

# Chemical Modification of Polystyrene. V. Sulfonic Acid Resins from Anhydride Substituted Polystyrene

MUKUL BISWAS\* and SHAKUNTALA CHATTERJEE, *Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India*

## Synopsis

Chemically modified polystyrenes based on the condensation of polystyrene with phthalic anhydride, trimellitic anhydride, and *cis*-1,2,3,6-tetrahydrophthalic anhydride have been processed into sulfonic acid cation exchange resins. The effects of variation of sulfuric acid amount and the temperature of sulfonation on the synthesis and the ion-exchange capacities of the resins have been established. The resins have finally been characterized with respect to their structures by IR and elemental analyses data. The total ion exchange capacity as well as the salt-splitting capacity and the pH-metric titration characteristics of these resins have also been determined. These resins possess better ion-exchange capacities than the conventional styrene based resins.

## INTRODUCTION

In earlier publications in this series, Biswas and Chatterjee reported the electrophilic substitution reactions between polystyrene (PS) and phthalic anhydride (PA),<sup>1</sup> pyromellitic dianhydride (PMDA),<sup>1</sup> trimellitic anhydride (TMA),<sup>2</sup> and *cis*-1,2,3,6-tetrahydrophthalic anhydride (THPA).<sup>3</sup> These modified resins, PSPA, PSTMA, and PSTHPA, have further been processed into cation exchange sulfonic acid resins. This article highlights the preparation of sulfonic acid resins from PSPA, PSTMA, and PSTHPA and the results of the evaluation of the structural characteristics, ion-exchange, and related properties of these resins. Significantly, these resins compare favorably with the commercial PS-based ion-exchange resins. The general reaction scheme followed in the preparation of these resins is illustrated in Figure 1.

## EXPERIMENTAL

### Materials

Polystyrene (DP = 480, PolyChem, India, Ltd.) was used in all the experiments. Phthalic anhydride (BDH) was purified by sublimation. Trimellitic anhydride and *cis*-1,2,3,6-tetrahydrophthalic anhydride (Fluka AG, Buches, Switzerland) were used without further purification. Nitrobenzene was fractionally distilled. Anhydrous aluminium chloride (Riedel, West Germany) certified as "sublimed for synthesis" was used without further purification. H<sub>2</sub>S<sub>2</sub>O<sub>7</sub> (containing 20% SO<sub>3</sub>) was used for sulfonation.

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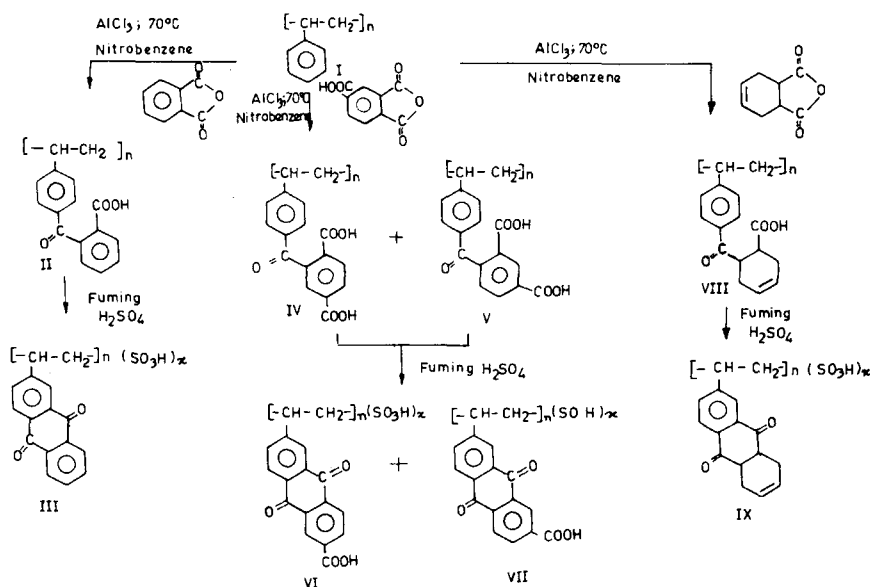


Fig. 1. Scheme for the synthesis of PSPAS (III), PSTMAS (VI, VII), and PSTHPAS (IX) from PS (I).

