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Arylsulfone Derivatives of Polystyrene

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ABSTRACT

Arylsulfonyl chlorides have been found to react quantitatively with polystyrene in the presence of Friedel-Crafts catalysts at room temperature. Polymers having the general structure I, where R = H, CH_3, Cl, Br, F and OCH_3, were prepared and characterized by NMR and IR spectroscopy, differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and thermogravimetric analysis (TGA).

I
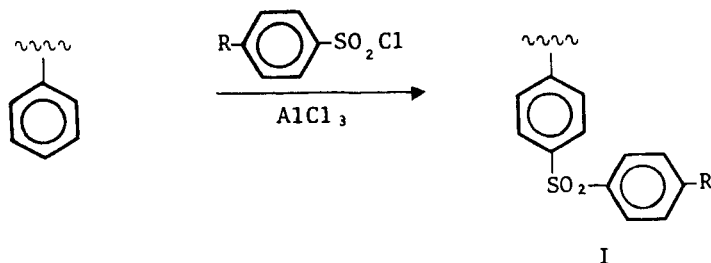
INTRODUCTION

Polystyrene is known to be readily substituted by electrophilic re-
agents. It is easily nitrated [1], brominated [2], iodinated [3], acyl-
ated [4], chloromethylated [5], sulfonated [6], and phosphorylated [7].
Such electrophilic substitutions often occur quantitatively with a high
preference for the p-position. In view of this, it is surprising that no
studies on the reaction of polystyrene with alkyl- or arylsulfonyl chlo-
rides in the presence of Friedel-Crafts catalysts have been reported.
The preparation of aryl sulfones and diaryl sulfones by the Friedel-
Crafts reaction is, of course, well known [8, 9] and has been used for
the preparation of poly(arylene sulfones) by polycondensation [10-13].
However, the only aryl sulfone derivatives of polystyrene that are
known have been prepared by homopolymerization of the correspond-
ing styrene derivatives [14] or by derivatization of poly(styrenesul-
fonyl chloride) [15].

During the course of studies on the methine proton resonance spec-
tra of polystyrene derivatives [16], we had occasion to prepare a num-
ber of arylsulfone derivatives of polystyrene via the Friedel-Crafts
reaction. The purpose of this paper is to present the results obtained
and to report some of the properties of the arylsulfone derivatives
that were prepared.

Experimental

Polystyrene having a number-average molecular weight of 153,000
was prepared in low conversion (20%) by bulk polymerization at 60°C
using 1 wt% benzoyl peroxide as initiator. It was reprecipitated twice
from chloroform solution into methanol. The sulfonyl chlorides em-
ployed in this study were obtained from the Aldrich Chemical Company.

Sulfonation Procedure

Methylene chloride (50 mL), anhydrous aluminum chloride (3.17 g,
0.02376 mol), and the aromatic sulfonyl chloride (0.0216 mol) were
introduced under nitrogen into a carefully dried 250 mL flask. The
mixture was stirred for 30 min at room temperature. A clear pale
yellow solution was obtained. A solution of polystyrene (1.50 g,
0.0144 mol of repeating units) in methylene chloride (25 mL) was
then added slowly to the stirred reaction mixture during 20 min. An
immediate coloration (varying from orange to red) was observed,
which darkened with time. The reaction mixture was stirred at room
temperature for 48 h and was then poured into a mixture of ice and
10% hydrochloric acid. After the ice had melted, the organic layer
was separated and slowly added to methanol to precipitate the product.
This was collected by filtration, washed with water, dried, and repre-
cipitated twice from chloroform solution into methanol. The product
was then dried under vacuum at 40° for 24 h.

Polymer Characterization

400-MHz ^{1}H-NMR spectra of the sulfonated polymers in CDCl$_3$ solution (2% w/v) were recorded at 50°C using a Varian XL-400 NMR spectrometer. A pulse width of 90° and an acquisition time of 2.0 s were used. Four transients were accumulated in each case. Resonance areas were measured by cutting and weighing spectra tracings. Infrared spectra of the polymers dispersed in KBr pellets or in the form of films cast from chloroform solution were recorded on a Perkin-Elmer 521 infrared spectrometer.

