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A series of model polyurethane ionomers containing uniform placement of the ionic groups along the chain has been synthesized in order to study the ionomer structure-property relationship in a well defined system. The materials were synthesized to vary in anion type (sulfonate vs. carboxylate), ionization level, and backbone soft segment polarity. The sulfonated ionomers possessed a higher degree of phase separation and superior mechanical properties compared to their carboxylated analogs. A critical minimum ionization level was found to be necessary for the development of good elastomeric properties.

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COMPARISON OF CARBOXYLATED AND SULFONATED MODEL POLYURETHANE IONOMERS

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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 (eg., 1-4). Even though the unusual qualities of ionomers are directly attributable to their ionic moieties, relatively little attention has been focused on the affect of pendant anion type on ionomer morphology and properties. Notable exceptions are the papers of Lundberg and Makowski(5), comparing carboxylated and sulfonated polystyrene ionomers, and of MacKnight and coworkers, who studied sulfonated, carboxylated and phosphonated polypentenamers (2,6,7). All these ionomers contained random placement of the ionic groups along the chain backbone.

A series of model polyurethane ionomers containing uniform placement of the ionic groups along the chain has been synthesized in order to study the effect of ionic group type on ionomer properties in a well-defined system. The effect of backbone polarity, ionic group content, and degree of ionization was examined as well. A comparison of the mechanical and thermal properties of sulfonated and carboxylated ionomers is presented here.

Experimental

The model ionomers are 1:1 copolymers of either poly(tetramethylene oxide) (PTMO) or poly(propylene oxide) and tolylene diisocyanate (TDI), which were post-polymerization derivatized with either γ-propane sultone, for sulfonated ionomers, or β-propiolactone, for carboxylated ionomers. The structure of the model ionomer is shown in Figure 1. The synthesis procedure for the sulfonated ionomers has been described previously (8). The carboxylated ionomers are synthesized using an identical procedure, with the substitution of β-propiolactone for γ-propane sultone in the ionization step. Structures were verified by Fourier transform infrared spectroscopy and elemental analysis (Galbraith Laboratories).

Sulfonated ionomers were prepared for testing by spin-casting at 60 C from N,N dimethylacetamide (DMA). Because of the insolubility of the carboxylated ionomers in all single organic solvents tested, carboxylated ionomers were spin cast at room temperature from 4:1 v/v toluene/methanol solutions, except for the 98% carboxylated PTMO(1000)/TDI ionomers, because of solubility constraints. The 98% carboxylated PTMO(1000)/TDI ionomers were cast from 2:1 v/v toluene/methanol solutions. Films were dried in a vacuum oven at 60 C for at least one week before testing.

Samples for uniaxial stress-strain testing were stamped out with a standard ASTM D1708 die and were tested using an Instron TM model at room temperature in air, with a crosshead speed of 0.5 inches/minute. Differential scanning calorimetry thermograms were recorded 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.

Samples are designated with the first letter indicating the soft segment type (M=PTMO; P=PPO), 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, as drawn Figure 1.

Results and Discussion

Uniaxial Stress Testing

Stress-strain curves for PTMO-based ionomers are shown in Figure 2, and the results are summarized in Table 1. Since sulfonic acid is a much strong acid than carboxylic acid, the physical crosslinks formed in the sulfonated ionomer are expected to be stronger than in the carboxylated ionomer, leading to polymers with increased physical properties. As predicted, M1SNa has a higher tensile strength than M1CNa (98% ionized), primarily because of the strain hardening behavior exhibited in the sulfonated but not the carboxylated ionomer.

Strain hardening generally results from strain-induced crystallization or finite extensibility of the polymer chains. Since strain hardening behavior is not seen in the analogous PPO-based ionomers, it seems likely that the upturn in the stress-strain curves of the PTMO-based ionomers results from strain-induced crystallization. Strain-induced crystallization has been demonstrated in PTMO-based polyurethane by wide-angle x-ray scattering (9), and sulfonate groups have been shown to disturb the crystalline matrix less than carboxylate groups in hydrogenated polypentenamers(6). The stronger physical crosslinks in the sulfonated ionomers result in fewer ionic groups dispersed in the PTMO matrix which could interfere with strain-induced crystallization. Thus, the sulfonated ionomers exhibited increased physical properties.

A similar difference between carboxylated and sulfonated ionomers is seen for the PTMO(2000) and PPO-based ionomers. M2CNa has a lower Young's modulus and a more rubbery character than M2SNa. Stress-strain curves for PPO ionomers in Figure 3 also show greatly reduced physical properties for the carboxylated ionomers. PPO ionomers also show qualitatively different behavior than the PTMO ionomers, due to their inherent inability to crystallize under strain, as discussed above.

The percentage of ionization also 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 PTMO(1000) and MDI previously; a two-fold decrease in modulus was found when the ionization level was decreased from 81% to 49%. (10) In the work presented here, M1CNa (98% ionized) has a Young's modulus approximately three times greater than that of M1CNa (57% ionized). A critical degree of ionization is apparently necessary before the full effects of the carboxylation are observed in the bulk polymer properties. The strain-induced crystallization behavior of M2CNa, which is only 59% ionized, support this conclusion.

Differential Scanning Calorimetry

DSC thermograms for PTMO-based ionomers are shown in Figure 4, and the DSC data for all the ionomers is summarized in Table 2. All the ionomers examined exhibited only a well-defined glass trasition, except the carboxylated PTMO(2000) ionomers, which show soft segment melting.

