Chemical Modification of Polystyrene. II. A Cation Exchange Resin from Polystyrene Electrophilically Substituted with Pyromellitic Dianhydride

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Synopsis

Crosslinked polystyrene based on condensation of polystyrene and pyromellitic dianhydride has been processed into a sulfonic acid cation exchange resin of improved thermal properties. The resin has been characterized in respect to its structure ion exchange and thermal stability by IR and elemental analysis data, total and salt-splitting capacity measurements, pH-titration characteristics, and TGA and DTA studies.

INTRODUCTION

As part of our continuing program on chemical modification of polymers,[1-6] we have studied a novel electrophillic substitution reaction between polystyrene (PS) and aromatic anhydrides, such as phthalic anhydride (PA),[7] pyromellitic dianhydride (PMDA),[7] and trimellitic[8] and *cis*-1,2,3,6 tetrahydrophthalic anhydride.[9] The polystyrene, thus modified, shows some attractive physicochemical properties compared to the unmodified polymer. A further modification of polystyrene–pyromellitic dianhydride condensate (PSPMDA) has now been possible through sulfonation (Fig. 1) leading to a cation-exchange resin of improved thermal and ion-exchange properties, which are highlighted in this paper.

EXPERIMENTAL

Materials

Polystyrene ($\overline{DP}$ 480) was supplied by Poly Chem, India Ltd. Pyromellitic dianhydride was obtained from Fluka AG, Buches, Switzerland, and purified by sublimation under vacuum. Aluminum chloride supplied by Riedel was purified following Howie and Macmillian.[10] Nitrobenzene, supplied by BDH, was distilled, and a middle fraction collected. Sulfuric acid (BDH, 98.8%) and $H_2S_2O_7$ (containing 20% SO_3) from International Chemical Industries, India, were used.

Preparation of PSPMDA

The condensation of PS with PMDA was first carried out using the procedure of Biswas and Chatterjee.[7]
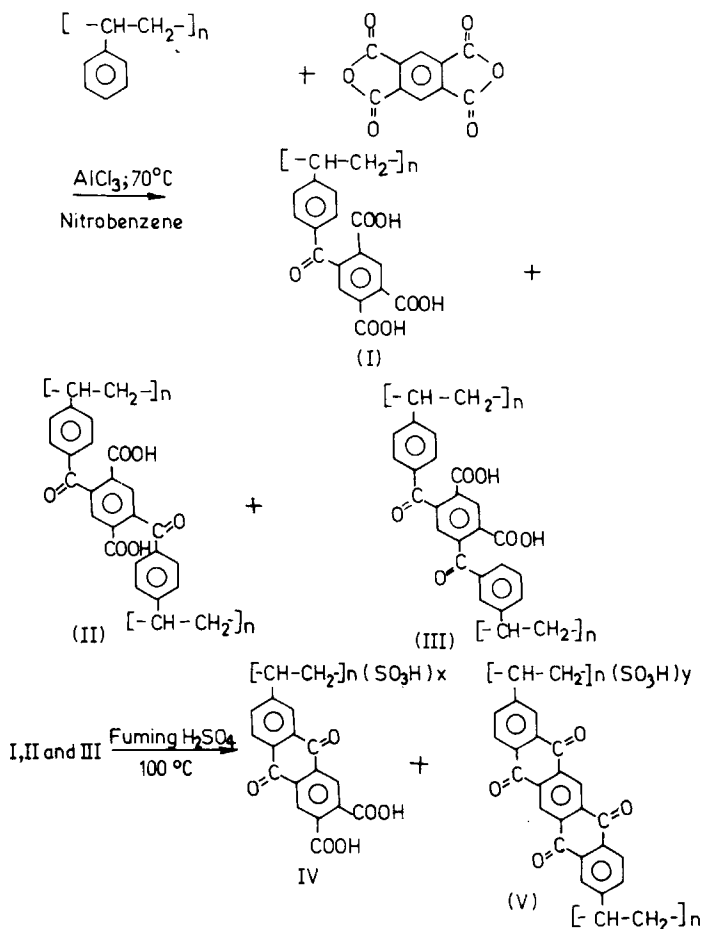
CCC 0021-8995/82/124645-09$01.90

Fig. 1. Route for the synthesis of a sulfonated resin from polystyrene substituted with pyromellitic dianhydride.

