

Preliminary Study of Sulfonation of Polystyrene by Homogeneous and Heterogeneous Reaction

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The experimental details of homogeneous sulfonation of polystyrene in solution of dichloroethane using acetyl sulfate as sulfonating agent were summarized in this work. The effect of H_2SO_4 concentration on the sulfonation yield was analyzed for homogeneous sulfonation. Two samples of polystyrene-sulfonated beads were prepared in a heterogeneous reaction and analyzed.

Sulfonation of polystyrene (PS) has been attempted by a number of researchers, however, little has been written about details of the sulfonation reactions. Although there are numerous references to the patent of *Makowski et al.* [1] in the literature, this patent does not give any details about the actual procedure.

Polystyrene was first sulfonated in a homogeneous phase by a method developed by *Turbak* [2] via reacting polystyrene with complexes of triethyl phosphate and sulfur trioxide in dichloroethane. *Makowski et al.* [1] prepared lightly sulfonated polystyrene by using acetyl sulfate complexes as sulfonation reagent in a solution of dichloroethane. In this reaction, random ionic functionality along the polymer chains was generated without significant degradation or crosslinking of the reaction product [3]. *Vink* [4] described preparation of polystyrenesulfonic acid (PSSA) in an inert cyclohexane solvent using Ag_2SO_4 or phosphorous pentoxide as an accelerator. The reaction was carried out at a slightly elevated temperature (40°C) to prevent phase separation in the cyclohexane solution. In the method of *Thaler* [5] sulfonation was also carried out in cyclohexane solution, however, hydrocarbon-soluble acyl sulfates produced by reaction with sulfur trioxide and chlorosulfonic acid (for example lauric acid) were used as the sulfonating agents. Such a sulfonating agent is more effective than acetyl sulfate due to its higher solubility in hydrocarbon solvents. Other homogeneous reagents were hydrocarbon-soluble complexes of sulfur trioxide with a high molecular mass phosphate ester ($2\text{SO}_3 \cdot \text{OP}(\text{OR})_3$).

It seems more practical to avoid problems with solvents by sulfonating PS in a heterogeneous phase, *i.e.* solid-liquid (s-l) or solid-gas (s-g). Heterogeneous sulfonation brings about substantial experimental complications, which seems to be reflected by a limited number of published papers dealing with such a re-

action. Only *Carrol* and *Eisenberg* [6] and *Kim* and *Salovey* [7] mentioned heterogeneous phase sulfonation reaction in their papers. In the method of *Carrol* and *Eisenberg* [6], fine polystyrene powder was rapidly mixed at room temperature with 100 % sulfuric acid containing a fairly high concentration of silver ion catalyst. Reaction was completed in 5–15 min, however, a separation of polystyrenesulfonic acid from the solution is a complicated procedure. *Kim* and *Salovey* [7] described s-g heterogeneous sulfonation of monodisperse crosslinked polystyrene beads which have been treated with sulfur trioxide above fuming sulfuric acid to sulfonate the beads surface. Unlike the solution reactions, gas phase sulfonation prevents swelling of polystyrene beads [7].

The aim of our work was to develop a new method for preparing PSSA by heterogeneous reaction of porous PS or solid PS beads with SO_3 . In order to gain insight into the reactions governing sulfonation itself and techniques for reaction product separation and characterization, homogeneous sulfonation experiments have been carried out first.

EXPERIMENTAL

Commercial grade PS under the trade name *Kras-ten 127/9001* (Kaučuk Kralupy, Czech Republic) had a number average molar mass $\bar{M}_N = 215000 \text{ g mol}^{-1}$. Sulfuric acid (95–97 %), P_4O_{10} , acetic anhydride, and methanol had a reagent grade purity. 1,2-Dichloroethane (DCE) was dried with CaCl_2 and P_4O_{10} and distilled. Acetyl sulfate, which was the sulfonating reagent, was prepared by reacting concentrated sulfuric acid with acetic anhydride in a solution of DCE. A little excess of acetic anhydride was used to scavenge the residual water.

Infrared spectra were measured using a Nicolet Impact 400D FTIR spectrometer (Thermometrics,

USA). KBr pellets technique and DRIFT technique were used to obtain the FTIR spectra. Spectra were taken over the interval of wavenumbers ranging from 400 to 2000 cm^{-1} . Peaks at about $\bar{\nu} = 1040 \text{ cm}^{-1}$ and 1180 cm^{-1} were used to indicate the SO_3H group qualitatively.