GPC measurements were made with a Waters Ana-Prep instrument that was equipped with a seven-column Styragel set with a continuous porosity range of 2×10^3 to 5×10^6 Å. THF was employed as the solvent, and a calibration based on polystyrene samples was used to characterize the approximate molecular weights and molecular weight distributions of the polymers.

Intrinsic viscosities in THF solution of most of the polymers were measured at 30°C with a Cannon-Ubbelhode viscometer. These values were obtained by extrapolating η_{sp}/c vs c and ln η_r/c vs c plots to zero concentration. Chloroform was used when poly(4-(4' methoxybenzenesulfonyl)styrene) was studied.

Glass transition temperatures (T_g) were determined from DSC thermograms that were recorded on a Du Pont 1090 differential scanning calorimeter. Measurements were made by using 10 mg of each sample under nitrogen at a heating rate of 10°C/min. The intersection method [17] was used to determine the T_g as this gave the best reproducibility.

Thermal stability measurements were made on a Du Pont 951 thermogravimetric analysis apparatus with the samples under nitrogen, with a heating rate of 20°C/min. The thermal decomposition temperature was taken as the point where rapid decomposition just started.

RESULTS AND DISCUSSION

Conditions previously reported for the acylation of polystyrene [4] were found to be suitable for the reaction of polystyrene with arylsulfonyl chlorides. The reactions occurred almost quantitatively when R was H, CH$_3$, OCH$_3$, Cl, Br, and F, based on the yields of recovered products and on the proportion of aromatic proton resonance areas observed in the ^{1}H-NMR spectra of the products. Table 1 lists the poly(arylsulfonylstyrenes) prepared along with intrinsic viscosities, molecular weights as estimated by GPC, glass transition temperatures, thermal decomposition temperatures, and relative NMR resonance areas.

The glass transition temperatures of the polymers range from 153 to 177°C and are influenced by the size of the substituent R. The polymers decomposed rapidly at 300-365°C, which is lower than the ther-

TABLE 1. Properties of Arylsulfonated Polystyrenes

$+CH_2-CH+_n$
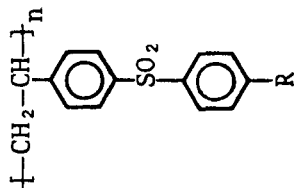
R	$[\eta]^a$	$\bar{M}_n^{\ b}$	$\bar{M}_w^{\ b}$	$\bar{M}_w/\bar{M}_n$	T_g (°C)	T_{dec} (°C)	Aromatic proton resonance area (%)	
							Observed	Calculated
H	0.33	140,000	381,000	2.7	153	340	68.8	75.0
CH_3	0.36	155,000	260,000	1.7	169	325	54.6	57.1
OCH_3	0.50	-	-	-	164	360	55.5	57.1
F	0.15	60,000	173,000	2.9	176.5	325	68.3	72.7
Cl	0.14	44,000	160,000	3.6	169	330	65.9	72.7
Br	0.21	105,000	478,000	4.5	172	335	69.0	72.7

[a]In THF at 30°C. The value for the parent polystyrene sample was 0.65.
[b]Based on GPC data obtained with THF as the solvent at 30°C. A polystyrene calibration was used. $\bar{M}_n$ and $\bar{M}_w$ values for the parent polystyrene were 153,000 and 230,000, respectively.

$$[\sim\sim CH_2-CH\sim\sim]_n \quad + \quad R-\text{⟨○⟩}-SO_2Cl \quad \xrightarrow[CH_2Cl_2]{AlCl_3} \quad [\sim\sim CH_2-CH\sim\sim]_n + HCl$$
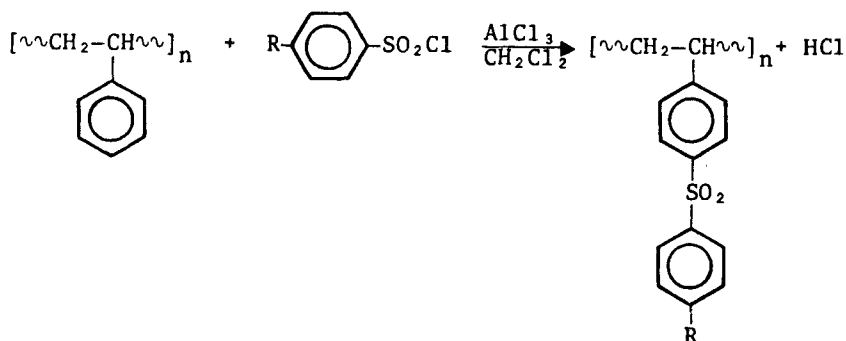
mal decomposition temperature of polystyrene (375°C) under the same conditions. This is believed to be a manifestation of the weakness of carbon-sulfur linkages, which has already been noted for polysulfones prepared by condensation polymerization.

