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Thermal, Dynamic Mechanical, and Dielectric Properties of Hydrogenated, Sulfonated Polypentenamers

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Hydrogenated, sulfonated polypentenamers containing from 2.9 to 19.1 mol % pendant groups in the form of sodium salts were examined by differential scanning calorimetry (DSC) and dynamic mechanical and dielectric relaxation techniques. DSC results display two endotherms and provide evidence of a room-temperature annealing phenomenon. Four relaxations, α , β , γ' , and γ , in order of decreasing temperature, are observed dynamic mechanically. The α relaxation is composite in origin but appears to arise partially from an ionic-phase mechanism which suggests the existence of ionic clusters. The β relaxation is related to the glass transition and is affected by the crystalline content. Large increases in ϵ' and $\tan \delta_\epsilon$ accompany the dielectric results. A dielectric α relaxation displays behavior that parallels that of the mechanical α peak.

We have reported previously the sulfonation of a polypentenamer (PP) under reaction conditions that preclude the formation of covalent cross-links (1). The sulfonated materials are isolated in the form of sodium salts to give ion-containing elastomers. The thermal and dynamic mechanical properties of the sulfonated PP's indicate the existence of phase-separated ionic clusters above a sulfonate concentration of roughly 10 mol % (2). It has been shown (1) that the unsaturation in the sulfonated PP's can be removed by a diimide hydrogenation reaction to yield a material that is essentially linear polyethylene with pendant sulfonate groups. In this manner the effect of backbone crystallinity on

the ability of an ion-containing polymer to form phase-separated domains can be investigated.

By conducting a study on sulfonated PP's and their hydrogenated derivatives, it is possible to look at materials that have identical chain backbones. As a result, such complications as variations in molecular weight, molecular weight distribution, and monomer sequencing can be eliminated. In this study we have used thermal, dynamic mechanical, and dielectric relaxation techniques to investigate four series of hydrogenated, sulfonated PP's. The level of sulfonation present in these systems ranges from 2.9 to 19.1 mol %. By varying the sulfonate concentrations and thermal histories of the samples in this study, much can be learned about the origins of the various relaxations that these materials display. The results of this investigation can then be compared with the results of previous investigations carried out in this laboratory on the properties of phosphonylated (3) and thioglycolate-substituted (4) PP's. This comparison will yield a better understanding of the effects of the nature and concentration of pendant ionic groups on the behavior of ion-containing polymers.

The desired comparisons of this study are obscured somewhat by three factors. The first and most serious of these is the fact that elemental analysis of the hydrogenated, sulfonated PP's indicates the presence of nitrogen in these materials. While the weight percent of nitrogen is low, its exact origin cannot be determined. It is found that the amount of nitrogen present increases as the degree of sulfonation increases. This suggests that the nitrogen results either from a side reaction during the hydrogenation step which is aided by the pendant sulfonate groups or from dimethyl formamide (DMF), the solvent used in the hydrogenation reaction, which is "bound" to the polar polymer. A second drawback is the fact that the degree of ionization in these materials varies from a low of 64% to a high of 100%. A third factor is that the sulfonate salts pendant to the hydrogenated-PP backbone have a propensity to absorb water from the atmosphere. As a result the materials investigated in this study are not completely dry but do hold some water.

The dynamic mechanical results of this study demonstrate that backbone crystallinity plays an important role in the properties of these materials. Moreover, it is observed that thermal history affects the properties of the materials investigated in a more complex manner than can be explained by simple changes in the degree of crystallinity. At low levels of sulfonation the materials generally behave very much like linear polyethylene, but this behavior is modified significantly as the level of sulfonation is increased. Evidence is clearly present for the existence of an ionic-phase relaxation that supports the proposed model for micro-phase-separated domains (5,6,7). However, owing to the effects of crystallinity the concentration at which the ionic-phase relaxation first

occurs cannot be determined unambiguously. While the dielectric results are consistent with the conclusions drawn from the dynamic mechanical investigation, the known presence of impurities in these systems and the occurrence of an undetermined interfacial phenomenon prohibit a rigorous interpretation of the data obtained in the dielectric experiments.

Experimental

Materials. The starting PP was kindly provided by the Goodyear Tire and Rubber Company. It contains 82% trans and 17% cis double bonds with fewer than 1% vinyl side groups. The molecular weight averages are $\bar{M}_n = 172,000$ and $\bar{M}_w = 470,000$. The PP was sulfonated using a 1:1 complex of sulfur trioxide to triethyl phosphate in chloroform at room temperature. The sulfonated material was neutralized by precipitating the reaction mixture into a 0.25M solution of NaOH in ethanol. The unsaturated product was then stabilized with hydroquinone, dried, put into solution using a mixed solvent system of DMF with a chlorinated aromatic (either chlorobenzene or 1,2,4-trichlorobenzene), and treated with *p*-toluenesulfonyl hydrazide (TSH). The reaction scheme is detailed elsewhere (1) and summarized below:

Characterization data for the samples investigated in this study are collected in Table 1.