Preparation of Cation Exchange Resin

Sulfonation of the PSPMDA was first carried out by varying the weight of H_2SO_4 (98.8%) with stirring in a pyrex flask at 60°C. In an alternative procedure sulfonation was also carried out with oleum at 60°C and other temperatures. The contents were cooled to 20°C and were subsequently poured dropwise into crushed ice with constant stirring. The resin (PSPMDAS) was filtered, washed several times with deionized water until free from sulfate ions, and finally dried at 100°C for 8 h.

Characterization

IR Spectra

Infrared spectrum was taken on a Perkin-Elmer 237B Grating IR Spectrophotometer in KBr pellet.

Elemental Analysis

Estimation of sulfur was done by standard method.[11]

Evaluation of Capacity

The total ion-exchange capacity and the salt-splitting capacity in equilibrium with an electrolyte like NaCl were determined by recommended procedures.[12,13]

pH-Metric Titration

pH values were measured by a Digilog pH Meter. Incremental quantities of NaOH solution (0.1N) were added to different mixtures containing a known weight of PSPMDAS and 10 mL NaCl (1N), keeping the total volume at 50 mL by the addition of deionized water and measuring the equilibrium pH of the solution[12-14] in each case. The capacities were evaluated after the attainment of a constant pH, after about 24 h.

Thermal Characteristics

The DTA of the sample was studied with a MOM derivatograph over temperatures up to 800°C in air. The TGA of PSPMDAS was studied both in air and nitrogen with a Stanton Red Croft TG-750 (U.K.) model up to 1000°C. In both the cases, heating rate was 10°C/min.

RESULTS AND DISCUSSION

Physical Properties

The resin is brittle and black in color and insoluble in organic solvents, including aliphatic and aromatic hydrocarbons, alcohols, acetone, acetonitrile, nitrobenzene, halogenated hydrocarbons, and also in inorganic acids and alkalies. In the wet forms, PSPMDAS is a gel of blackish-brown mass. On heating to 100°C the gel nature disappears, and the mass changes to brittle black in color.

Elemental Analysis

Elemental analysis reveals the presence of sulfur in PSPMDAS (Figs. 2 and 3).

IR Characteristics

The IR spectrum of PSPMDAS (structures IV and V) reveals band typical of aromatic C=C stretching at 1600 cm^{-1} and sulfonic acid group stretching at 650 cm^{-1}, 1040 cm^{-1}, and 1175 cm^{-1} [15-18] (Fig. 4).

The IR spectrum does not reveal any stretching band due to the —COOH group, but the sharp band at 1710 cm^{-1} appears to be rather consistent with the
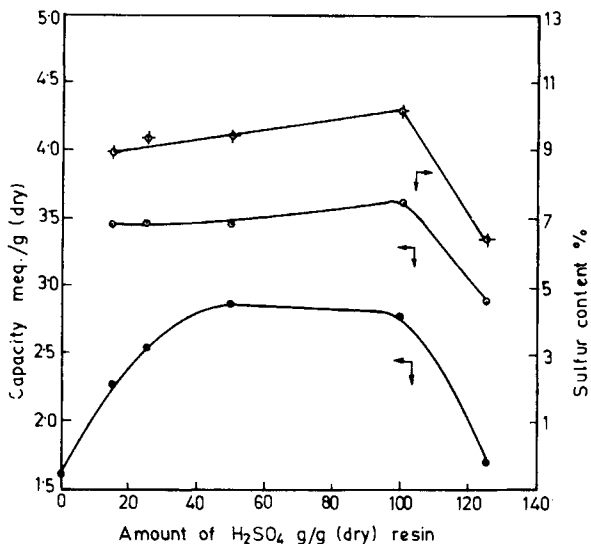
Fig. 2. Effect of variation of sulfuric acid (98.8%) amount of capacity: (◇) sulfur content; (⊙) total capacity; (●) salt-splitting capacity.

