	157.0	12.8
E1SNa	-34	103	-5.7	43.5	173.0	5.78
E1CNa	-40	*a*	-16.7	151.0	48.0	20.8

[a] Onset of flow could not be measured.

The glass transition temperatures derived from the DMTA analysis do not agree quantitatively with the T_g values obtained from the DSC scans because the scan rates of the DMTA (15.9 Hz) and the DSC (20 °C/min) are not of comparable time scales.[46] Nevertheless, the trends in the glass transition temperatures are the same as in the DSC analysis. The carboxylated ionomers based on 1000 molecular weight soft segments give significantly higher T_g's than the sulfonated ionomers, as well as exhibiting broader glass transition regions, attributable to the lower degree of phase separation in the carboxylated systems. The ionomers based on 2000 molecular weight soft segments exhibited approximately the same T_g's for the sulfonated and carboxylated ionomers of identical backbone type.

The value of the storage modulus E'_{in} at the inflection point of the rubbery plateau was combined with the density (ρ) values given above to calculate the average molecular weight between cross-links according to the equation[47]

$$M_c(\text{exp}) = 3\rho R T_{in}/E'_{in} \tag{4}$$

as reported in Table III. The cross-linking efficiency of the ionic aggregates may be expressed as the ratio $M_c(\text{calc})/M_c(\text{exp})$, where $M_c(\text{calc})$ is the theoretical value calculated for strictly multiplet-type interactions and is taken as the molecular weight of the soft segments. The advantage of this method is that it allows comparison of the effect of ionic aggregation on the samples with respect to a reference state, in this case a state in which ion pairs interact to form multiplets [$M_c(\text{calc})$] only. Larger values of the ratio $M_c(\text{calc})/M_c(\text{exp})$ indicate enhanced states of aggregation.

As the data show, for the 1000 molecular weight soft segment ionomers, the cross-linking efficiency $M_c(\text{calc})/M_c(\text{exp})$ of the carboxylated ionomers is much greater than that of the sulfonated ionomers, matching the E_0 trends seen in the large-deformation tensile analyses. The larger ionic aggregates present in the carboxylated ionomers, as noted in the SAXS results,[38] give rise to the higher cross-linking efficiencies. The different aggregate sizes may be related to the planar nature of the carboxylate anions, which may allow for more efficient packing arrangements in the ionic aggregates than are present with the tetrahedral sulfonate groups.

Comparing the soft-segment types, the PEO-based ionomers show the lowest cross-linking efficiencies. The higher polarity of the PEO matrix provides a lower barrier to aggregate dissociation upon the application of stress than the PTMO- or PPO-based ionomers. The cross-linking efficiencies of the M2SNa and M2CNa ionomers are similar, as are their tensile properties, with the lower cross-linking efficiency of the carboxylated ionomer giving rise to weaker mechanical properties.

The flow of the ionomers, resulting from the decreased effectiveness of the ionic aggregates to act as physical cross-links, occurs at a much higher temperature for the M2SNa than the M2CNa ionomer and is, in general for the model polyurethane ionomers, dependent on pendant anion type and matrix character. The failure of the carboxylate groups as physical cross-links at lower temperatures than the sulfonate groups could be predicted from the weaker acid strength of the carboxylate groups; less energy is needed to disturb the physical cross-links. The inability to observe flow behavior in the M1CNa, P1CNa, P2CNa, and E1CNa ionomers at temperatures greater than the flow temperatures of their sulfonated analogues may result from the highly entangled nature of these systems. While the physical cross-links may have failed at lower temperatures, no significant decreases in modulus prior to sample failure are observed because the polymer chains are too highly entangled to slip past one another into a liquidlike flow state.

The temperature of the onset of flow for the sulfonated ionomers decreases in the order PTMO > PPO > PEO for identical soft-segment molecular weights. This is a reflection of the effect of matrix polarity on ionic aggregation. The high polarity of the PEO matrix provides the lowest driving force for ionic aggregation and, therefore, allows the onset of flow at the lowest temperatures.