The hydrogenated, sulfonated PP's were compression molded into films suitable for differential scanning calorimetry (DSC), dynamic mechanical, and dielectric measurements. Films were prepared by preheating at 140°–145°C for 5 min and then pressing at 140°–145°C and 20,000 lb for 5 min. Annealed samples were prepared by placing air-cooled films between two metal platens and storing them in a vacuum oven at 80°C for 3 days. The platens were necessary to prevent the films

Table I. Characterization Data for Hydrogenated, Sulfonated PP's

Sample	Mol % Sulfonation	% Neutralization	Wt % Nitrogen
HyPPSO ₃ Na (2)	2.9	66	0.37
HyPPSO ₃ Na (5)	6.3	84	1.02
HyPPSO ₃ Na (10)	9.4	> 100	1.54
HyPPSO ₃ Na (20)	19.1	64	3.48

from becoming fluted during the annealing process. Quenched materials were prepared by submerging the films in a dry ice-isopropanol bath immediately after they were removed from the press. The resulting quenched and annealed films were stored in a desiccator under vacuum at room temperature and in the absence of light until use.

Water-saturated samples were prepared by storing film samples overnight in distilled water at room temperature. The rate of water uptake was not measured.

Measurements. DSC measurements were carried out on a Perkin-Elmer instrument, Model DSC II. The scanning speed was 20°C/min in all cases, and indium was used as a standard. The temperature range scanned was -50°-180°C. The peak temperature of the melting endotherm was taken as the melting point of the polymer crystals.

Dynamic mechanical measurements were carried out on a Vibron dynamic viscoelastometer, Model DDV-II (Toyo Measuring Instruments Co.). The temperature range was from -160° to 150°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.

Dielectric measurements were carried out using a General Radio Corporation capacitance-measuring assembly of the transformer-ratio-arm bridge type (Model 1620 A), in conjunction with a three-terminal cell (Balsbaugh type LD-3) having 53-mm diameter electrodes. Capacitance and $\tan \delta_e$ measurements were carried out at 0.1, 1, 10, and 100 kHz over a temperature range of -160°-100°C. Low-temperature variation was achieved by cooling the cell with liquid nitrogen and then regulating the flow of dry, chilled nitrogen gas through the cell. Heating above room temperature was achieved with a heating element regulated by two variacs, and was accompanied by a steady flow of dry nitrogen through the sample chamber. The temperature was increased at a rate of 1°-2°C/min throughout the experiment. DC resistance measurements were made using a General Radio megohmmeter, Type 1852A. To prevent the films from sticking to the electrode surface, one side was covered with a thin layer of aluminum foil.

Results

Differential Scanning Calorimetry. The DSC traces obtained at a scan rate of 20°C/min for the hydrogenated, sulfonated PP's are somewhat unique in that two distinct endotherms are present in all of the samples. Figure 1 shows the DSC behavior of the quenched HyPPSO₃Na samples. From this figure it can be seen that the low-temperature endotherm occurs between 55° and 60°C for each sample and increases in

Figure 1. DSC results for quenched films of HyPPSO₃Na

Figure 2. DSC results for $\text{HyPPO}_3\text{Na}(10)$ films with the following thermal histories: (A) annealed 3 days at 80°C and stored 30 days at room temperature; (B) quenched and immediately observed; (C) annealed $1/2$ hr at 25°C ; (D) annealed 1 hr at 25°C ; (E) quenched and stored at room temperature for 30 days.

magnitude as the degree of sulfonation increases. The higher-temperature endotherm, on the other hand, decreases in both magnitude and temperature as the level of sulfonation increases. The existence of a second, low-temperature endotherm in the DSC curves of ethylene-based ionomers has been observed previously (8) and has been related to a room-temperature annealing phenomenon. As a result, the effect of room-temperature annealing on the DSC behavior of Sample $\text{HyPPO}_3\text{Na}(10)$ was investigated. The results are shown in Figure 2. It is clear from these data that increasing the time a sample is maintained at room temperature causes a resulting increase in the magnitude of the endotherm that occurs around 55°C . However, no significant change takes place in the higher-temperature endotherm.

Table 2 lists the weight percent crystallinities determined for the samples in this study. These represent the ratio of $\Delta H_t/\Delta H_u$, where ΔH_t is the experimental enthalpy of fusion and ΔH_u the enthalpy of fusion for the hypothetical 100% crystalline polymer. Since the samples in this study display two endotherms, ΔH_t is based on the entire area enclosed by the two peaks, including the area between the two peaks, since the DSC curve does not return to the original baseline over this portion of the scan. Owing to the bulkiness of the sulfonate group, it is assumed that these groups are excluded completely from the crystalline phase. As a result, the value of ΔH_u determined by the polymer-diluent technique for fully hydrogenated PP's, evaluated as 59 cal/g (9), was used. While this value is appropriate for an unsubstituted, fully hydrogenated-PP crystal of infinite thickness, it might be reduced if the crystals are small. In addition, while the sulfonate groups may be excluded from the crystal lattice, their presence at the crystalline surface may distort the crystal lattice and thereby reduce ΔH_u further. However, in spite of these drawbacks the DSC results seem to give a good relative determination of the crystallinity present in these systems.