stretching $\gtrless$C=O group, which is formed in structures IV and V obviously due to cyclization of —COOH groups in the presence of fuming sulfuric acid, which is a well-known cyclizing agent. A similar cyclization of a polyketo acid form of N-vinyl carbazole phthalic anhydride condensate to the corresponding poly quinonic structure has been reported.[1]

Effect of Variation of Sulfuric Acid Amount on Capacity

Figure 2 shows that a total capacity of 3.61 meq/g and a salt-splitting capacity of 2.78 meq/g are realized when PSPMDA is sulfonated using H_2SO_4, 100 g/g (dry) PSPMDA, at 60°C for 10 h. With further increase in the quantity of H_2SO_4, the values of total capacity and salt-splitting capacity decrease sharply, which indicates that the degradation of the polymer is taking place with excess of H_2SO_4. However, when the sulfonation was repeated with fuming sulfuric acid (20% SO_3), 100 g/g (dry) PSPMDA, higher values of total capacity (4.38 meq/g) and salt-splitting capacity (3.72 meq/g) could be realized.

Effect of Temperature of Sulfonation

Figure 3 represents the effect of variation of temperature and ion-exchange characteristics of the resin sulfonated for a period of 10 h in fuming sulfuric acid 100 g/g (dry). It follows that both the total and the salt-splitting capacities increase with increasing temperature over the range 30–100°C. The sulfur content also consistently increases in this range. This trend suggests that the introduction of ionizable —SO_3H group in the polymer matrix is increasingly favored in this range.

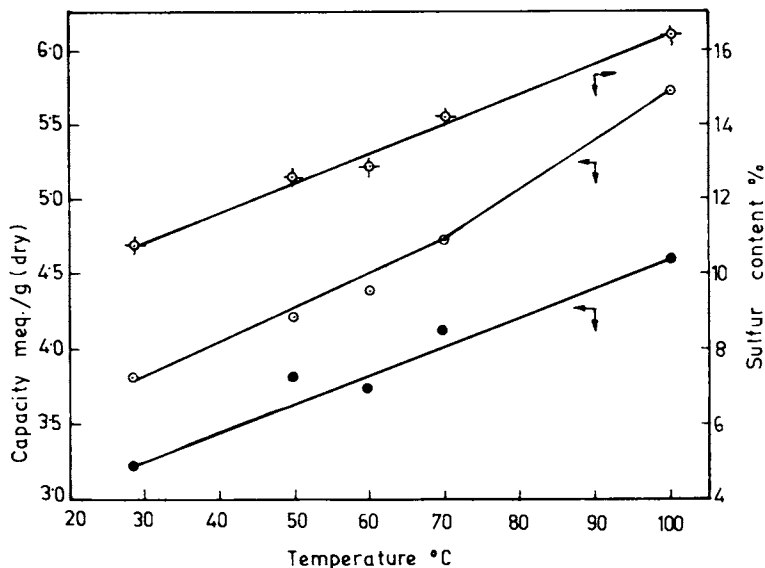Interestingly, in N-vinyl carbazole based cation exchange resins, the capacities

Fig. 3. Effect of variation of temperature of sulfonation (with fuming sulfuric acid) on capacity: (◇) sulfur content; (◉) total capacity; (●) salt-splitting capacity.

have been observed[1,12-14] to decrease with increase in temperature due to inactive sulfone formation.