Conclusions

A series of carboxylated and sulfonated model polyurethane ionomers was examined to determine the influence of pendant-anion type on their physical properties. Backbone type was varied to study the effect of polarity and crystallizability on properties. The initial moduli were seen to be much greater than would be predicted by rubber elasticity theory. The modulus enhancement was attributed to trapped entanglements and the formation of additional interlocking loops during ionic aggregation. The weaker overall tensile properties of the carboxylated ionomers were attributed to the weaker acid strength of carboxylate groups. The higher than expected tensile moduli of the carboxylated ionomers were attributed to their high cross-linking efficiencies and the larger size of the ionic aggregates in the carboxylated compared to the sulfonated ionomers. It should be noted that some of the observed differences between the carboxylated and sulfonated ionomers could result from the different casting solvents used to prepare the samples. As identical trends were seen for sulfonated and carboxylated compression-molded samples prepared under identical conditions, however, it is expected that the observed differences arise primarily from changes in pendant-anion type.

The ion content of the model ionomers was an important factor in distinguishing the T_g behavior of carboxylated and sulfonated ionomers. For the higher ion content polymers based on 1000 molecular weight soft segments, a 9–10 °C difference in T_g was seen between the carboxylated and sulfonated ionomers in the DSC scans. The lower T_g's of the sulfonated ionomers were attributed to a higher degree of phase separation, as confirmed by the narrower temperature range of the glass transition in the DMTA data. In contrast, the ionomers based on 2000 molecular weight soft segments displayed equivalent T_g's and similar degrees of phase separation regardless of anion type.

The thermal energy required to disrupt the ionic aggregates in their role as physical cross-links, as determined by the onset of flow in the DMTA experiments, was shown to be higher for sulfonated than carboxylated ionomers and to depend on anion type and matrix polarity. The PTMO-based polymers gave the highest tensile strengths and the highest flow temperatures, followed by the PPO-based ionomers and finally the PEO-based ionomers. The ability to stress crystallize contributed greatly to the higher tensile properties of the PTMO-based ionomers, whereas the high polarity of the PEO soft segments and their increased compatibility with the ionic groups gave the PEO-based ionomers the lowest tensile properties and the earliest onset of flow.

Overall, the use of carboxylate groups rather than sulfonate groups was seen to decrease the tensile strength, increase the degree of phase mixing, and increase the cross-linking efficiency of the model polyurethane ionomers. The differences in physical properties and morphologies between sulfonated and carboxylated ionomers point out advantageous features of both systems and opens the question of how the two types of pendant ionic group could be combined to reap the benefits of both functionalities. This issue will be addressed in a future paper.

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References and Notes

(1) Eisenberg, A.; King, M. *Ion Containing Polymers: Physical Properties and Structure*; Academic Press: New York, 1977.

(2) MacKnight, W. J.; Earnest, T. *Macromol. Sci., Rev. Macromol. Chem.* **1981**, *16*, 41.

(3) Eisenberg, A., Bailey, F., Eds. *Coulombic Interactions in Macromolecular Systems*; ACS Symposium Series No. 302; American Chemical Society: Washington, D.C., 1986.

(4) Tant, M.; Wilkes, G. *J. Macromol. Sci., Rev.* **1988**, *C28*, 1.

(5) Lantman, C. W.; MacKnight, W. J.; Lundberg, R. D. *Annu. Rev. Mater. Sci.* **1989**, *19*, 295.

(6) Fitzgerald, J. J.; Weiss, R. A. *J. Macromol. Sci., Rev.* **1988**, *C28*, 99.

(7) Ding, Y. S.; Register, R. A.; Yang, C.-Z.; Cooper, S. L. *Polymer* **1989**, *30*, 1204.

(8) Brockman, N. L.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1145.

(9) Yarusso, D. J.; Cooper, S. L. *Macromolecules* **1983**, *16*, 1871.

(10) Gauthier, M.; Eisenberg, A. *Macromolecules* **1989**, *22*, 3754.

(11) Gauthier, M.; Eisenberg, A. *Macromolecules* **1990**, *23*, 2066.