Dynamic Mechanical Measurements. The dynamic mechanical results for both quenched and annealed samples of the four materials investigated are presented in the form of E' and E'' plots against temperature in Figures 3–6. These figures show the presence of four relaxation regions (α , β , γ' , and γ in order of decreasing temperature) in each of the samples examined. The labeling of these relaxations is based on the nomenclature used for polyethylene. For Sample HyPPSO₃Na(2) shown in Figure 3 it is seen that the temperature and magnitude of the α relaxation increase with annealing, while the β and γ relaxations demonstrate virtually no change associated with the thermal history. The

Table II. Wt % Crystallinities and Melting Points of HyPPSO₃Na Films for Rheovibron and Dielectric Studies

Sample	Mechanical		Dielectric	
	Wt % Crystallinity	T_m (°C)*	Wt % Crystallinity	T_m (°C)*
HyPPSO ₃ Na(2)A	54	127	54	126
HyPPSO ₃ Na(2)Q	47	122	39	124
HyPPSO ₃ Na(5)A	52	120	46	119
HyPPSO ₃ Na(5)Q	37	120	32	118
HyPPSO ₃ Na(10)A	34	115	27	116
HyPPSO ₃ Na(10)Q	22	107	21	107
HyPPSO ₃ Na(20)A	13	96	4	96
HyPPSO ₃ Na(20)Q	9	97	—	—

* Taken as the point where the melting endotherm displays maximum excursion from the baseline in the DSC scan.

Figure 3. Dynamic mechanical results for HyPPO₃Na(2) at 11 Hz: (●) annealed; (○) quenched

Figure 4. Dynamic mechanical results for HyPPSO₃Na(5) at 11 Hz: (●) annealed; (○) quenched

Figure 5. Dynamic mechanical results for HyPPSO₃Na(10) at 11 Hz: (●) annealed; (○) quenched

Figure 6. Dynamic mechanical results for HyPPSO₃Na(20) at 11 Hz: (●) annealed; (○) quenched

relaxation labeled γ' does appear somewhat larger for the annealed case than for the quenched sample. Samples HyPPSO₃Na(5) and HyPPSO₃Na(10) react identically to their changing thermal histories. The α relaxation is observed to increase in both magnitude and temperature on annealing, while the β and γ' relaxations remain relatively unchanged with respect to temperature, though somewhat greater in magnitude in going from the annealed to the quenched case. The thermal history of both samples has essentially no effect on the behavior of the α relaxation. A discussion of the effect of thermal history on the behavior of Sample HyPPSO₃Na(20) must be prefaced by noting that the annealing temperature of 80°C used in this study is very close to the melting temperature observed by DSC for this material. Therefore the change in crystallinity between the quenched and annealed samples is quite small, as shown in Table II. Nonetheless Figure 6 demonstrates the fact that the α relaxation increases somewhat in magnitude while decreasing just slightly in temperature with annealing. The β relaxation, which is distinct in the quenched case, merges with the α relaxation peak to become virtually indistinguishable in the annealed sample. Both the γ' and γ relaxations increase in magnitude on annealing, while displaying no change in position. A summary of the relaxation temperatures determined for these samples at 11 Hz is given in Table III. From this table it can be seen that the temperatures of both the α and γ' relaxations clearly decrease as the degree of sulfonation is increased. For both the quenched and annealed cases the β relaxation is seen to increase in temperature on going from Sample HyPPSO₃Na(2) to Sample HyPPSO₃Na(5), but then drop as the degree of sulfonation is increased above the level found in Sample HyPPSO₃Na(5). The temperature of the γ relaxation displays no significant change with variations in the sulfonation level.

The effect of water on the dynamic mechanical behavior of a hydrogenated, sulfonated PP is displayed in Figure 7 for a quenched film of Sample HyPPSO₃Na(20). The sample labeled "dry" had been stored in

Table III. Temperatures* of Mechanical Relaxations in Hydrogenated, Sulfonated PP's (°C at 11 Hz)

Sample	γ	γ'	β	α (E'')	α ($\tan \delta$)
HyPP	-115	—	-3	80	100
HyPPSO ₃ Na(2) A	-115	-45	20	60	95
HyPPSO ₃ Na(5) A	-113	-50	30	55	80
HyPPSO ₃ Na(10) A	-115	-80	15	50	68
HyPPSO ₃ Na(20) A	-133	-83	-20	15	45
HyPPSO ₃ Na(2) Q	-133	-60	10	43	80
HyPPSO ₃ Na(5) Q	-110	-60	12	43	62
HyPPSO ₃ Na(10) Q	-120	-65	0	46	55
HyPPSO ₃ Na(20) Q	-120	-90	-33	25	45

