Sulfonation of Syndiotactic Polystyrene for Model Semicrystalline Ionomer Investigations

E. Bruce Orler, Dorie J. Yontz, and Robert B. Moore*

Department of Polymer Science, University of Southern Mississippi, Southern Station, Box 10076, Hattiesburg, Mississippi 39406-0076

Received May 3, 1993; Revised Manuscript Received June 30, 1993[◆]

ABSTRACT: Syndiotactic polystyrene was lightly sulfonated in 1,2,4-trichlorobenzene using acyl sulfate complexes. The sulfonation efficiency of the acyl sulfate increased significantly when anhydrides containing long aliphatic groups were used to complex sulfuric acid. The high sulfonation efficiencies, relative to acetyl sulfate, were attributed to the increased solubility of the longer hydrocarbon complexes in trichlorobenzene. The incorporation of small quantities (less 3.4 mol %) of sulfonic acid groups onto the syndiotactic polystyrene backbone was found to have little effect on the glass transition temperatures of these new materials. However, a much more pronounced effect of sulfonation was observed in the ionomer crystallization. Increasing the level of sulfonation decreased the melting point, degree of crystallinity, and apparent rate of crystallization due to a rejection of sulfonated styrene units from the crystalline domains.

Introduction

Numerous studies of lightly sulfonated, atactic, polystyrene (SaPS)[1-8] have provided a wealth of experimental and theoretical information regarding ionic aggregation in ionomers. The functionalization of these ionomers usually involves a postpolymerization sulfonation reaction of polystyrene with acetyl sulfate in chlorinated solvents such as 1,2-dichloroethane.[9] Polystyrene has also been sulfonated in hydrocarbon solvents using a variety of acyl sulfate complexes.[10] These methods of sulfonation offer the advantage of a homogeneous reaction which yields a random placement of sulfonic acid groups along the polymer chains. Moreover, since sulfonation occurs without significant degradation or cross-linking of the polymer,[11] structure–property relationships of the ionomer may be directly compared to that of the unmodified polymer.

We have recently begun investigations aimed at ascertaining the fundamental link between ionic aggregation and crystallization in semicrystalline ionomers (SCI's).[12] Since each polymer chain in a typical SCI is likely to be involved in the formation of both crystalline and ionic domains, crystallization is expected to be influenced by ionic aggregation, just as ionic aggregation may be influenced by crystallization. Previous investigations of SCI's have focused primarily on the industrially important ethylene-*co*-methacrylic acid systems (i.e., Surlyn). However, undesirable microstructural characteristics (e.g., variable molecular weight distributions for different ion contents, and random, polydisperse alkyl chain branching along the backbone) of the resulting copolymers prevents Surlyn from being an acceptable model system for systematic morphological studies.

Based on the information gained from previous studies of SaPS ionomers, the optimum choice of a semicrystalline ionomer for fundamental investigations is lightly sulfonated, stereoregular polystyrene. For example, isotactic polystyrene has been sulfonated using a modified version of the standard SaPS procedure[9] by first melt quenching the polymer to create a noncrystalline solid which is subsequently soluble in 1,2-dichloroethane.[13] To date, however, information regarding the morphological link between ionic aggregation and crystallization in sulfonated isotactic polystyrene has been severely limited by the slow crystallization kinetics of isotactic polystyrene.

The recent discovery of a synthetic route for producing syndiotactic polystyrene[14,15] has yielded a material which crystallizes approximately 40–80 times faster than the isotactic isomer.[16] While this behavior may be desirable in enhancing the formation of crystalline domains under standard melt-processing conditions, the rapid crystallization (particularly in the presence of solvent) adds a formidable barrier to dissolving the polymer. Thus, solubility and gelation characteristics of syndiotactic polystyrene are critical parameters which must be considered in developing a homogeneous, solution-state, sulfonation procedure. In this communication, we report a method for lightly sulfonating syndiotactic polystyrene. In addition, the effect of low levels of sulfonation on the thermal properties of these semicrystalline ionomers will be discussed.

Experimental Section

Materials. The syndiotactic polystyrene (with greater than 99% syndiotactic purity) was obtained from the Dow Chemical Co. and had a weight average molecular weight of 609 000. All other chemicals and solvents were obtained from Aldrich and were used without further purification.