The degree of crosslinking in an ion-exchanger is an important factor which affects ion-exchange capacity and the stability of the resin.   In the present instance, enhanced crosslinking[7] through PMDA moiety is possible, which implies a greater possibility of occupation of more positions in the polymer molecule[12,13] by the ionizable —SO_3H group than is feasible in polystyrene alone.
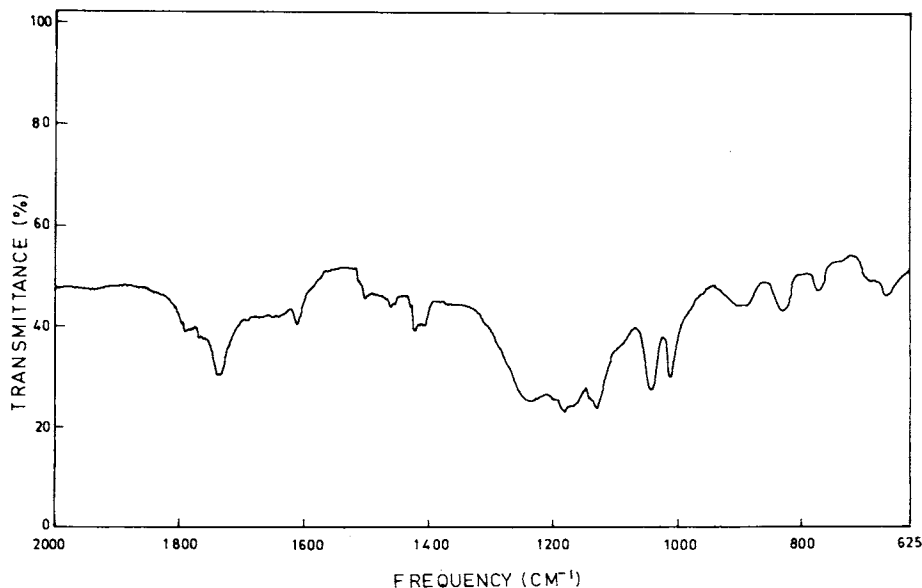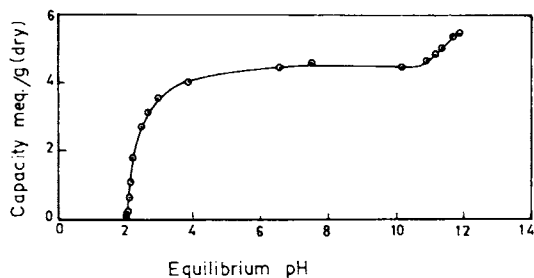

Fig. 4. IR spectra of PSPMDAS.

Fig. 5. Capacity vs. equilibrium pH curve.

pH-Metric Titration Curve

Figure 5 represents a typical pH-metric titration curve of PSPMDAS resin. The capacity sharply increases from 0.05 to 4.01 meq/g, corresponding to a pH change from 2.08 to 3.82 and thereafter remains more or less the same over the pH range 6.73–10.86. Above pH 11.10 the capacity increases slowly up to pH 11.87. The pH titration curve shows only one inflection. The apparent pK value of the resin calculated by applying the procedure of Helfferich[13] to the data of Figure 5 turns out to be about 1.98, which falls in the range of sulfonic acid resins.[13] The absence of a second inflection rules out the existence of a weakly dissociable group such as —COOH under conditions of sulfonation. The curve has a plateau after pH 11.73, which corresponds to complete conversion of the resin to the Na^+ form.

Effect of Heating on Capacity

Table I represents the effect of heating on capacity. No loss in capacity is realized when the resin is heated in water up to 80°C. However, a loss of ca. 3.47% occurs at 100°C. This information is significant in regard to the use of PSPMDAS in ion exchange at higher temperatures.

Thermal Properties

Figures 6 and 7 compare the thermograms of PSPMDAS in nitrogen and in air along with the corresponding data for PSPMDA.[7] In PSPMDA the weight loss starting from 200°C is presumably connected with the degradation of least thermally stable oxygen containing bonds.[16] The very considerable rate of

TABLE I
Effect of Heating[a] on Capacity

Temp (°C)	Total capacity (meq/g)		Loss in capacity (%)
	Before heating	After heating	
60	5.75	5.75	No loss
80	5.75	5.75	No loss
100	5.75	5.55	3.47