A noticeable difference in glass transition behavior was seen between the carboxylated and sulfonated ionomers. Two factors may be responsible for the differences: the length of the hydrocarbon chain attaching the ionic group to the polymer backbone or 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 which are incapable of crystallization, as are the side chains under investigation here, lower the glass transition to a greater degree. 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 some of the differences in Tg's between the carboxylated and the sulfonated ionomers.

However, the primary cause of the differing Tg's must be attributed to the ionic group type. For the 1000 molecular weight soft segment PPO and PTMO ionomers, a difference of 9C in the Tg's can be see for the fully ionized polymers, with the Tg's of the carboxylates always greater. As was described above for the tensile testing results, the sulfonated ionomers form stronger physical crosslinks in the material and results in a more phase-separated structure. Because the soft segment phase contains fewer ionic 'contaminants,' the Tg approaches the Tg of the pure soft segment material, -84 C for PTMO and -73 C for PPO (11). Similar thermal behavior has been observed for sulfonated and carboxylated polystyrene ionomers(5). 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 C difference in Tg's seen for the PTMO- and PPO-based ionomers.

The Tg's of the 2000 molecular weight soft segment materials more closely approach the Tg's of the pure soft segments, as expected for ionomers with lower ionic group concentrations. In addition, the differences in Tg between the carboxylated and sulfonated ionomers have disappeared, indicating, that a minimum concentration of ionic groups is necessary to distinguish between the two ionic group types in glass transition behavior. Since the Tg of the 57% carboxylated PTMO(1000) ionomer is still much less than that of the sulfonated ionomer, the critical ion concentration must be less than approximately one ionic group per TDI unit.

Conclusion

The choice of pendant anion type was shown to have a substantial influence on ionomer properties. The carboxylated ionomers gave consistently poorer mechanical properties, with the carboxylate groups dispersing in the backbone matrix and disrupting strain-induced crystallization in the PTMO(1000) ionomers. The stronger physical crosslinks in the sulfonated ionomers gave rise to stronger, more highly phase separated ionomers, as evidenced by the tensile testing and DSC results. A critical ion concentration was found to be necessary to observe certain unusual mechanical and thermal behavior in these ionomers. Further work probing the properties and morphology of these ionomers using dynamic mechanical thermal analysis and small angle x-ray scattering is in progress.

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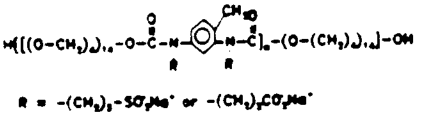

$R = -(CH_2)_3-SO_3^-Na^+$ or $-(CH_2)_?CO_2^-Na^+$

Fig. 1 Structure of model polyurethane ionomer based on PTMO soft segment.

Table 1. Tensile Properties of Polyurethane Ionomers

Sample	Percent[a] Ionization	Young's[b] Modulus (MPa)	Stress at break (MPa)	Elongation at break (%)
M1SNa	93	39.6	32.0	710
M1CNa	98	38.7	5.4	310
M1CNa	57	12.8	19.2	930
M2SNa	94	9.3	25.3	740
M2CNa	99	5.9	26.7	1160
P1SNa	95	14.6	0.50	430
P1CNa	100	5.36	0.80	15
P2SNa	93	5.50	‡	‡
P2CNa	98	8.10	0.97	31

[a] From elemental analysis for sulfur, in the case of sulfonated ionomers, or for sodium, for carboxylated ionomers

[b] Determined as slope of stress-strain curve at 5% elongation.

[‡] PPO(2000) sulfonated ionomers did not break within the extension limits of the instrument.

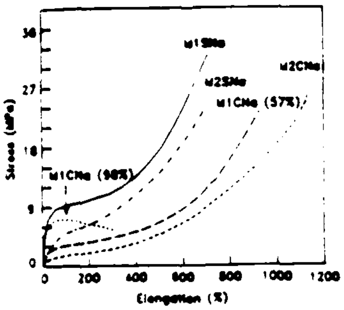

Figure 2. Tensile properties of PTMO/TDI ionomers. Numbers in parentheses indicate percent carboxylation.

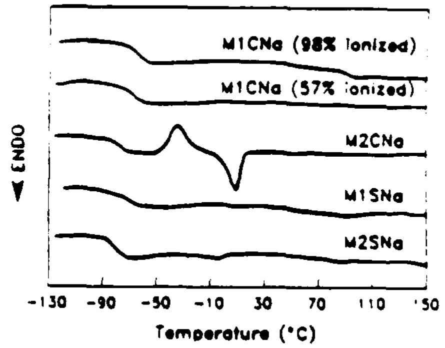

Figure 4. DSC results for PTMO/TDI ionomers

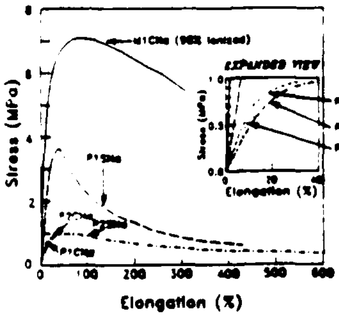

Figure 3. Tensile properties of PPO/TDI ionomers.

Table 2. DSC Results for Polyurethane Ionomers

Sample	Glass transition temperature, Tg			Crystallization peak	Crystalline melting peak
	Onset	Midpoint	Endpoint		
M1SNa	-84°C	-76°C	-69 °C	-	-
M1CNa (57% Ionized)	-77	-70	-60	-	-
M1CNa (98% Ionized)	-80	-67	-60	-	
M2SNa	-88	-80	-75	-	-
M2CNa	-85	-79	-74	-38°C	14°C
P1SNa	-61	-52	-46	-	-
P1CNa	-50	-43	-37	-	-
P2SNa	-66	-62	-58	-	-
P2CNa	-67	-63	-58	-	-