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**PREPARATION OF ARYLSULFONE DERIVATIVE OF POLYSTYRENE
with P-TOLUENE SULFONYL CHLORIDE**

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ABSTRACT

The arylsulfone derivative of polystyrene was prepared by p-toluene sulfonyl chloride in the presence of anhydrous aluminum chloride in methylene chloride at three different temperatures. The sulfonated polystyrenes were characterized by IR spectrophotometer, $^1\text{H-NMR}$ spectrometer and sulfur analyzer. Activation energy of the sulfonation reaction was found to be $38,0 \text{ kJ mol}^{-1}$ and $36,5 \text{ kJ mol}^{-1}$ from the results of HCl and sulfur determinations, respectively. Solubility parameters and densities of some sulfonated polystyrenes were also determined.

INTRODUCTION

It is known that polystyrene can react readily with electrophilic reagent. It can be easily nitrated(1), chlorinated(2), brominated(3), acylated(4), chloromethylated(5), phosphorylated(6) and sulfonated(7). Such electrophilic substitutions on polystyrene often occur almost quantitatively with a high preference for the p-position. No more

studies on the reaction of polystyrene with arylsulfonyl chlorides which is an electrophilic reagent, in the presence of Friedel-Crafts catalysts, have been reported(8). However, the aryl sulfone derivatives of poly(styrenesulfonyl chloride)(9) or homopolymerization of the corresponding styrene derivatives are well known.

In the present study the arylsulfone derivative of polystyrene was prepared by p-toluen sulfonyl chloride in the presence of anhydrous aluminum chloride. The purposes of this study are to present how the conversion changes with time and temperature and to calculate activation energy of the reaction and to report the some structure characteristics and some of the properties of the product.

EXPERIMENTAL

Chemicals

Polystyrene supplied by YARPET (Turkish, Petrochemical Ind. Inc.) was used. Its viscosity average molecular weight was about 200000. It was purified before use by dissolving in CH_2Cl_2 and by precipitation by ethanol followed by vacuum drying for two days at 50 °C. Methylene chloride (Merck product) was used as solvent without additional purification. P-toluene sulfonyl chloride (produced by Fluka) was recrystallised from petroleum ether. Anhydrous AlCl_3 was used as Friedel-Crafts catalyst.

Sulfonation Procedure

The sulfonation reaction was carried out as described by Desgupta et. al. (8). Methylene chloride (50ml), anhydrous AlCl_3 (0,024 mol), and p-toluene sulfonyl chloride (0,022 mol) were introduced under dry nitrogen into a carefully dried 250 ml flask. The mixture was stirred for 30 min at the desired temperature. A solution of polystyrene (0,0144 mol repeating units) in methylene chloride (25 ml) was then added slowly to the stirred reaction mixture over 20 min. The mixture was colored immediately. The reaction mixture was stirred at desired temperatures (+18 °C, 0 °C and -20 °C) under nitrogen stream for 28 h and was then poured into a mixture of ice and 10 % HCl. After the ice had

melted, the organic layer was separated and slowly added to excess ethanol to precipitate the sulfonated polymer. Then the product was filtered, washed with water, dried, and reprecipitated from methylene chloride solution into ethanol. The product was then dried under vacuum at about 50 °C for a few days. During the sulfonation reaction, liberated HCl was trapped in 0,1 N NaOH solution. After the reaction, excess NaOH solution was titrated with 0,1 N HCl solution, and then percentage of sulfonation was calculated.

Instruments and Methods

¹H-NMR spectra of the sulfonated polymers in CDCl₃ solution were recorded at room temperature using a Perkin-Elmer EM 360 L model 60 MHz NMR spectrometer. IR spectra of the polymers were recorded using a film deposited on a salt plate from methylene chloride solution on a Pye Unicam SP3-100 IR spectrophotometer. Leybold-Heraeus CSA 2003 carbon-sulfur analyser was used for sulfur determinations in the sulfonated polymers.

The density of the sulfonated polymer was measured by the flotation method with the use of a mixture of ethanol and formic acid as the floating agent. The solubility parameter of the sulfonated polymer was estimated from solubility test by using chloroform, nitromethan and n-heptane, according to the methode adapted from McCaffer (10).

RESULTS and DISCUSSION

Table I shows % conversion with time at three different temperatures (+18 °C, 0 °C and -20 °C) for production of sulfonated polymer, which is a styrene-p-(p-toluenesulfonyl) styrene copolymer, as estimated by removed hydrogen chloride during the reaction.