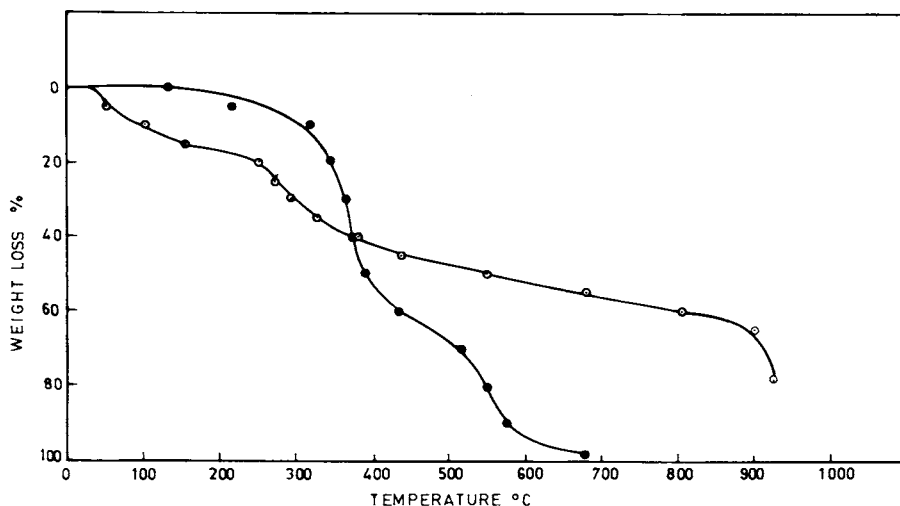[a] All samples were heated with deionized water for 24 h.

Fig. 6. TG curves of: (●) PSPMDA; (⊙) PSPMDAS in air.

weight loss in the range 300–400°C is reminiscent of the situation encountered by Leikin et al. in their study of the thermal stability of S–DVB copolymer[16] and is possibly due to the diffusion of the monomer evolved during the thermal degradation—a feature typically characteristic of PS with crosslinks. In the present instance, introduction of sulfogroup and cyclization of aromatic Keto acids to a polyquinone structure (V) are brought about by treatment of PSPMDA with fuming H_2SO_4. This causes some improvement in the thermal stability of PSPMDAS. Remarkably, PSPMDAS undergoes only 60% maximum weight loss at 950°C, while the sulfo-cationite from PS (10% DVB)[16] degrades 60% at ≃ 600°C.

Comparison of DTA curves for PSPMDAS in H^+ and Na^+ forms, Figures 8 and 9, respectively, in air indicates a better thermal stability of the Na form of
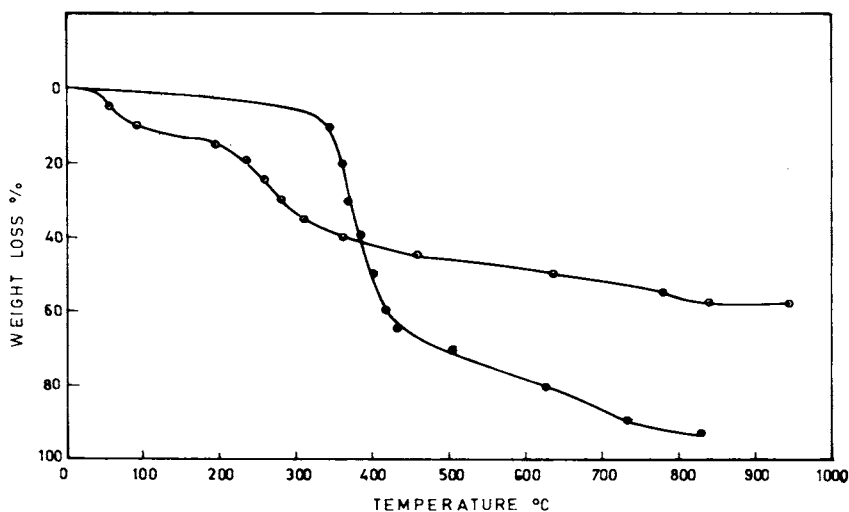