Figure 1 shows the 400-MHz ^{1}H-NMR spectra of the arylsulfonated polystyrenes prepared in this study. In contrast to the behavior of acetylated polystyrene [18], the methine proton resonances of the polymers are not separated from the methylene proton resonances. The aromatic proton resonances of the polymers consist of many signals due to a combination of spin-coupling and tacticity effects, and perhaps also due to the presence of substitution on meta as well as para positions of the parent polymer. Based on the strong tendency noted for para-substitution in other electrophilic substitutions of polystyrene, this latter possibility is considered remote, however. The highest field resonance area in each aromatic resonance pattern is attributed to protons that are ortho to the polymer backbone, but definite assignments cannot be made at this time for the other signals.

The infrared spectra of the polymers are shown in Fig. 2. In all cases they contain strong absorptions characteristic of O=S=O stretching. An antisymmetric doublet (1290 and 1310 cm^{-1}) was noted in the spectra of most of the polymers, but a sharp singlet occurred in this region in the case of the p-chlorobenzenesulfonated and p-bromobenzenesulfonated derivatives. In all cases a strong symmetric O=S=O absorption was noted at 1140 cm^{-1}. The p-methoxybenzenesulfonated and p-fluorobenzenesulfonated derivatives showed, in addition, characteristic OCH$_3$ (1250 cm^{-1}) and C–F (1220 cm^{-1}) absorptions.

The intrinsic viscosities of the arylsulfonated derivatives are lower than that of the parent polymer. This is partly due to the change in polymer-solvent interaction that results from incorporating highly polar sulfone groups in a polymer. However, it is also possible that some viscosity reduction may be due to chain degradation. Polystyrene and its derivatives are known to degrade under conditions that enable carbenium ions to be generated on their backbones, viz.
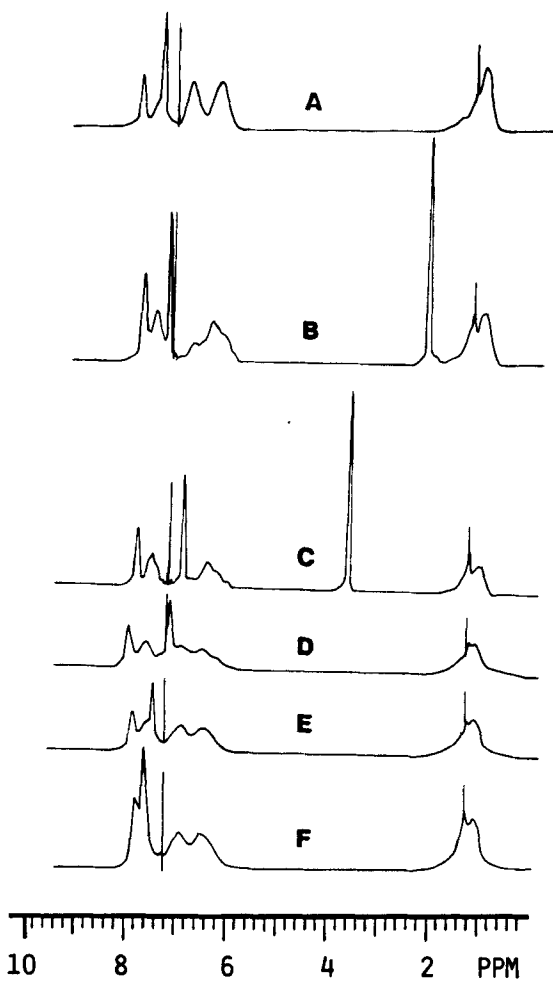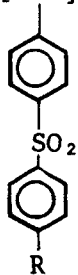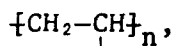
FIG. 1. 400-MHz ^{1}H-NMR spectra of arylsulfonated polystyrenes,