At the end of the 28 h of reaction time, sulfur content of the product and % conversions were calculated and presented in Table II. Conversion % values (by mol) found from removed HCl have been approximately agreed with those of sulfur determination.

The estimations of solubility parameter (δ) and density (φ) of the highly and poorly sulfonated PS are summerized in Table III.

TABLE I. Changing of % conversion with time. Solvent: CH_2Cl_2 ,
catalyst: anhydrous AlCl_3

time (h)	% conversion (by mol)		
	-20°C	0°C	+18°C
4	2.8	15.0	13.2
8	3.2	26.3	30.6
12	3.6	36.9	47.7
20	5.2	55.6	59.1
24	5.4	55.9	59.7
28	6.3	56.2	59.8

TABLE II.

t°C	S%	% Conversion (by mol)
-20	1.980	7.1
0	9.251	54.2
+18	9.959	62.1

TABLE III.

% Conversion (by mol) ^a	$\delta(\text{cal}/\text{cm}^3)^{1/2}$	$\varphi(\text{g}/\text{cm}^3)$
7.1	9.6	0.9812
62.1	9.8	0.9205

a : Calculated by sulfur determination

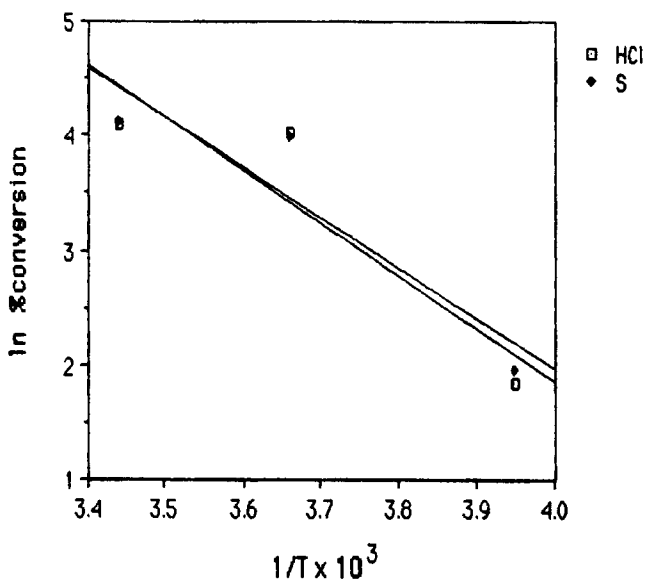


Fig 1. A plot of $\ln(\% \text{Conversion})$ vs $1/T$

Solubility parameter and density for PS had been reported in literature as $8,5-9,5 (\text{cal}/\text{cm}^3)^{1/2}$ and $1,05-1,15 \text{ g}/\text{cm}^3$ (11), respectively. These results show that the solubility characteristics do not almost change but the density decreases during the sulfonation of PS.

The activation energy of the sulfonation reaction on aromatic ring of polystyrene was found to be $38,0 \text{ kJ mol}^{-1}$ and $36,5 \text{ kJ mol}^{-1}$ from Figure 1, by HCl and sulfur determinations, respectively.

% conversion given in Table I shows that the reaction did not occur quantitatively under these conditions. Specially, % conversion at 0°C and $+18^\circ \text{C}$ did not almost change after the the period of time of 20 h.

Fig 2 a, b and c show the 60-MHz $^1\text{H-NMR}$ spectra of the original polystyrene (a), poorly (b) and highly (c) sulfonated polystyrene

