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Thermal and Dynamic Mechanical Properties of Sulfonated Polypentenamers

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A series of sulfonated polypentenamers containing from 1.9 to 17.6 mol % pendant groups in the form of sodium salts was studied by differential scanning calorimetry (DSC) and dynamic mechanical techniques. The composition dependencies of the glass transition temperatures (T_g 's) measured by DSC show typical random copolymer behavior at low levels of sulfonation but deviate significantly from this behavior above 10 mol %. The dynamic mechanical results exhibit an ionic-phase relaxation α that is believed to originate within ionic clusters. The fact that the α relaxation is only present in samples sulfonated above 10 mol % is taken as evidence, along with the T_g behavior, that clustering occurs only above a critical sulfonate concentration of 10 mol % or two sulfonate groups per 100 backbone carbon atoms.

It is usually not possible to alter the nature or concentration of salt groups without significantly affecting such variables as molecular weight, molecular weight distribution, and monomer sequencing, since most ionomers are prepared by copolymerization reactions. This factor presents a serious obstacle to a meaningful study of the effects of the nature and concentration of salt groups on the properties of ionomeric materials. One method of avoiding this drawback is to prepare materials by postpolymerization reactions on a common precursor. It is this concept that has led to our continuing investigation of the properties of modified polypentenamers (PP's).

We reported previously the modification of a PP by phosphorylation (1) and by the addition of thioglycolate side groups (2), and exam-

Table I. Characterization Data for Sulfonated PP's

Sample	% Sulfonation	% Neutralization	T_g ($^{\circ}\text{C}$)
PPSO ₃ Na(2)	1.9	89	-95
PPSO ₃ Na(5)	6.7	72	-85
PPSO ₃ Na(10)	10.8	73	-72
PPSO ₃ Na(15)	14.3	78	-38
PPSO ₃ Na(20)	17.6	74	+31

for dynamic mechanical and DSC measurements. Film preparation was carried out by pressing at 130°–140°C and 10,000 psi for 20 min under nitrogen. The resulting films were stored in a desiccator under vacuum at room temperature in the absence of light until use.

Water-saturated samples were prepared by storing film samples overnight in distilled water at room temperature. Water uptake in these samples was not observed to increase significantly after 4 hr. The rate of water uptake was not measured.

Measurements. DSC measurements were carried out on a Perkin-Elmer Model DSC II. The scanning speed was 20°C/min in all cases, and cyclohexane and indium were used as standards. The temperature range scanned was -120°–100°C.

Dynamic mechanical measurements were carried out on a Vibron Dynamic Viscoelastometer, Model DDV-II (Toyo Measuring Instruments Co.). The temperature range was -160°–200°C and the frequencies used were 3.5, 11, and 110 Hz. Samples were heated at a rate of 1°–2°C/min under dry nitrogen.

Results

The DSC results for three of the sulfonated PP samples are displayed in Figure 1. Sample PPSO₃Na(2) exhibits a very distinct glass transition at -95°C, followed by an exotherm that is centered around -65°C and an endotherm that appears around 11°C. The DSC traces of the remaining sulfonated PP samples display neither an exotherm nor an endotherm, though all of these samples display readily observable glass transitions. The glass transitions detected by DSC for these materials become broadened and increase in temperature as the degree of sulfonation increases. This trend is demonstrated in the scans shown in going from sample PPSO₃Na(5), with a relatively narrow glass transition centered at -85°C, to the most highly sulfonated material in this study, sample PPSO₃Na(20), which displays a glass transition spread over several decades of temperature centered at 31°C. A summary of the DSC-determined T_g 's is given in Table I. When these T_g 's are plotted against the mol % sulfonation determined by elemental analysis, the plot in Figure 2 is obtained. For low levels of sulfonation this plot demonstrates a linear relationship with slightly positive slope, but above 10 mol % sulfonation the DSC-determined T_g 's differ significantly from such linear behavior.