Preparation of the Sulfonating Reagents. Acyl sulfate complexes from acetic anhydride and caproic anhydride were prepared in an identical manner. Concentrated sulfuric acid (0.018 moles) was slowly added, with vigorous stirring, to 25 mL of a 1,2,4-trichlorobenzene solution containing 0.03 mol of the anhydride. After complete mixing, these reagents were equilibrated at room temperature and then diluted with 1,2,4-trichlorobenzene to 50 mL in a volumetric flask.

Due to the extreme reactivity of SO_3, the acyl sulfate complex from lauric acid was prepared, in a glovebag, under a dry nitrogen atmosphere. Lauric acid (0.04 mol) was dissolved in 1,2,4-trichlorobenzene at ca. 50 °C. Sulfur trioxide (0.025 mol) was then slowly added, with vigorous stirring, to 25 mL of the lauric acid solution. After complete mixing, these reagents were equilibrated at room temperature and then diluted with 1,2,4-trichlorobenzene to 50 mL in a volumetric flask.

Sulfonation of Syndiotactic Polystyrene. In a 500-mL round bottom flask, 5.0 g of syndiotactic polystyrene (sPS) was mixed with 350 mL of 1,2,4-trichlorobenzene and heated under reflux (ca. 210 °C) until all the sPS dissolved. The solution was cooled to 70–80 °C and then purged with nitrogen. Note that at 70 °C, solution-state crystallization and subsequent gelation occurred for sPS solution concentrations greater than ca. 2%

---

* Author to whom all correspondence should be addressed.

[◆] Abstract published in *Advance ACS Abstracts,* August 15, 1993.

0024-9297/93/2226-5157$04.00/0 © 1993 American Chemical Society

Table I. Efficiency of Sulfonation Reagents in Trichlorobenzene

				degree of sulfonation (mol %)[c]		
complexing agent	reaction time (h)	tacticity[a]	solvent[b]	theoretical	titration	sulfonation efficiency (%)
acetic anhydride	1	A	DCE	5	4.7	94
acetic anhydride	1	S	TCB	10	2.0	20
lauric acid	1	S	TCB	6	1.8	30
lauric acid	3	S	TCB	6	1.8	30
caproic anhydride	1	S	TCB	6	2.7	45

[a] Tacticity of samples is referred to as A for atactic and S for syndiotactic. [b] The solvents used were 1,2-dichloroethane (DCE) and 1,2,4-trichlorobenzene (TCB). [c] All sulfonation reactions were conducted at ca. 70 °C.

(w/v). Furthermore, sPS gelation was observed if the temperature of the 1.5% solution was allowed to drop below 70 °C.

Depending on the degree of sulfonation desired (see Table I), a specific amount of an acyl sulfate reagent in 1,2,4-trichlorobenzene was slowly added to the sPS solution with rapid stirring. The reaction was allowed to proceed for 1 h at ca. 70 °C, and then terminated by the addition of 2 mL of methanol. As is usually observed during the standard atactic polystyrene sulfonation reaction,[9] the sPS solution acquired a slight brown tint. To avoid gelation after the reaction was terminated, the warm solution was immediately precipitated into 1200 mL of methanol. The white precipitate was then filtered and dried under vacuum, at 70 °C, overnight.

To facilitate the complete removal of residual sulfonating reagent from the functionalized polymer, the sulfonated syndiotactic polystyrene (SsPS) samples were redissolved in trichlorobenzene and reprecipitated in methanol. The precipitate in methanol was then ground into a fine slurry using a Waring blender. This powder was vacuum filtered and placed in a Soxhlet extractor. The polymer was then washed with refluxing methanol for 14 h. Finally, the polymer was removed from the extractor and dried in a vacuum oven, at 70 °C.

Characterization Methods. The degree of sulfonation was determined by nonaqueous titration, in a 95:5 (v/v) 1,2,4-trichlorobenzene–ethanol mixed solvent, using a methanolic KOH titrant, to the phenolphthalein end point. The titrant was calibrated at 70 °C using a benzoic acid standard dissolved in the 1,2,4-trichlorobenzene–ethanol solvent. All sample titrations (performed in triplicate) were conducted at 70 °C in solutions containing 0.5 g of SsPS in 100 mL of the mixed solvent.