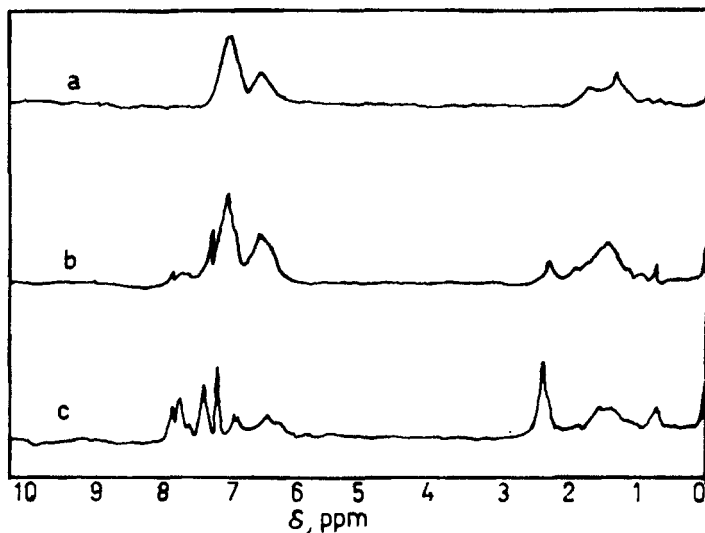


Fig 2. ^1H -NMR Spectra of (a) PS, (b) poorly and (c) highly sulfonated PS

prepared in this study. The broad signal at δ 1,0-1,8 ppm is due to methine and methylene protons in the polymer backbone.

The signals of protons on $-\text{CH}_3$ groups in reacted styrene units are seen at δ 2,3 ppm. It is difficult to say which signals are belong to which aromatic protons at between δ 6-8 ppm. However, signals at low field area (at δ 7,2-8,0 ppm) may be assigned to ortho protons to the sulfone group which is an electron acceptor.

The infrared spectra of the highly sulfonated polymer and the original polystyrene are shown in Fig 3. In the case of the sulfonated polymer it contains strong absorptions characteristics of $\text{O}=\text{S}=\text{O}$ stretching which is not present in that of original polystyrene. These

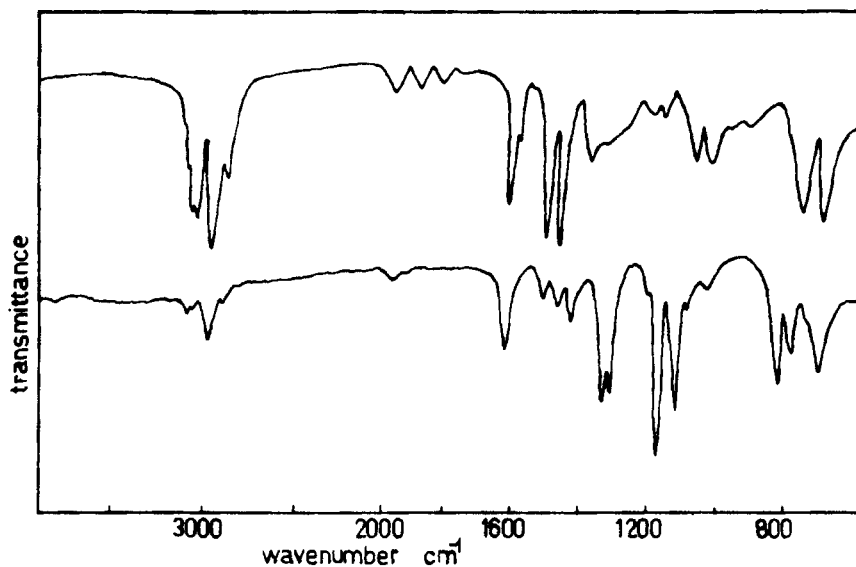
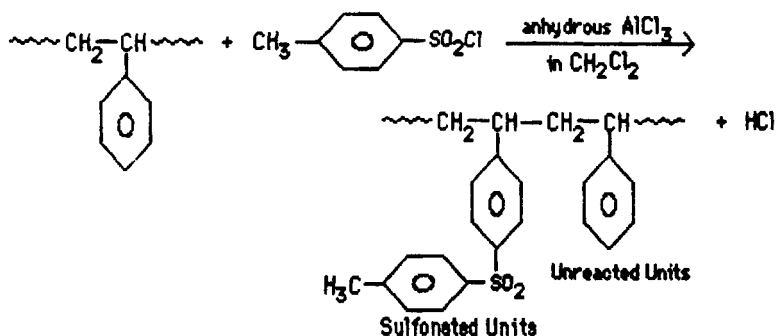


Fig 3. IR Spectra of (a) PS and (b) highly sulfonated PS

bands are due to antisymmetric (1295 cm^{-1} and 1310 cm^{-1}) and symmetric (1150 cm^{-1}) stretching absorptions of the $-\text{SO}_2-$ group. The strong absorption at 805 cm^{-1} and the weak absorption at 1890 cm^{-1} which are not present in that of polystyrene are characteristics of the *p*-disubstituted ring. Although these evidences are not enough for fully *para*-substitution, it may be noted that the reaction carried out in *para* position because of the steric effect of *ortho* to polymer backbone and also the electrophile is a large group.

The electrophilic substitution is as follows:



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