### Preparation of Sulfonic Acid Resins PSPAS, PSTMAS, and PSTHPAS and Their Sodium Salts

The condensation of PS with PA, TMA, and THPA were carried out using the procedure of Biswas and Chatterjee.<sup>1-3</sup> The sulfonation of PSPA, PSTMA, and PSTHPA was carried out directly by reacting the powdered condensate (100-mesh size) with fuming sulfuric acid for 10 h in a Pyrex flask under varied conditions such as using different temperatures (35°C, 50°C, 70°C, and 100°C) and different quantities of fuming sulfuric acid (25, 50, 75, and 100 g acid/g dry resin). The contents were cooled to 20°C and were subsequently poured onto crushed ice with constant stirring. The resins, PSPAS, PSTMAS and PSTHPAS, were filtered, washed several times with deionized water till the washings were free of SO<sub>4</sub><sup>-</sup> ions and finally dried at 100°C for 8 h. Synthesis of PSTHPAS has been described earlier.<sup>4</sup>

The sodium salts of the above resins were prepared by keeping them in *N* NaOH solution for 24 h, filtering, and washing the solid resins with deionized water till free of alkali. The resins were finally washed with alcohol and dried at 100°C.

### Characterization

**IR Spectra.** IR spectra were taken on a Perkin-Elmer 237B Grating IR Spectrophotometer in KBr pellets.

**Elemental Analysis.** Estimation of sulfur in the resins was done by a standard method.<sup>4</sup>

**Evaluation of Total Ion-Exchange Capacity.** The total ion-exchange

TABLE I  
Characteristic IR Absorptions ( $\text{cm}^{-1}$ )

Bands common to PSPAS, PSTMAS, and PSTHPAS	Assignments
1600	C=C aromatic stretching
1710	One strong C=O stretching vibration of quinonic structure
1750, 1775	Two small stretching for cyclic anhydrides
650	One band for $-\text{SO}_3\text{H}$
1035	Sharp and broad for $>\text{SO}_2$ and $-\text{SO}_3\text{H}-\text{SO}_3\text{H}$
1100-1300	

capacity and the salt splitting capacity in equilibrium with an electrolyte such as NaCl were determined by procedures described in earlier publications.<sup>5-7</sup>

**pH-Metric Titration.** pH values were recorded on a Digilog pH meter. Incremental quantities of NaOH solution (0.1*N*) were added to different mixtures containing a known weight of the resins and 10 mL NaCl (1*N*)—keeping the total volume at 50 mL by the addition of deionized water. The equilibrium pH and the ion-exchange capacities were measured after 24 h of equilibration.<sup>5-8</sup>

## RESULTS AND DISCUSSION

**Physical Properties.** The resins are brittle and black in color and insoluble in organic solvents such as aliphatic and aromatic hydrocarbons, alcohols, acetone, acetonitrile, nitrobenzene, halogenated hydrocarbons, and dimethylsulfoxide, also in inorganic acids and alkalis. The sodium salt forms of the resins are brittle and brownish black in color and exhibit the same solubility characteristics as the H form resins. The latter swell considerably in organic solvents compared to the Na forms.

**IR Characteristics.** Table 1 summarizes the pertinent IR absorptions in PSPAS, PSTMAS, PSTHPAS, and their assignments. Incorporation of sulfonic acid moieties is also endorsed by the results of sulfur analysis (Figs. 2 and 3).

Significantly, no stretching band due to  $-\text{COOH}$  groups appears in the IR spectra. This observation does not contradict structures VI and VII since the  $\text{COOH}$  moiety possibly exists as intra- and/or intermolecularly H-bonded. Pertinently, pH metric titration curves [Figs. 3(a), 3(b), and 3(c)] do not reveal any characteristic inflexion due to any weak acid moiety.

The appearance of rather sharp absorptions at 1750 and 1775  $\text{cm}^{-1}$ , assigned to anhydride, suggests the possibility of interchain anhydride formation during sulfonation through the dehydrating action of sulfuric acid.