Figure 1. DSC scans recorded at $20^{\circ}\text{C}/\text{min}$ for (a) sample $\text{PPSO}_3\text{Na}(2)$; (b) sample $\text{PPSO}_3\text{Na}(5)$; and (c) sample $\text{PPSO}_3\text{Na}(20)$

Figures 3–6 represent the temperature dependencies of the tensile storage and loss moduli (E' and E'') at 11 Hz for the sulfonated PP's. The E'' behavior of sample $\text{PPSO}_3\text{Na}(2)$ shown in Figure 3 displays three relaxation regions. These three relaxations are labeled α , β , and γ in order of decreasing temperature. Sample $\text{PPSO}_3\text{Na}(5)$ exhibits only two relaxations, a β relaxation at -72°C and a γ relaxation centered around -130°C . As shown in Figure 4, the α relaxation is absent in the E'' plot of sample $\text{PPSO}_3\text{Na}(5)$, but is present around 0°C for sample $\text{PPSO}_3\text{Na}(10)$. In addition, sample $\text{PPSO}_3\text{Na}(10)$ displays a β relaxation at -49°C and a γ relaxation at -120°C . Figures 5 and 6 show the dynamic mechanical responses of both dry and water-saturated samples of materials $\text{PPSO}_3\text{Na}(15)$ and $\text{PPSO}_3\text{Na}(20)$, respectively. In this context “dry” means the sample was stored in a desiccator under vacuum and only exposed to atmospheric moisture, while “water-saturated”

means the sample was allowed to stand submerged in distilled water at room temperature until it reached a constant weight. The dynamic mechanical spectra of the $\text{PPSO}_3\text{Na}(15)$ samples given in Figure 5 show that the dry material displays three relaxations, with the α occurring at 25°C , the β at -35°C , and the γ at -123°C . The water-saturated sample absorbed 72% of its dry weight in water, corresponding to roughly 23 water molecules per sulfonate group. It is seen in Figure 5 that the α relaxation is not observable when the material is saturated with water, but the β and γ relaxations remain at the same temperatures as for the dried samples. Also very noticeable in the dynamic mechanical behavior of sample $\text{PPSO}_3\text{Na}(15)$ is the fact that the tensile storage modulus decreases rapidly at the temperature of the β relaxation for the water-

Figure 2. Composition dependence of the DSC-determined T_g 's for the sulfonated PP's

Figure 3. Temperature dependencies of E' and E'' at 11 Hz for sample $\text{PPSO}_3\text{Na}(2)$

Figure 4. Temperature dependencies of E' and E'' at 11 Hz for samples $\text{PPSO}_3\text{Na}(5)$ (●) and $\text{PPSO}_3\text{Na}(10)$ (○)

Figure 5. Temperature dependencies of E' and E'' at 11 Hz for dry (●) and water-saturated (○) samples of $\text{PPSO}_3\text{Na}(15)$

Figure 6. Temperature dependencies of E' and E'' at 11 Hz for dry (●) and water-saturated (○) samples of $\text{PPSO}_3\text{Na}(20)$

saturated case. However, it decreases much more gradually and in two steps for the dry sample, with these two steps coinciding with the temperatures of the β and α relaxations. For sample PPSO₃Na(20) Figure 6 shows α , β , and γ relaxations for both the dry and water-saturated cases. The E'' plot for the dry material demonstrates that at this level of sulfonation the α relaxation occurring at 12°C is the dominant relaxation mechanism; the β relaxation is reduced in magnitude relative to the less highly sulfonated samples studied, and appears almost as a shoulder on the α relaxation peak. The tensile storage modulus shows virtually no change at the temperature of the β relaxation, but decreases rapidly at the temperature of the α relaxation. At this level of sulfonation the material absorbed 84% of its initial weight when submerged overnight in distilled water. This, as in sample PPSO₃Na(15), corresponds to roughly 23 molecules of water per sulfonate group. The dynamic mechanical behavior of the water-saturated sample as shown in Figure 6 displays an 80°C decrease in the temperature of the α relaxation, from 12°C for the dry sample to -68°C for the water-treated material. At the same time the temperature of the β relaxation remains unaffected, though its magnitude is observed to increase slightly. The γ relaxation becomes narrower and decreases slightly in temperature with water uptake. The tensile storage modulus exhibits a catastrophic decrease in conjunction with the β relaxation at -35°C, rather than at the temperature of the α relaxation as it does in the dry materials. A summary of the temperatures at which each of the relaxations is observed to occur at 11 Hz for the materials investigated in this work is compiled in Table II.