Thin films of the SsPS samples were prepared by compression molding the polymers at temperatures above the sPS melting point (ca. 270 °C) in a Carver lab press. To confirm sulfonation of the aromatic rings, FTIR spectra of these films, having thicknesses of ca. 50–100 μm, were obtained using a Perkin-Elmer 1600 FTIR.

The thermal properties of the sPS and SsPS samples were compared using a Perkin-Elmer DSC 7 differential scanning calorimeter, with a nitrogen purge. All DSC samples were first heated to 330 °C, rapidly quenched (−200 °C/min) to the start temperature, and then scanned from 50 to 330 °C at 20 °C/min. The glass transition temperatures, T_g's, were taken as the midpoint of the step change in the heat flow, and the melting and crystallization temperatures were defined as the peak maximum or minimum in endothermic or exothermic transitions, respectively.

Results and Discussion

Since syndiotactic polystyrene is insoluble in 1,2-dichloroethane (i.e., the standard solvent for sulfonation of atactic polystyrene), the sPS sulfonation reactions were conducted in 1,2,4-trichlorobenzene (TCB). This solvent interacts strongly with the polystyrene chains and offers a high boiling point which is required to break down the crystalline domains. In addition, the polychlorinated solvent is deactivated toward sulfonation.

Table I lists the results of sulfonation reactions on syndiotactic polystyrene using a variety of sulfate complexing agents in TCB. For comparison, the results of a standard sulfonation of atactic polystyrene in 1,2-dichloroethane are also included. In agreement with the work of Thaler,[10] the low sPS sulfonation efficiency of acetic anhydride may be attributed to a low solubility of acetyl sulfate in TCB. To increase the solubility of the sulfonating reagent in TCB, the organic character of the acyl sulfate was increased.

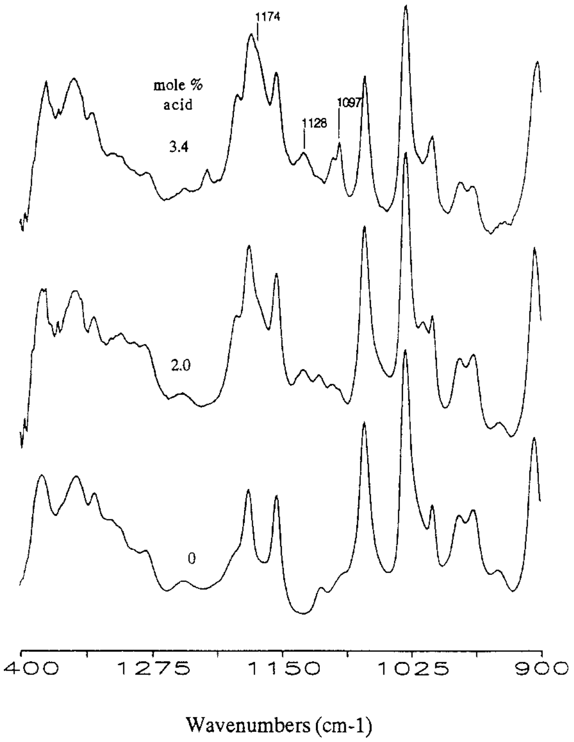

Figure 1. FTIR spectra of (A) 3.4 mol % SsPS, (B) 2.0 mol % SsPS, and (C) pure sPS.

Data for the sulfonation with the lauric acid complex show an increase in the sulfonation efficiency; however, this slight improvement over acetyl sulfate does not outweigh the difficulty in preparing the sulfonating reagent with pure SO_3.[10] Furthermore, increasing the reaction time showed no improvement in the sulfonation efficiency. In contrast to the lauric acid system, preparation of the caproic anhydride complex by adding H_2SO_4 to the anhydride solution is much more desirable, and this system yields a substantial improvement in the sulfonation efficiency.