**Effect of Temperature of Sulfonation on the Total Ion-Exchange Capacity of the Resins.** Figure 2 shows that, with a fixed quantity of fuming sulfuric acid (100 g/g of resin), the highest values of the total ion-exchange and salt-splitting capacities are realized when the sulfonation is conducted at 70°C. Significantly, the percentage of sulfur incorporated in the resin also assumes the highest value at this temperature. This feature implies that the introduction of the ionizable  $-\text{SO}_3\text{H}$  groups in the polymer matrix is most favored under these conditions. However, in the case of PSPMDAS resins the most efficient sulfonation is realized at 100°C under otherwise identical conditions. This difference

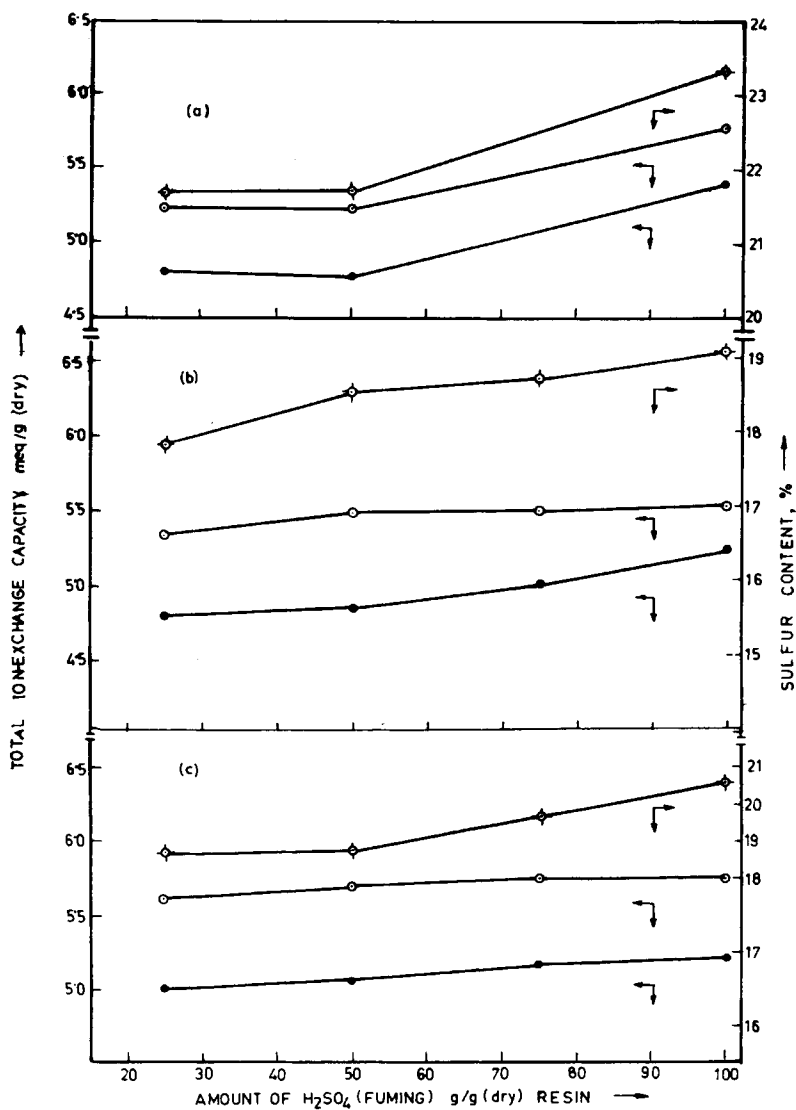


Fig. 2. Effect of variation of sulfuric acid amount for (a) PSPA, (b) PSTMA, and (c) PSTHPA on: ( $\diamond$ ) sulfur content; ( $\circ$ ) total ion-exchange capacity; ( $\bullet$ ) salt-splitting capacity.

is reasonable since the latter polymer matrix is more crosslinked than the others, so that sulfonation requires somewhat more drastic conditions.

**Effect of Variation of the Amount of Sulfuric Acid on the Total Ion-Exchange Capacity.** Figure 3 indicates that at a sulfonation temperature of 70°C the total ion-exchange and the salt-splitting capacities of the resins depend on the amount of the sulfonating agent. Thus, under the present conditions, 100 g fuming sulfuric acid/g dry resin, yield maximum sulfonation as evidenced by sulfur analysis data and the highest ion-exchange capacity value exhibited.