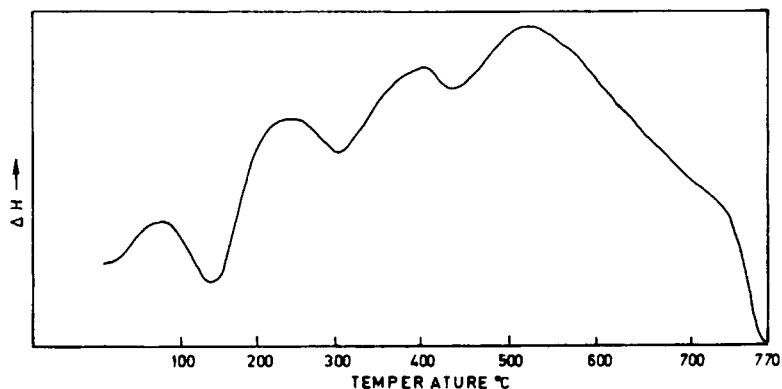Fig. 7. TG curves of: (●) PSPMDA; (⊙) PSPMDAS in nitrogen.

Fig. 8. DTA curve of PSPMDAS, H$^+$ form.

PSPMDAS relative to the acid form. However, the sharp endothermic peak at 630°C in the Na$^+$ form is conspicuously absent in the H$^+$ form, which indicates that the decomposition of the resin in the acid form apparently follows a different trend than that in the Na$^+$ form. Pertinently, Bothe et al.[21] observed similar trends in their DTA study of the H$^+$ and Na$^+$ forms of S–DVB sulfonated resins. However, these features are receiving closer attention for a better understanding of the decomposition processes involved.

Comparison with Other PS-Based Cation Exchangers

Table II compares the present resin with several other styrene based resins. Significantly, PSPMDAS registers a higher capacity and, as already discussed earlier, possesses better thermal stability than the styrene–divinyl benzene sulfonated resins reported by Korshak et al.[16] and by Bothe et al.[21]

CONCLUSION

The cation exchange resin prepared by sulfonation of polystyrene–pyromellitic dianhydride condensate exhibits attractive thermal stability and ion exchange
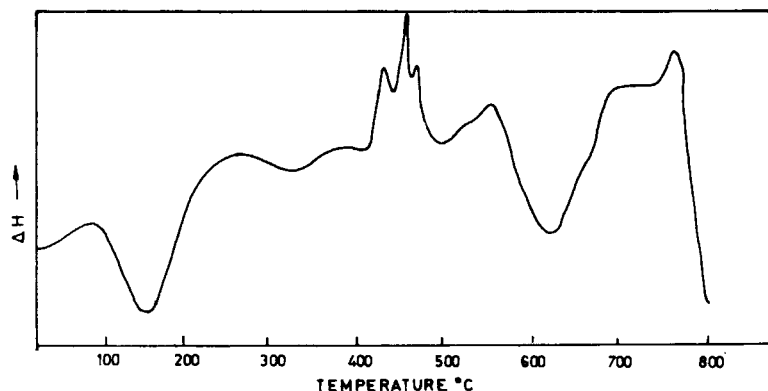

Fig. 9. DTA curve of PSPMDAS, Na$^+$ form.

TABLE II
Comparison of Capacities of Various Polystyrene-Based Sulfonic Acid Cation Exchangers

Resin	Ionogenic groups	Capacity (meq/g, dry)	Ref. no.
PSPMDAS	$SO_3^-H^+$	5.75	This work
SFS[a]	$SO_3^-H^+$	4.0–4.2	19
(styrene-furfural sulfonated)	COO^-H^+		
Amberlite	COO^-H^+	4.20	20
IR-120 (styrene– divinylbenzene)	$SO_3^-H^+$		
Amberlyst 15[b]	COO^-H^+	4.8	21
	$SO_3^-H^+$		
Styrene– divinylbenzene copolymer[c]	COO^-H^+	4.2–5.1	21
	$SO_3^-H^+$		

[a] Sulfonation temp, 100°C.
[b] Rohn and Haas.[21]
[c] Bayer.[21]

capacity relative to styrene–divinyl benzene or styrene furfural sulfonic acid resins.

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