Discussion

The behavior of sample PPSO₃Na(2) when studied by DSC can be explained readily by the fact that PP's containing a high content of trans double bonds are known to form trans double bond-containing crystals (4, 8). Since these crystals have a melting point below room temperature,

Table II. Temperatures* of Relaxations in Sulfonated PP's
(°C at 11 Hz)

Sample	$\alpha(E'')$	$\beta(E'')$	$\gamma(E'')$
PPSO ₃ Na(2)	-8	-77	-130
PPSO ₃ Na(5)	—	-72	-130
PPSO ₃ Na(10)	0	-49	-120
PPSO ₃ Na(15)	25	-35	-123
PPSO ₃ Na(20)	12	-35	-120
PPSO ₃ Na(15);H ₂ O	—	-36	-123
PPSO ₃ Na(20);H ₂ O	-68	-35	-134

* All temperatures have error bounds of $\pm 3^\circ\text{C}$.

the rapid cooling used in the DSC experiment ($\sim 320^\circ\text{C}/\text{min}$) quenches the sample and inhibits crystal formation during the cooling cycle. Upon heating the sample at a rate of $20^\circ\text{C}/\text{min}$ starting from -120°C , crystals form once the temperature of the materials is adequately above T_g . The formation of these trans double bond-containing crystals accounts for the exotherm seen at -65°C , while the endotherm present at 11°C results from the melting of such crystals. Therefore, it is seen in this study that at 1.9 mol % sulfonation, the concentration of pendant sulfonate groups is not high enough to completely disrupt the formation of crystals. However, at 6.3 mol % sulfonation and above, the pendant group concentration is sufficient to suppress crystallization.

The plot of T_g vs. mol % sulfonation shown in Figure 2 is unusual with respect to typical copolymers, but has been observed previously in ion-containing copolymers (9,10). Matsuura and Eisenberg have reported that for ethyl acrylate-based ionomers, the T_g increases linearly with the concentration of salt groups at low concentrations of such groups, but eventually begins to deviate substantially from this typical copolymer-type behavior by rising sharply. Furthermore, it was observed that the concentration of salt groups at which the T_g begins to deviate from the typical copolymer-type linearity is the same concentration at which the time-temperature superposition of viscoelastic behavior is observed to break down. Since such nonsuperposability is taken as evidence for ion clustering (11,12), this seems to suggest that the deviation of T_g from typical copolymer behavior correlates with the critical concentration of salt groups necessary for the formation of microphase-separated domains. If such is the case, the plot of T_g vs. mol % sulfonation shown in Figure 2 indicates the presence of ionic clusters in PP's sulfonated above a level of roughly 10 mol %.

The dynamic mechanical properties of the sulfonated PP's combine with the DSC results to give a much clearer idea of the transition behavior of these materials. However, a discussion of the dynamic mechanical behavior of these derivatives is best understood by examining each relaxation region individually.

α Relaxation. As shown in the results section of this chapter, the α relaxation is present in sample PPSO₃Na(2), disappears for sample PPSO₃Na(5), but then reappears in sample PPSO₃Na(10) and is present in all samples sulfonated above 10 mol %. In addition, for samples sulfonated above 10 mol % the magnitude of the α relaxation increases as the degree of sulfonation increases. In view of the DSC results for these materials and dynamic mechanical studies on PP's with other pendant groups (3,4), it is concluded that the origin of the α relaxation in sample PPSO₃Na(2) differs from that for the more highly substituted materials. For PP's with a high content of trans double bonds that are

either unsubstituted or only substituted to a low degree, an α relaxation is present owing to the melting of the trans double bond-containing crystals. Since sample PPSO₃Na(2) is known from the DSC results to crystallize, it seems likely that the α relaxation for this materials is attributable to the melting of these crystals. The absence of an α relaxation in PPSO₃Na(5), which is known from DSC to be noncrystalline, tends to verify this assignment.

The concentration of sulfonate groups at which the DSC-determined T_g 's begin to deviate from typical copolymer behavior corresponds with the concentration of sulfonate groups at which the mechanical α relaxation reappears. The fact that the magnitude of the α relaxation increases as the degree of sulfonation increases suggests that it is related to a separate ionic phase. This postulate is reinforced further by the fact that the α relaxation is "plasticized" or decreases substantially in temperature when the sulfonated PP samples are saturated with water. If a separate ionic phase, such as the proposed ionic clusters (6, 7), is present in these materials one would expect water to migrate to this phase and avoid the hydrocarbon matrix. Such behavior would result in a preferential plasticization of ionic-phase relaxations with little or no effect on hydrocarbon relaxations. This is exactly the type of phenomenon observed in these samples if the α relaxation is assigned to the ionic phase and the β relaxation to the amorphous hydrocarbon matrix. This leads to the conclusion that the α relaxation observed in samples sulfonated above 10 mol % is in fact attributable to a relaxation mechanism that occurs in a separate ionic phase and is evidence for the presence of ionic clusters in the sulfonated PP's. Moreover, the dependence of the ionic-phase α relaxation on sulfonate concentration suggests that ionic clusters occur only above a critical concentration of roughly 10-mol % sulfonation. This conclusion is consistent with the interpretation given for the T_g behavior of these materials.