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

Figure 7. Effect of water on the dynamic mechanical results for a quenched film of HyPPSO₃Na(20) at 11 Hz: (●) dry; (○) water saturated

a desiccator under vacuum at room temperature until studied and had been exposed only to the moisture in the air. The water-plasticized sample, on the other hand, had been stored overnight in a beaker of distilled water at room temperature. This process resulted in a water uptake equivalent to 43% of the initial weight of the sample, which corresponds to roughly 11 water molecules per sulfonate group. It can be seen in Figure 7 that the α relaxation, which is the dominant relaxation mechanism in this material, is shifted from a temperature of 25°C for the dry sample to -70°C for the water-plasticized sample. This result parallels the behavior seen previously in water studies on the unhydrogenated, sulfonated PP's (2).

The α relaxation region undergoes significant changes as the degree of sulfonation is increased. This is best demonstrated in the plot of $\tan \delta$ vs. temperature given in Figure 8 for annealed films of the four materials studied. The magnitude of the α relaxation peak is seen to increase steadily with increasing sulfonation, while its position clearly decreases in temperature. Figure 9 shows the $\tan \delta$ vs. temperature behavior of both quenched and annealed films of Sample HyPPSO₃Na(10). Thermal history alters the behavior of the α relaxation in a different fashion than does the level of sulfonation. While increasing the level of sulfonation causes the magnitude of the α relaxation to increase with a corresponding temperature decrease, annealing causes both magnitude and temperature to increase. The α relaxation temperatures determined from $\tan \delta$ measurements are included in Table III.

Dielectric Measurements. Dielectric measurements on the hydrogenated, sulfonated PP's suffer from several drawbacks. Among these are the fact that (1) these materials are known to possess some absorbed water; (2) they contain a small amount of nitrogen in an undetermined form; and (3) they are heterogeneous in that they contain both an amorphous and a crystalline phase as well as an apparent ionic phase. A comparative plot of $\tan \delta_e$ values against temperature for three of the samples is displayed in Figure 10. It is seen that the behavior of the observed relaxation, which we have labeled α , correlates well with the behavior of the mechanical α relaxation. Both are found to increase in magnitude and decrease in temperature as the degree of sulfonation increases. For Sample HyPPSO₃Na(2) the $\tan \delta_e$ vs. temperature plot does not display a relaxation maximum in this region, though the magnitude of $\tan \delta_e$ does increase continuously above -40°C and reaches a value of 0.15 at 100°C. However, the $\tan \delta_e$ values measured for Samples HyPPSO₃Na(5), (10), and (20) are extremely large and clearly continue to increase sharply above the relaxation region. Correcting for dc conductivity results in only a moderate decrease in the $\tan \delta_e$ values. It appears that the α relaxation is superimposed on some other phenomenon occurring in these materials, obscuring the dielectric relaxation studies.

Figure 8. Comparative $\tan \delta$ results for annealed HyPPSO_3Na films in the region of the α relaxation: (●) $\text{HyPPSO}_3\text{Na}(2)$; (○) $\text{HyPPSO}_3\text{Na}(5)$; (▲) $\text{HyPPSO}_3\text{Na}(10)$; (△) $\text{HyPPSO}_3\text{Na}(20)$

The behavior of the $\tan \delta_\epsilon$ below 0°C for all four of the materials investigated is displayed in Figure 11. A low-temperature dielectric relaxation centered between -70° and -80°C appears to exist in these systems. This relaxation is labeled β . The magnitude of the β relaxation clearly increases as the degree of sulfonation increases. For the more highly sulfonated samples the β relaxation appears as a low-temperature shoulder on the much larger α relaxation, but in all cases the β relaxation is distinguishable. No evidence for any dielectric relaxations other than the α and β is present in these materials.

Figure 10. The $\tan \delta_\epsilon$ behavior for annealed HyPPSO_3Na materials in the region of the α relaxation: (●) $\text{HyPPSO}_3\text{Na}(5)$; (○) $\text{HyPPSO}_3\text{Na}(10)$; (▲) $\text{HyPPSO}_3\text{Na}(20)$

Figure 11. The $\tan \delta_\epsilon$ behavior for annealed HyPPSO_3Na materials at low temperatures: (●) $\text{HyPPSO}_3\text{Na}(2)$; (○) $\text{HyPPSO}_3\text{Na}(5)$; (▲) $\text{HyPPSO}_3\text{Na}(10)$; (△) $\text{HyPPSO}_3\text{Na}(20)$

While the $\tan \delta_\epsilon$ values measured for the materials in this study are unusually large, the dielectric constants measured likewise increase tremendously in the region of the α relaxation. Figure 12 shows the temperature dependence of ϵ' at 0.1 kHz for an annealed film of Sample $\text{HyPPSO}_3\text{Na}(10)$. The value of ϵ' for this material increases so rapidly that the figure was prepared by plotting $\log \epsilon'$ against temperature. Such a large change in the ϵ' value cannot be accounted for by a simple orientational dielectric relaxation mechanism. Similar ϵ' behavior was seen for Samples $\text{HyPPSO}_3\text{Na}(5)$ and $\text{HyPPSO}_3\text{Na}(20)$.