Sulfonation Reaction

First, 10.4 g of PS was dissolved in 50 cm^3 of dried DCE in a bottom glass flask reactor (250 cm^3) equipped with mechanical agitation, vertical condenser, and thermometer. The flask containing the solution was heated in the silicone oil bath to 48–52°C. Acetyl sulfate as sulfonating agent was prepared in a separate flask: 6.0 cm^3 of acetic anhydride was added to 50 cm^3 of DCE. The solution was cooled to about 5–10°C and 3.0 cm^3 of 95–97 % sulfuric acid was carefully added. The prepared acetyl sulfate in solution of DCE was poured through the vertical condenser to the solution of PS in the DCE. The reaction mixture was heated to about 50°C and stirred for 1 h. Then the sulfonated polymer was isolated.

Isolation of Sulfonated PS

The method of isolating sulfonated PS was dependent on the sulfonation level achieved. For sulfonation levels below about 15 mole %, no problems were encountered regarding separation of the sulfonated PS. The product was precipitated by dripping into a large quantity of water or methanol, followed by washing several times in water using a high-speed mixer for liquids. Isolated sulfonated PS was filtered and dried at 50°C in vacuum for 3 d. For sulfonation levels higher than 15 mole % substantial problems with the formation of an emulsion in water or methanol were encountered. In order to prevent them, solvent was evaporated, the solid polymer was ground to powder and washed with water. At sulfonation levels higher than about 30 mole % the product was completely water-

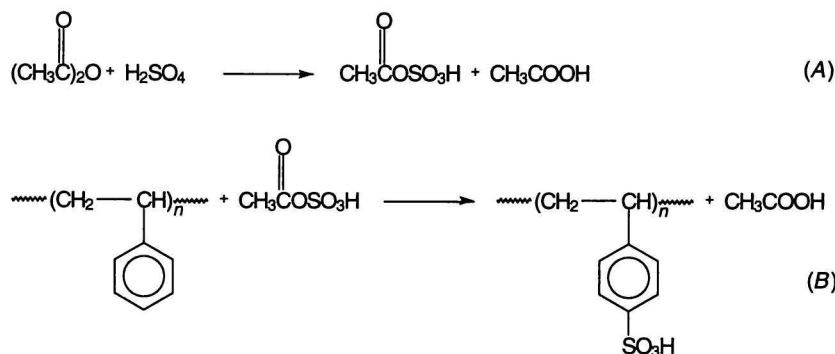
soluble and could be isolated after evaporating the solvent and then purified with nonaqueous solvent. Dichloroethane was the solvent of choice in this case. Finally, the sulfonated PS was dried in a vacuum oven at about 50°C for 3 d.

Characterization of the Sulfonated PS

The sulfonation level can be determined by titration of solution of PSSA in toluene–methanol-blended solvent ($\varphi_r = 9 : 1$) to a phenolphthalein end point using sodium hydroxide solution in methanol as the titration agent. Provided that the PSSA was completely soluble in ethanol (sulfonation level higher than about 20 mole %) it could be titrated in solution of ethanol. In order to standardize a solution of sodium hydroxide, benzoic acid or toluenesulfonic acid was used. The atomic absorption spectroscopy was another method used to determine the sulfonation level. It was measured using the IRISH AP Plasma Spectrometer (Thermo Jarrell Ash Corporation, USA). At first, the sulfonated material was mineralized in oxygen atmosphere by the method of Schoniger [9]. Then, the formed SO_2 was converted to SO_3 using H_2O_2 and then absorbed in water. Finally, this solution was transported into a volumetric flask. The mineralization procedure was done in an Erlenmeyer flask (250 cm^3) equipped with a special glass stopper with sealed platinum wire for holding the sample.