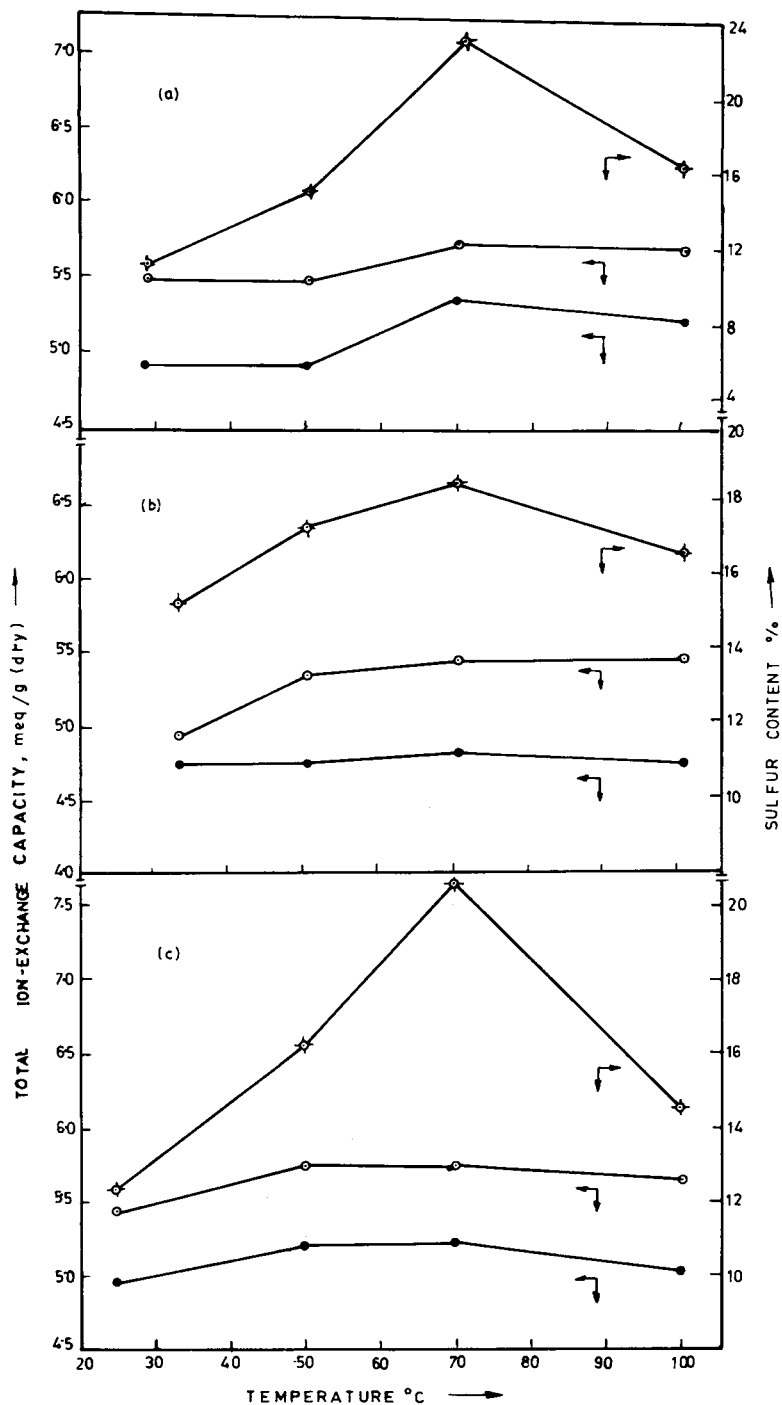


Fig. 3. Effect of variation of temperature of sulfonation for (a) PSPA, (b) PSTMA, and (c) PSTHPA on: (◇) sulfur content; (○) total ion-exchange capacity; (●) salt-splitting capacity.