Figure 12. Temperature dependence of $\log \epsilon'$ for an annealed film of Sample HyPPSO₃Na(10)

Discussion

Thermal Properties. The results of the DSC experiments on the HyPPSO₃Na systems display both a high-temperature and a lower-temperature endotherm for all samples investigated. The nature of the high-temperature peak is unaffected by annealing at room temperature for long periods of time. However, annealing at 80°C for three days causes this high-temperature endotherm to increase in both magnitude and temperature, and become significantly sharpened. While the high-temperature endotherm is independent of effects occurring at room temperature, the lower-temperature peak exists only when the material has been maintained at ambient conditions for a moderate period of time. The magnitude of this endotherm is related both to the amount of time a sample spends at room temperature and to the level of sulfonation. Its temperature is independent of composition, but it does appear to be a function of the time maintained at room temperature.

According to Flory (10) the dependence of the equilibrium melting point on the concentration of crystallizable units in a random copolymer should be given by the equation

$$1/T_m - 1/T_m^\circ = -(R/\Delta H_u) \ln N_A \quad (3)$$

where T_m is the melting point of the copolymer, T_m° that of the crystalline homopolymer, N_A the mole fraction of crystallizable units in the copolymer, and ΔH_u the heat of fusion per mole of homopolymer repeat unit. A plot of $1/T_m$ vs. $-\ln N_A$ for annealed films of the HyPPSO₃Na copolymers is given in Figure 13, where T_m is taken as the temperature at which the high-melting endotherm displays maximum excursion from the baseline. It is seen that a straight line results and that the intercept gives a T_m° value of 132.5°C. This agrees well with the T_m of 131°C determined experimentally for the completely hydrogenated PP (9). The slope yields a ΔH_u value of 347 cal/mol of $-\text{CH}_2-$, which is less than half of the ΔH_u value of 802 cal/mol of $-\text{CH}_2-$ determined by the polymer-diluent technique for fully saturated PP. However, it is commonly seen for polymers that the ΔH_u value determined by the copolymer method is less than that determined by the diluent method (11). This discrepancy is generally attributed to both the inability to measure the equilibrium melting point in such systems and the inability to achieve equilibrium conditions during the crystallization process. It is seen then that the position of the high-temperature endotherm depends qualitatively on composition in the manner predicted by theory for random copolymers. Its failure to comply quantitatively with theory is typical of most copolymer systems.

Marx and Cooper have demonstrated that in ethylene-based ionomers, the ease of forming a low-temperature melting peak in the DSC

Figure 13. Plot of $1/T_m$ vs. $-\ln N_A$ for annealed films of hydrogenated, sulfonated PP's ($1/T_m - 1/T_m^\circ = (-R/\Delta H_\mu) \ln N_A$; $\Delta H_\mu = 347 \text{ cal/mol } (-CH_2-)$; $T_m^\circ = 132.5^\circ C$)

scan by annealing at room temperature increases slightly in going from low-density polyethylene to ethylene-methacrylic acid copolymers, but is augmented dramatically when the methacrylic acid units are neutralized to sodium salts (8). Since the acid and salt groups are assumed to be excluded from the crystal lattice, Marx and Cooper suggest that the distance between the noncrystallizable repeat units in each chain segment is the maximum lamellar thickness into which that chain segment can fit. They propose that long, uninterrupted runs of ethylene repeat units give rise to the crystals that melt at the higher temperatures while crystallites composed of short, imperfect polyethylene segments between more closely spaced acid or salt groups result in the lower-melting crys-

tals. However, this does not explain the reason for discrete endotherms as opposed to one quite broad melting peak, nor does it address the question of why the effect is more distinct for the ion-containing systems than for the ethylene-methacrylic acid copolymers.

It has been shown that in ethylene-methacrylic acid copolymers, the supercooling required before crystallization occurs increases as the acid groups are neutralized (12, 13). This phenomenon has been attributed to the increase in melt viscosity, which has been shown to be significantly higher in ionomers than in ethylene-methacrylic acid copolymers or in unsubstituted polyethylene (14). If the changes in supercooling and melt viscosity are considered along with the ideas proposed by Marx and Cooper, an explanation for the thermal behavior of the HyPPSO_3Na systems can be proposed. The longer, uninterrupted runs of polyethylene repeat units crystallize on cooling to yield the higher-melting crystals. The average length of such runs, and therefore the resulting lamellar thickness, decreases as the level of sulfonation increases. This explains the dependence of the high-temperature endotherm position on composition. High local viscosity causes the shorter polyethylene segments between closely spaced pendant groups to refrain from crystallizing initially on quenching. When the samples are annealed at 80°C for three days, the annealing temperature causes all but the longest polyolefin sequences to melt. However, when the samples are stored at room temperature for reasonable periods of time these smaller polyethylene segments gradually crystallize. The size of these secondary crystals is so small, though, that their lamellar thickness is undisturbed by increased levels of substitution. This explains the failure of the lower-temperature endotherm to display a temperature dependence on composition. Annealing at room temperature results in thickening of the small lamellae, which accounts for the slight increase in the melting point of the small crystals after several days at room temperature. The increased magnitude of the low-temperature endotherm with increasing sulfonation simply reflects the greater number of short ethylene sequences as the number of pendant groups is raised.