(12) Register, R. A.; Foucart, M.; Jerome, R.; Ding, Y. S.; Cooper, S. L. *Macromolecules* **1988**, *21*, 1009.

(13) Broze, B.; Jerome, R.; Teyssie, P.; Marco, C. *Macromolecules* **1983**, *16*, 996.

(14) Yarusso, D. J.; Ding, Y. S.; Pan, H. K.; Cooper, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 2073.

(15) Hashimoto, T.; Fujimura, M.; Kawai, H. In *Perfluorinated Ionomer Membranes*; Eisenberg, A., Yeager, H. L., Eds.; ACS Symposium Series No. 180; American Chemical Society: Washington, D.C., 1982; p 217.
(16) Rahrig, D.; MacKnight, W. J.; Lenz, R. W. *Macromolecules* **1979**, *12*, 195.
(17) Rahrig, D.; MacKnight, W. J. In *Ions in Polymers*; Eisenberg, A., Ed.; ACS Symposium Series No. 187; American Chemical Society: Washington, D.C., 1980; p 91.
(18) Rahrig, D.; MacKnight, W. J. In *Ions in Polymers*; Eisenberg, A., Ed.; ACS Symposium Series No. 187; American Chemical Society: Washington, D.C., 1980; p 77.
(19) Sanui, K.; MacKnight, W. J. *Brit. Polym. J.* **1974**, *8*, 22.
(20) Sanui, K.; Lenz, R. W.; MacKnight, W. J. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1965.
(21) Azuma, C.; MacKnight, W. J. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 547.
(22) Rahrig, D.; Azuma, C.; MacKnight, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 59.
(23) Lundberg, R. D.; Makowski, H. S. In *Ions in Polymers*; Eisenberg, A., Ed.; ACS Symposium Series No. 187; American Chemical Society: Washington, D.C., 1980.
(24) Yarusso, D. J.; Cooper, S. L. *Polymer* **1985**, *26*, 371.
(25) Horrion, J.; Jerome, R.; Teyssie, P. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 153.
(26) Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098.
(27) Ding, Y. S. Ph.D. Thesis, University of Wisconsin, 1986.
(28) Ding, Y. S.; Register, R. A.; Yang, C.-Z.; Cooper, S. L. *Polymer* **1989**, *30*, 1213.
(29) Lee, D. C.; Register, R. A.; Yang, C.-Z.; Cooper, S. L. *Macromolecules* **1988**, *21*, 998.
(30) Andrews, G. D.; Vatvars, A.; Pruckmayr, G. *Macromolecules* **1982**, *15*, 1580.
(31) Dickinson, L. C.; Chien, J. C. W.; MacKnight, W. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*, 80.
(32) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(33) Graessley, W. W. *Macromolecules* **1975**, *8*, 186.
(34) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(35) Vallance, M. A.; Cooper, S. L. *Macromolecules* **1984**, *17*, 1208.
(36) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 480.
(37) Mark, J. E. *Rubber Chem. Technol.* **1975**, *48*, 495.
(38) Visser, S. A.; Cooper, S. L. *Macromolecules*, following paper in this issue.
(39) Clough, S. B.; Schneider, N. *J. Macromol. Sci., Phys.* **1968**, *2*, 553.
(40) Mooney, M. *J. Appl. Phys.* **1940**, *11*, 582.
(41) Rivlin, R. *Philos. Trans. R. Soc. London* **1948**, *A241*, 379.
(42) Miller, R. L. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; p IV-72.
(43) Brandrup, J., Immergut, E., Eds. *Polymer Handbook*, 2nd ed.; Wiley: New York, 1975; pp 11-157.
(44) MacKnight, W. J.; McKenna, L. W.; Read, B. E. *J. Appl. Phys.* **1967**, *38*, 4208.
(45) Read, B. E.; Carter, E. A.; Conner, T. M.; MacKnight, W. J. *Brit. Polym. J.* **1969**, *1*, 123.
(46) Sperling, L. H. *Introduction to Physical Polymer Science*; Wiley: New York, 1986.
(47) Treloar, L. R. G. *The Physics of Rubber Elasticity*; Oxford University Press: Oxford, 1958; Chapter 9.