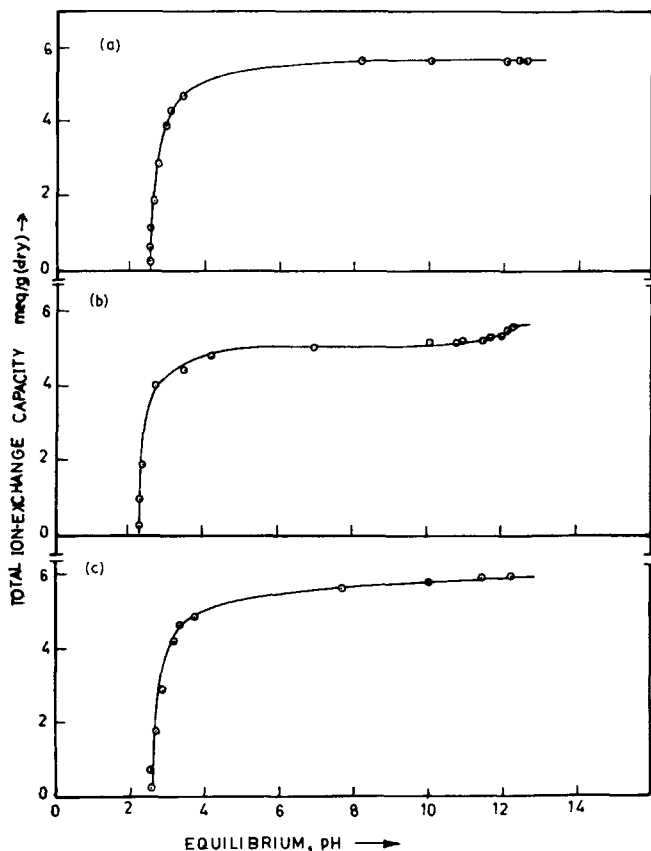


Fig. 4. Capacity vs. equilibrium pH curves of: (a) PSPAS; (b) PSTMAS; (c) PSTHPAS.

**pH-Metric Titration Curves.** Figure 4 represents the characteristic pH-metric titration curves for PSPAS, PSTMAS, and PSTHPAS resins. Table II compares the apparent pK values for these strong acid resins calculated from these data by applying the procedure of Helfferich.<sup>6</sup> Table II indicates that the pK values follow the trend: PSPMDAS > PSTHPAS > PSPAS > PSTMAS, which implies that the dissociation of the resins is somewhat suppressed along the series. Apparently, the different polymeric matrices will favor intra/intermolecular H bonding to different extents, depending on the nature of the sub-

TABLE II  
Comparison of Apparent pK Values of the Resins

Resin	Apparent pK Value
PSPAS	1.64
PSTMAS	1.31
PSTHPAS	1.74
PSPMDAS	1.98

TABLE III  
Comparison of the Capacities (Ion-Exchange) of Various Polystyrene-Based Sulfonic Acid Cation Exchangers

Resin	Ionogenic group	Capacity [meq/g (dry)]	Reference
PSPAS	SO <sub>3</sub> H <sup>+</sup>	5.80	This work
PSTMAS	COO-H <sup>+</sup>		
	SO <sub>3</sub> H <sup>+</sup>	5.49	This work
PSTHPAS	SO <sub>3</sub> H <sup>+</sup>	5.74	This work
PSPMDAS	SO <sub>3</sub> H <sup>+</sup>	5.75	8
SFS <sup>a</sup>			
(Styrene-Furfural)	COO-H <sup>+</sup>		
sulfonated	SO <sub>3</sub> H <sup>+</sup>	4.0-4.2	9
Amberlite	COO-H <sup>+</sup>		
IR-120	SO <sub>3</sub> H <sup>+</sup>	4.20	10
(S-DVB)			
Amberlyst 15 <sup>b</sup>	COO-H <sup>+</sup>		
	SO <sub>3</sub> H <sup>+</sup>	4.8	11
S-DVB <sup>c</sup>	COO-H <sup>+</sup>		
	SO <sub>3</sub> H <sup>+</sup>	4.2-5.1	11

<sup>a</sup> Sulfonation temperature, 100°C.

<sup>b</sup> Rohm and Haas.

<sup>c</sup> Bayer.

stituent, the structure of the polymeric network, and the extent of sulfonation undergone. However, the situation is indeed too complex for isolating the contribution of each of these factors.

**Comparison with Other PS-Based Strong Acid Resins.** Table III compares the total ion-exchange capacities of various PS based strong acid resins. Notably, the four anhydride modified PS-based sulfonic acid resins exhibit significantly higher total ion-exchange capacity values relative to the conventional PS-based resins. However, between PSPAS, PSPMDAS, PSTMAS, and PSTHPAS the total ion-exchange capacity values remain more or less the same. Furthermore, it has been reported in earlier publications that anhydride-substituted PS polymers exhibit significantly higher thermal stability compared to the unmodified PS. Accordingly, it would be interesting to find out how these sulfonated resins would compare with the conventional resins in respect of thermal stability. Results of comprehensive thermal stability studies of these resins will be reported in Paper VI of this series.

## CONCLUSION

Sulfonic acid resins processed from polystyrene electrophilically substituted with phthalic anhydride, trimellitic anhydride, and *cis*-1,2,3,6-tetrahydrophthalic anhydride exhibit better ion-exchange capacities than the unmodified styrene based resins.

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