Since the lower-melting crystallites are assumed to be in the form of chain-folded lamellae, a first approximation of the thickness expected for these lamellae can be obtained from the equation

$$T_m = T_m^\circ (1 - 2\sigma_e/l\Delta H_u) \quad (4)$$

where T_m is the measured melting temperature, T_m° the melting point of an infinitely thick crystal, σ_e the surface free energy, l the lamellar thickness, and ΔH_u the heat of fusion. This equation has been derived in several crystallization theories including those of Lauritzen and Hoffman (15), Frank and Tosi (16), and Sanchez and DiMarzio (17). Using

values of the variables determined for polyethylene, the lamellar thickness of those crystallites melting at 57°C is calculated to be between 35 and 42 Å, depending on which values of σ_e , T_m° , and ΔH_u are used. Since the polyethylene unit cell displays a spacing of 2.53 Å along the fiber axis, and since this unit-cell distance incorporates two methylene groups (18), the lamellar thickness determined using this equation corresponds to between 27 and 33 methylene groups. Obviously the average spacing between sulfonated groups will depend on the degree of sulfonation for the HyPPSO₃Na materials, but from synthetic work it is known that sulfonation occurs preferentially across the cis double bonds (1). If successive cis bonds are sulfonated, then the average distance between the sulfonate groups should be roughly six repeat units, based on the cis/trans ratio of the starting PP. For the hydrogenated derivatives this corresponds to 28–30 methylene groups. It would appear from these rough calculations, then, that the polyethylene segments between the more closely spaced pendant groups are long enough to account for the lower-melting crystals.

The fact that crystals can be formed and annealed at room temperature in these systems can also be cited as evidence that the glass transition temperature (T_g) of these materials is sufficiently below room temperature. If the amorphous material were glassy at room temperature, there could not be sufficient large-scale motion to allow the formation of such crystals. This information can be applied in the interpretation of the dynamic mechanical relaxations as will be seen. No indication of a glass-to-rubber relaxation was found in the DSC scans of these materials.

Dynamic Mechanical Properties. Hydrogenation of sulfonated PP's to give a crystallizable backbone results in significant changes in the dynamic mechanical properties of the materials. When the unsaturated linkages are converted to methylene groups, the rather clear-cut behavior of the ion-containing elastomers is transformed to a much more complex behavior affected by such variables as thermal history and degree of crystallinity. As a result, the dynamic mechanical behavior of the HyPPSO₃Na materials should be examined in the light of previous studies on polyethylene, ethylene-based ionomers, and hydrogenated PP's as well as unsaturated, sulfonated PP's. This is best accomplished by analyzing each relaxation region independently as is done in the following discussion.

α RELAXATION. The α relaxation in polyethylene (19), hydrogenated PP's (20, 21), and ethylene-based copolymers (22) is found to depend on the presence of polyethylene crystals. This relaxation generally is accepted as being composite in nature, arising from both an interlamellar slip process (23, 24) and intracrystalline motion involving the simultaneous rotation and translation of chains within the crystal (25). For hydrogenated PP's, three partially merged α peaks are observed in the samples

with a sufficient level of crystallinity. All three of these peaks display a general increase in both magnitude and temperature with increasing crystallinity (20).

The behavior of the α relaxation is more complex for the HyPPSO₃Na materials. At any fixed level of sulfonation, annealing succeeds in increasing the temperature and magnitude of the α process. However, as the level of sulfonation is increased, the magnitude of the α relaxation peak also increases, despite the fact that crystallinity drops significantly in this direction. In addition it is observed that while the magnitude of the α peak increases with increasing sulfonation, the temperature decreases correspondingly. Such behavior indicates that this α mechanism differs from that detected in polyethylene. It is proposed that the α relaxation observed in the HyPPSO₃Na materials results from the superposition of two distinct processes. The one process is the composite α relaxation process normally observed in polyethylene-based systems of sufficient crystallinity. As the crystallinity of the materials studied decreases, the contribution of this complex process to the α peak also decreases. Accompanying this crystallinity-related process, though, is another relaxation mechanism originating in a separate ionic phase. It has been suggested previously (26, 27) that a relaxation reflecting motion in ionic clusters or domains should occur in ionomer systems and, in the case of monovalent salts, should appear in the temperature range of 50°–100°C. Such a relaxation has been observed in ethylene-methacrylic acid- and ethylene-acrylic acid-based ionomers (28, 29, 30, 31), in phosphonylated low-density polyethylene (32), and in the sodium salts of hydrogenated, thioglycolate-substituted PP's (4). Evidence in this study suggests that a similar process contributed greatly to the α relaxation observed in the HyPPSO₃Na systems.