β Relaxation. The β relaxation is believed to be created by the microbrownian segmental motion that accompanies the glass transition of the amorphous hydrocarbon matrix. The manner in which the β relaxation magnitude changes as the sulfonate concentration changes suggests its amorphous hydrocarbon-phase origin. For sample PPSO₃Na(2), which is slightly crystalline, the magnitude of the β relaxation is less than that of the completely amorphous sample PPSO₃Na(5). For samples PPSO₃Na(10), PPSO₃Na(15), and PPSO₃Na(20), the magnitude of the β relaxation decreases as the degree of sulfonation increases, attributable to the increasing volume of material present in the ionic phase. The large decrease in storage modulus accompanying the β relaxation further indicates that it arises from the glass-to-rubber transition. However, the most conclusive evidence is the correlation that exists between the DSC-

determined T_g 's and the β relaxation temperatures. With the exception of sample PPSO_3Na (20), this correlation is good. In the case of sample PPSO_3Na (20), it is possible that the second-order transition observed by DSC corresponds to the dominant α relaxation of the ionic phase rather than the glass transition of the amorphous hydrocarbon phase.

γ Relaxation. All of the sulfonated PP's display a well-defined mechanical γ relaxation. It has long been known that three or more CH_2 units in sequence are necessary for the appearance of a γ relaxation (13), and it has been proposed that a crankshaft motion of the three methylene groups between the double bonds, based on the mechanism of Boyd and Breitling (14), can account for the γ process observed in unsubstituted PP's (15,16). It seems likely that this same mechanism explains the mechanical γ relaxation observed for the sulfonated materials. The fact that the phosphonate- (3), thioglycolate- (4), and cyano- (17) substituted PP's exhibit identical behavior in this region further reinforces the proposal that the γ relaxation mechanism involves segments of the polymer chain other than the pendant groups.

Conclusions

The dynamic mechanical and DSC results for sulfonated PP's combine to give strong evidence for the existence of ionic clusters in these materials. In addition they suggest that these clusters are only present above a critical sulfonate concentration of 10 mol %. These conclusions are based on the existence of an ionic-phase α relaxation for materials sulfonated above 10% and the deviation of the T_g vs. % sulfonation plot from typical copolymer-type behavior at this same concentration.

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Literature Cited

1. Azuma, C.; MacKnight, W. J. *J. Polym. Sci., Polym. Chem. Ed.* 1977, 15, 547.
2. Sanui, K.; Lenz, R. W.; MacKnight, W. J. *J. Polym. Sci., Polym. Chem. Ed.* 1974, 12, 1965.
3. Rahrig, D.; Azuma, C.; MacKnight, W. J. *J. Polym. Sci., Polym. Phys. Ed.* 1978, 16, 59.
4. Sanui, K.; MacKnight, W. J. *Br. Polym. J.* 1976, 8, 22.
5. Rahrig, D.; MacKnight, W. J.; Lenz, R. W. *Macromolecules* 1979, 12, 195.

6. MacKnight, W. J.; Taggart, W. P.; Stein, R. S. *J. Polym. Sci., Polym. Symp.* 1974, 45, 113.
7. Eisenberg, A.; King, M. "Ion-Containing Polymers"; Stein, R. S., Ed.; Academic: New York; 1977.
8. Tucker, H.; Minchak, R. J.; Macey, J. H. *Polym. Eng. Sci.* 1975, 15, 360.
9. Matsuura, H.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* 1976, 14, 1201.
10. Noshay, A.; Robeson, L. M. *J. Appl. Polym. Sci.* 1976, 20, 1885.
11. Eisenberg, A.; Navratil, M. *Macromolecules* 1973, 6, 604.
12. Eisenberg, A.; Navratil, M. *Macromolecules* 1974, 7, 84.
13. McCrum, N. G.; Read, B. E.; Williams, G. "Anelastic and Dielectric Effects in Polymeric Solids"; Wiley: New York, 1967; Chapter 10.
14. Boyd, R. H.; Breitling, S. M. *Macromolecules* 1974, 7, 855.
15. Sanui, K.; MacKnight, W. J.; Lenz, R. W. *Macromolecules* 1974, 7, 101.
16. Earnest, Jr., T. R.; MacKnight, W. J. *Macromolecules* 1977, 10, 206.
17. Neumann, R.; Sanui, K.; MacKnight, W. J. *Macromolecules* 1975, 8, 665.

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