$\{CH_2-CH\}_n$,

where R = H (A), CH$_3$ (B), OCH$_3$ (C), F (D), Cl (E), and Br (F).
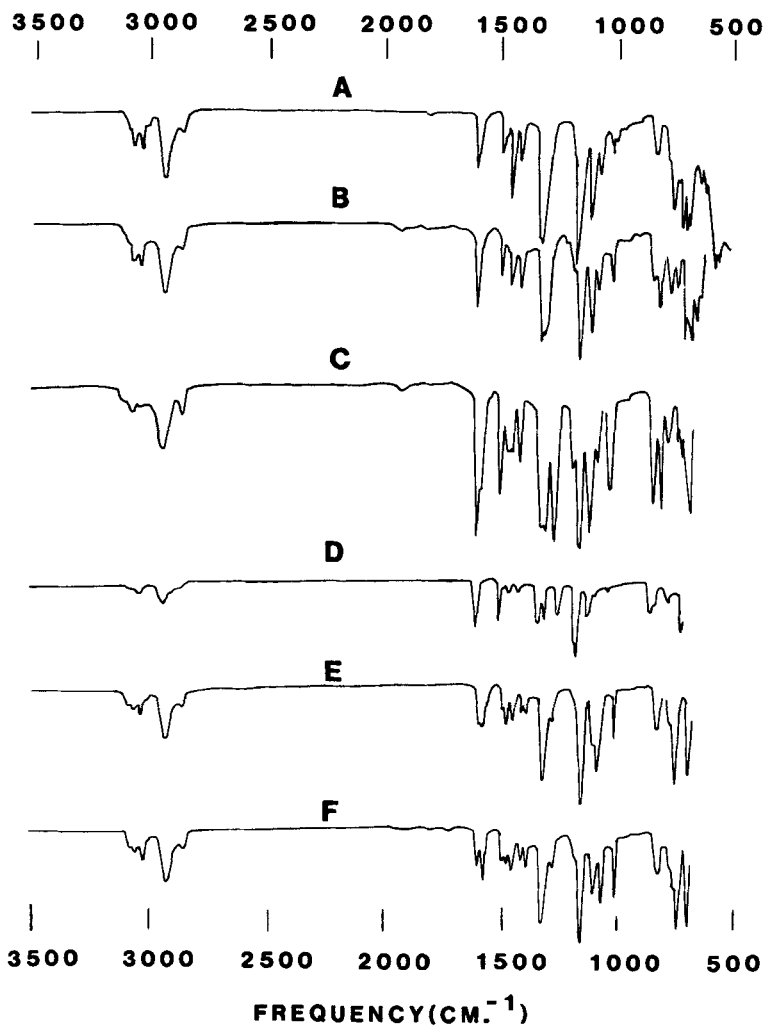
FIG. 2. Infrared spectra of arylsulfonated polystyrenes,

$-\!\!\left[CH_2\!-\!CH\right]\!\!-$,

where R = H (A), CH_3 (B), OCH_3 (C), F (D), Cl (E), and Br (F).

$$\sim\!\!\sim\!CH_2\!-\!CH\!-\!CH_2\!-\!CH\!\sim\!\!\sim \quad\longrightarrow\quad \sim\!\!\sim\!CH_2\!-\!\overset{\oplus}{C}\!-\!CH_2\!-\!CH\!\sim\!\!\sim \quad\longrightarrow$$

with ϕ–R substituents on the CH carbons

$$\sim\!\!\sim\!CH_2\!-\!C\!=\!CH_2 \quad+\quad \overset{\oplus}{C}\!H\!\sim\!\!\sim$$

with ϕ–R substituents
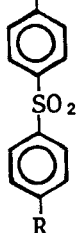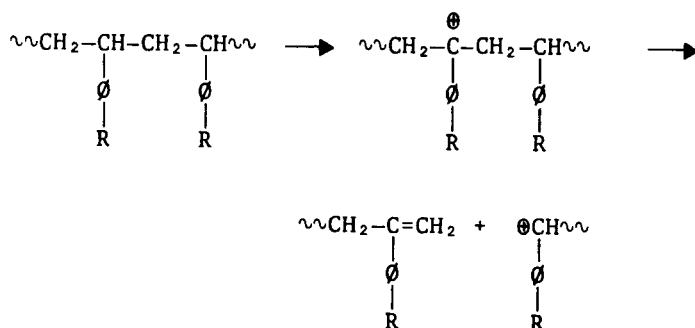
This might occur as shown below during arylsulfonation reactions:

$$R\!\!-\!\!\bigcirc\!\!-\!SO_2Cl \quad+\quad AlCl_3 \quad\longrightarrow\quad R\!\!-\!\!\bigcirc\!\!-\!\overset{\oplus}{SO_2}\ AlCl_4^{-}$$

$$\sim\!\!\sim\!CH_2\!-\!CH\!-\!CH_2\!-\!CH\!\sim\!\!\sim \ +\ R\!\!-\!\!\bigcirc\!\!-\!\overset{\oplus}{SO_2} \longrightarrow \sim\!\!\sim\!CH_2\overset{\oplus}{C}\!-\!CH_2CH\!\sim\!\!\sim \ +\ R\!\!-\!\!\bigcirc\!\!-\!SO_2H$$
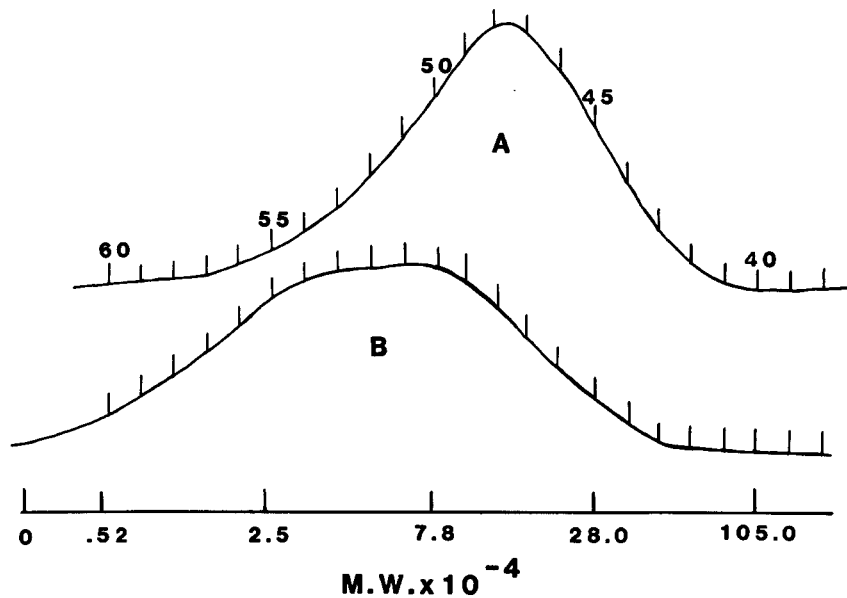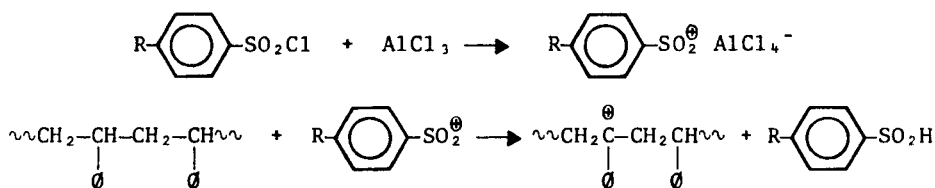

FIG. 3. Comparison of GPC chromatograms of parent polystyrene (A) and its p-bromosulfonated derivative (B).

If this is the case, it is interesting that the reaction is most pronounced with p-halobenzenesulfonyl chlorides, which may be expected to give the most electrophilic intermediates.

The GPC results also indicate that the arylsulfonated polymers are either more tightly coiled than the parent polystyrene or degraded. In addition, the arylsulfonated products have broader molecular weight distributions than the parent polystyrene, except for the p-toluenesulfonated derivative. This is evident from the comparison shown in Fig. 3, and from the $\overline{M}_w/\overline{M}_n$ ratios given in Table 1. This might also be a consequence of the backbone degradation reactions discussed above, since polystyryl carbenium ions generated by chain degradation processes might alkylate unsubstituted styrene units and cause the products to have branched structures. This could result in increased $\overline{M}_w/\overline{M}_m$ ratios.

ACKNOWLEDGMENT

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