The FTIR spectra of melt quenched SsPS films containing 0, 2.0, and 3.4 mol % sulfonic acid groups are shown in Figure 1. The most prominent band for confirming sulfonation on polystyrene is observed at 1175 cm^{-1} and has been attributed to the symmetric stretching vibration of the sulfonic acid group.[17] Due to the low concentrations of sulfonic acid groups in these materials, this band only appears as a distinct shoulder between the bands centered at 1179 and 1154 cm^{-1}. As expected, this shoulder becomes more prominent with an increase in the degree of sulfonation. Further evidence of sPS sulfonation is gained by observing the peaks at 1097 and 1128 cm^{-1}. These vibrational bands, which are absent in the spectrum of

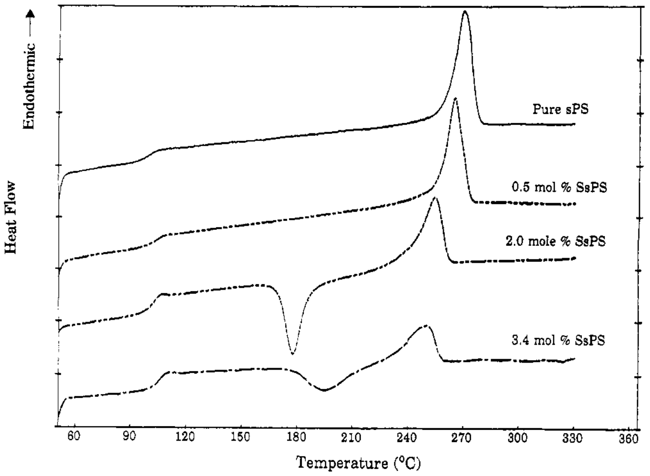

Figure 2. Effect of percent sulfonation on the DSC scans of melt-quenched sulfonated syndiotactic polystyrene. Prior to the collection of the above scans, all samples were heated to 330 °C and then rapidly cooled at −200 °C/min to 50 °C.

Table II. Summary of DSC Results for SsPS Ionomers

sample	T_g (°C)	T_m (°C)	ΔH_f (J/g)	%[a] crystallinity	T_c (°C)	ΔH_c (J/g)
pure sPS	99	269	22.4	27		
0.5 mol% SsPS	102	264	20.0	24		
2.0 mol% SsPS	101	254	17.7	21	177	13.5
3.4 mol% SsPS	104	249	10.3	12	194	9.6

[a] The weight percent crystallinity is based on the theoretical heat of fusion computed for sPS of 100% crystallinity (i.e. $\Delta H_f° = 82.6$ J/g).[21]

the unsulfonated sPS, have been attributed to the in-plane skeletal vibrations of the disubstituted benzene rings.[17]

The thermal behaviors of melt-quenched SsPS samples containing different amounts of sulfonation are displayed in Figure 2. The absence of a crystallization exotherm in the sPS thermogram indicates that the unsulfonated syndiotactic polystyrene rapidly reaches a state of maximum crystallinity during the quench. The thermal behavior observed for the 0.5 mol % SsPS sample is very similar to that of the pure sPS sample. In contrast, the crystallization exotherms observed in the thermograms of the 2.0 and 3.4 mol % SsPS samples indicate that crystallization was incomplete during the time frame of the quench and that a significant degree of crystallization occurs during the heating scan. This behavior suggests that the crystallization kinetics of these ionomers is retarded by the presence of covalently-attached sulfonic acid groups.

Table II lists the thermal data for each of the samples shown in Figure 2. For the SsPS materials containing up to 3.4 mol % sulfonation, the T_g varies only slightly with increasing acid content. However, in a manner similar to that observed with other semicrystalline ionomers,[18,19] the T_m and degree of crystallinity decrease significantly with increasing ion content. While the melting point depression shown with these ionomers is greater than that expected from Flory's theory for crystallizable random copolymers,[20] further information regarding equilibrium melting temperatures of the ionomers and specific interactions between the pendant sulfonic acid groups will be needed to evaluate the significance of this depression.

A measure of the extent of crystallization during the quench (i.e., the percentage of the total sample crystallinity which formed during the quench) may be obtained by subtracting ΔH_c from ΔH_f and dividing by ΔH_f. For the 2.0 and 3.4 mol % SsPS samples, this analysis indicates that the 2.0 mol % sample crystallized 24% during the quench, while the 3.4 mol % sample crystallized only 7% during the quench. This behavior is consistent with the trend of a decrease in the rate of crystallization with an increase in the level of sulfonation.