The proposal that the α relaxation is attributable in part to a relaxation mechanism occurring in microphase-separated ionic clusters is based on several factors. The fact that the α peak increases in magnitude with increasing sulfonation indicates that this relaxation is related either to the behavior of an ionic-phase or an amorphous-phase mechanism, since crystallinity decreases as the sulfonation level is raised. However, the trend of the α peak to increase in magnitude and temperature with annealing contradicts the assignment of this peak to an amorphous-phase origin. Previous small-angle x-ray work on ethylene-acrylic acid-based ionomers (33) suggests that annealing either increases or alters the morphology of phase-separated ionic clusters. Therefore the annealing behavior of the α relaxation is consistent with the ionic-phase assignment. However, the strongest support for the proposed assignment is found in the water studies conducted on these materials. If a separate ionic phase is present in the systems studied, one would expect water to migrate to the ionic clusters and avoid the more hydrophobic amorphous and crys-

talline hydrocarbon regions. As Figure 7 shows for the quenched film of Sample HyPPSO₃Na(20), the dominant α relaxation is shifted downward almost 95°C when the material is saturated with water. This demonstrates the significant plasticizing effect that water has on the α relaxation mechanism, and reinforces the assignment of the α relaxation to an ionic-phase origin.

The trend of the α relaxation to decrease in temperature with increasing sulfonation is related to the hydrophilicity of these materials. As the level of sulfonation is raised, the ability of the materials to absorb water from the air also is raised. Though attempts were made to keep these systems reasonably free from water, stringent drying procedures were not used nor were extraordinary handling precautions taken to prevent the samples from having normal contact with the atmosphere as they were being prepared for dynamic mechanical testing. As the water study on these materials demonstrates, moisture can reduce the temperature of the α relaxation significantly. Thus it would appear that the varying amounts of water absorbed by the HyPPSO₃Na materials from the atmosphere account for the decreasing temperature of the α relaxation with increasing sulfonation.

β RELAXATION. The mechanism that accounts for the β relaxation in polyethylene has been a matter of controversy for years (19, 34, 35). Studies on hydrogenated PP's (17, 18) have concluded that this relaxation is attributable to the microbrownian segmental motion accompanying the glass transition, and propose that the T_g is very dependent on crystallinity. Succeeding studies on substituted, hydrogenated PP's have likewise associated the observed β relaxations with motions accompanying the glass transition (3, 4, 36). In view of this background and the fact that the β relaxation in the HyPPSO₃Na materials appears to increase in magnitude as the degree of crystallinity decreases, the assignment of this relaxation to the glass-to-rubber transition seems reasonable.

The glass transition in a material of the type examined in this study is affected by several factors. On the basis of simple copolymer-type arguments (37, 38) one would expect the glass temperature to increase as the extent of sulfonation is increased. However, recent studies on ionomer systems demonstrate that the onset of clustering can cause a much more dramatic rise in T_g than can be explained on the basis of copolymer effects alone (2, 39, 40). Varying the level of sulfonation and thermal history alters the degree of crystallinity, which also affects the T_g in polymers of this type. The complex interaction of these variables then, must determine the behavior of the β relaxation if it is assigned correctly.

A view of the β relaxation temperatures given in Table III suggests that they are very dependent on the crystallinities of the samples studied. In every case the T_β was higher in the annealed film than in the quenched

film having the same sulfonation level. Superimposed on the crystalline contribution to the β relaxation temperature is the copolymer effect. Between Samples HyPPSO₃Na(2) and HyPPSO₃Na(5) it appears that the effect of the additional sulfonate groups outweighs the effect of the slight decrease in crystallinity. This causes higher β relaxation temperatures in the HyPPSO₃Na(5) material for both the quenched and annealed cases. However, above 6.3% sulfonation, it is seen that the temperature of the β relaxation is dominated by the effect of the decreasing crystallinity, as increasing sulfonation results in lower T_β values. Owing to the multiphase nature of these materials, no clear-cut effect of cluster formation on the β relaxation temperature is discernible.

The fact that the materials in this study exhibit a room-temperature crystallization process was suggested as evidence that the glass transition of these systems is below ambient temperatures. However, the β relaxation temperatures recorded in Table III are, in some cases, quite close to room temperature. This apparent contradiction results from the fact that the β relaxation is related not to a true amorphous-phase glass transition but to the apparent glass transition of a semicrystalline system, where T_g is altered significantly by the degree of crystallinity. From basic copolymer arguments alone, for example, one would expect the T_g of Sample HyPPSO₃Na(20) to be higher than that of Sample HyPPSO₃Na(2). However, such behavior is not displayed by the β relaxations of these materials because of the role that crystallinity plays in increasing the apparent T_g . Thus while the T_g 's of these materials would be considerably below room temperature if they were completely amorphous, crystallinity causes the values to be increased. The crystals that form at room temperature then increase the apparent T_g 's determined as the β relaxation temperatures.