RESULTS AND DISCUSSION

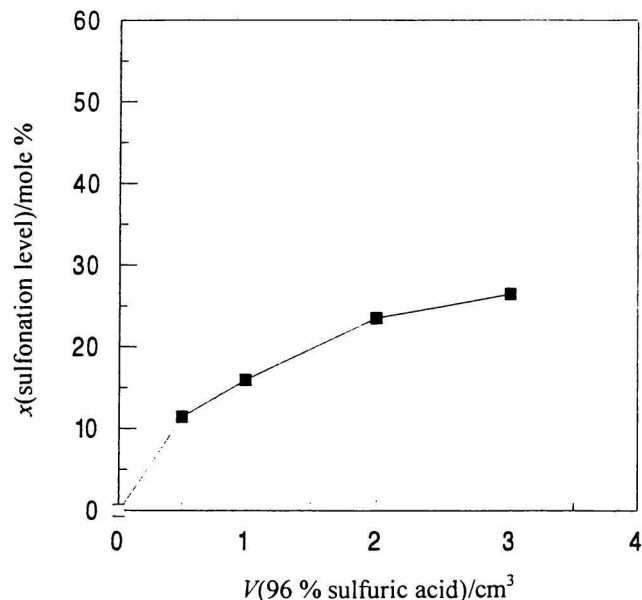
The sulfonation reaction was conducted at about 50°C for about 1 h [1, 10]. Initially, the degree of substitution of the SO_3H group to the phenyl ring increased rapidly in the first few minutes of the reaction and then it began to level off after about 1 h. It was assumed that the reaction yield of acetyl sulfate was quantitative (reaction A). The appropriate reaction scheme for the following sulfonation is given in [1] (reaction B).



Scheme 1

Table 1. Characterization of PSSA Prepared by Homogeneous Reaction

Designation of PSSA	$V(96\% \text{ sulfuric acid})$	$V(\text{acetic anhydride})$	ω_s
	cm^3	cm^3	%
SPS05	0.5	1.0	2.93
SPS1	1.0	2.0	4.09
SPS2	2.0	4.0	6.02
SPS3	3.0	6.0	6.77
SPS6	6.0	12.0	(13.89)

**Fig. 1.** The yield of sulfonation level against the volume of H_2SO_4 used for sulfonation. \square Theoretical, \blacksquare experimental.

In order to elucidate the effect of sulfuric acid concentration on the sulfonation yield, several PSSA's of different sulfur content were prepared (Table 1).

The experimental data for homogeneous sulfonation reaction plotted in Fig. 1 suggested that there existed a saturation effect for the dependence of sulfonation yield on the concentration of sulfuric acid which was used to generate acetyl sulfate as sulfonation agent. The theoretical line in Fig. 1 is calculated assuming quantitative sulfonation yield (100 %) and the experimental data are for the sulfonation yield of homogeneous reaction performed using the reaction procedure described by *Makowski* [1]. The apparent discrepancy between theory and experimental data for H_2SO_4 concentration above 17 % (1 cm^3) could be caused by either a different reaction mechanism

Table 2. Characterization of Sulfonated PS Beads Prepared by Gas Phase Sulfonation

Designation of PSSA	Reaction time	ω_p	x_p
	h	%	mole%
PSG 1	2	0.32	1.2
PSG 2	12	2.45	9.6

for sulfonation to a higher level or crosslinking of the product at the sulfonation level higher than about 20 mole %. Currently, experiments are conducted to elucidate this effect and determine the primary cause of the observed discrepancy.

In order to compare effectiveness of homogeneous and heterogeneous sulfonations, PS beads were sulfonated by gaseous SO_3 above the fuming sulfuric acid at concentrations at about 20 % SO_3 . The PS particles prepared by milling PS pellets were exposed to the sulfonating agent for a longer time than in the case of the homogeneous sulfonation in solution. It seemed reasonable to assume that the heterogeneous sulfonation reaction was proceeding only on the surface of the PS beads. As a result of the sulfonation, the colour of sulfonated PS became yellowish compared to white neat PS. Quantitative analysis of the sulfonated PS beads suggested a direct proportionality between sulfonation level and reaction time (Table 2). The concentration of SO_3H in the sulfonated PS was calculated for this case assuming that only the single sulfonation reaction took place. No side reactions were accounted for this work. Principally, diffusion of SO_3 into the PS beads is also probable, which can affect the result of sulfonation reaction in the gas phase. Further work on this project is in progress.

In conclusion, the effect of saturation was observed on the dependence of the sulfonation yield on the volume of H_2SO_4 used for the sulfonation of the PS in the case of homogeneous reactions. Preliminary data showed that the gas phase sulfonation reaction is a viable alternative to the homogeneous sulfonation and could be used for industrial production since it obviates problems associated with the use of large amounts of solvents.

Sulfonating PS in the gas phase we can produce a water-soluble polymer additive for polymer-modified concrete which may become an economically attractive way of recycling waste PS.

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