From the data in Figure 2 and Table II, it is interesting to note that, upon heating from 50 °C, the crystallization temperature for the 3.4 mol % sample is much higher than the T_c for the 2.0 mol % sample. This observation indicates that, under the time scale of the DSC experiment, more thermal energy is required to induce crystal growth in the 3.4 mol % sample. Again, these data are in agreement with the indirect evidence of decreased crystallization kinetics with sulfonation, and may be attributed to the disruptive effect of incorporating noncrystallizable styrenesulfonic acid units along the crystallizable polymer chains. As the level of sulfonation increases, more thermal energy is required to increase the rate of transport of pure sPS chain segments (of sufficient length) from the melt to the growing crystal interface. While this kinetic phenomenon has been observed in other copolymer systems,[22] it is important to note that specific interactions between the polar sulfonate groups may complicate the crystallization behavior of the SsPS materials (e.g., the formation of polymorphic crystalline structures).[12] Future investigations of SsPS ionomers neutralized with a wide variety of counterions will be aimed at understanding the effects of varying the strengths of specific interactions between the functionalized units (i.e., ionic aggregation) on the crystallization behavior of these new materials.

Conclusions

Syndiotactic polystyrene may be lightly sulfonated using acyl sulfate solutions in 1,2,4-trichlorobenzene. Due to enhanced solubility, the sulfonation efficiency of the acyl sulfate increases significantly when anhydrides containing long aliphatic groups are used to complex sulfuric acid. For sulfonation levels less than 3.4 mol %, there is little effect of sulfonation on the glass transition temperature. However, low levels of sulfonation significantly reduce the melting temperature, the degree of crystallinity, and the apparent rate of crystallization of these new materials. The dramatic change in the crystallization behavior with increasing sulfonation is attributed to the rejection of the sulfonated styrene units from the crystalline domains.

Acknowledgment. The research upon which this material is based was supported in part by the National Science Foundation through Grant No. EHR-9108767, the State of Mississippi, and the University of Southern Mississippi. The authors also gratefully acknowledge the Dow Chemical Co. for providing the syndiotactic polystyrene.

References and Notes

(1) Fitzgerald, J. J.; Weiss, R. A. *J. Macromol. Sci.: Rev. Macromol. Chem. Phys.* **1988**, *C28*, 99.
(2) Weiss, R. A.; Lefelar, J. A. *Polymer* **1986**, *27*, 3.
(3) Weiss, R. A.; Fitzgerald, J. J.; Kim, D. *Macromolecules* **1991**, *24*, 1071.
(4) Weiss, R. A.; Lefelar, J.; Toriumi, H. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 661.
(5) Galambos, A. F.; Stockton, W. B.; Koberstein, J. T.; Sen, A.; Weiss, R. A.; Russell, T. P. *Macromolecules* **1987**, *20*, 3091.
(6) Register, R. A.; Sen, A.; Weiss, R. A.; Cooper, S. L. *Macromolecules* **1989**, *22*, 2224.
(7) Register, R. A.; Cooper, S. L. *Macromolecules* **1990**, *23*, 310.
(8) Yarusso, D. J.; Cooper, S. L. *Macromolecules* **1983**, *16*, 1871.

(9) Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. US Patent 3,870,841, 1975.
(10) Thaler, W. A. *Macromolecules* **1983**, *16*, 623.
(11) Lundberg, R. D.; Makowski, H. S. *Polym. Prepr.* **1978**, *19* (2), 287.
(12) Orler, E. B.; Moore, R. B. *Polym. Prepr.* **1993**, *34* (1), 852.
(13) Peiffer, D. Personal communication.
(14) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2465.
(15) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 277.
(16) Cimmino, S.; Di Pace, E.; Martuscelli, E.; Silvestre, C. *Polymer* **1991**, *32*, 1080.
(17) Zundel, G. *Hydration and Intermolecular Interaction*; Academic Press: New York, 1969.
(18) Marx, C. L.; Cooper, S. L. *J Macromol. Sci.: Phys. Ed.* **1974**, *B9*, 19.
(19) Starkweather, H. W. *Macromolecules* **1982**, *15*, 320.
(20) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 223.
(21) Gianotti, G.; Valvassori, A. *Polymer* **1990**, *31*, 473.
(22) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1976; Vol. 2.