γ' RELAXATION. Unlike the other dynamic mechanical relaxations observed in this study, the γ' relaxation does not have an analog in the dynamic mechanical behavior of polyethylene, hydrogenated PP's, or other ionomer systems. In addition, it displays no definite trends in changing temperature or magnitude as the level of sulfonation and thermal history are altered. Coupled with the fact that these systems are known to contain water as well as nitrogen, it is not possible to assign this relaxation to any specific phase or mechanism. Additional studies are necessary before this task can be approached adequately.

γ RELAXATION. The previous publications on hydrogenated PP's (20, 21) and their derivatives bearing pendant ionic groups (3, 4, 36) all have concluded that the γ relaxation is a secondary relaxation of composite nature, involving both an amorphous and crystalline component. The results of this investigation suggest no reason to disagree with these conclusions. Therefore the γ relaxation observed in the dynamic mechanical spectra of the HyPPSO₃Na materials is believed to arise from the same

mechanisms. The amorphous contribution is envisioned as resulting from a crankshaft motion with three bonds between the stem bonds of the crankshaft (after the Boyd-Breitling proposal (41)), while the crystalline contribution is believed to result from motion around defects within the crystals (25, 42).

Dielectric Properties. The extremely large increases in $\tan \delta_e$ and ϵ' values accompanying increases in temperature dominate the results of the dielectric experiments. Since these materials are known to possess some absorbed water and to contain a small amount of nitrogen in an undetermined form, the potential for both impurity ionic conduction and space-charge localization at the electrodes exists. In addition the dynamic mechanical results suggest the presence of a separate ionic phase in these systems, so the possibility of Maxwell-Wagner absorption is real as well (43, 44, 45). Independent measurement of dc conductivity was carried out, and the resulting correction of ϵ'' values demonstrated that this factor was making only a minor contribution to the overall dielectric loss measured, besides which ϵ' values should be unaffected by dc conductivity. These factors combine to suggest that while impurity ionic conduction is playing a role in the dielectric behavior of these materials, it is not the most significant component. However, drawing a distinction between interfacial polarization which occurs either at the electrodes or on an occluded phase is not readily accomplished. As a result, the source of the phenomenon observed in these systems cannot be determined absolutely. It is known though, that the Maxwell-Wagner effect will cause ϵ' values to increase only by a factor of about 2-4 if the occluded phase is spherical (46, 47); therefore attempts to explain the observed behavior via the Maxwell-Wagner concept must assume that the domains are nonspherical.

From Figure 10 it appears that a dipolar relaxation labeled α is superimposed on the phenomenon we have just discussed. The behavior of this α peak correlates well with the behavior of the dynamic mechanical α relaxation since it increases in magnitude and decreases in temperature with increasing sulfonation. The presence of this peak in the dielectric spectra of these materials and its behavior as a function of sulfonate concentration are consistent with the assignment of the mechanical α relaxation to an ionic-phase mechanism. However, it is not possible to cite this dielectric peak as proof of the mechanical assignment; the known presence of ionic impurities in these systems and the unknown origin of the large increases in $\tan \delta_e$ and ϵ' dictate that the dielectric results be interpreted with caution.

On the basis of similar arguments, an assignment of the dielectric β peak is not suggested. The magnitude of the $\tan \delta_e$ values in the region of the β peak, the fact that the magnitude of this peak appears to increase roughly in proportion to the increase in sulfonate groups, and the fact

that the temperature of this peak remains relatively constant combine to suggest that it does arise from an actual dipolar relaxation. This peak is in the same temperature range as the unassigned mechanical γ' relaxation, which might imply some relationship between the two. However the data are not sufficient to propose a mechanism for this apparent dielectric relaxation or a relationship between it and the mechanical γ' process.

Conclusions

The DSC results for HyPPSO₃Na materials demonstrate the existence of low-melting crystals that form when these polymers are maintained at room temperature. The volume fraction of such crystals increases as the degree of sulfonation is increased, but the melting temperature is unaffected by the level of sulfonation. The higher-melting crystallites qualitatively obey the Flory equation for melting-point depression in random copolymers.

The α relaxation observed by dynamic mechanical techniques is attributable in part to an ionic-phase mechanism. The existence of this relaxation is suggested as evidence for the presence of phase-separated clusters in these materials. The temperature at which the β relaxation occurs is found to result from the complex interaction of crystallinity and ionic group concentration.

The high-temperature phenomenon present in the dielectric results for these materials is believed to arise from an interfacial effect either at the electrodes or on an occluded phase. No assignment is made for the origins of the α and β relaxations observed dielectrically.

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