

# Chemical Modification of Polystyrene. I. Electrophilic Substitution of Polystyrene with Aromatic Anhydrides\*

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## Synopsis

Polystyrene has been modified by electrophilic substitution reaction with phthalic anhydride and pyromellitic dianhydride. The products have been characterized by physical characteristics, solubility differences, elemental analysis, infrared spectra, ion-exchange capacity, and pH metric titration. The ultimate thermal stabilities of these modified polymers are better than the same for the unmodified polystyrene.

## INTRODUCTION

In continuation of our recent studies<sup>1-4</sup> on chemical modification of polymers, we now report electrophilic substitution reactions between polystyrene (PS) and phthalic anhydride (PA), and pyromellitic dianhydride (PMDA), respectively. The polystyrene, thus modified, exhibits some interesting physicochemical properties as compared with the unmodified polymer, which are also highlighted in this paper.

The substitution reactions involving polystyrene and PA or PMDA were carried out following the steps illustrated in Scheme I.

## EXPERIMENTAL

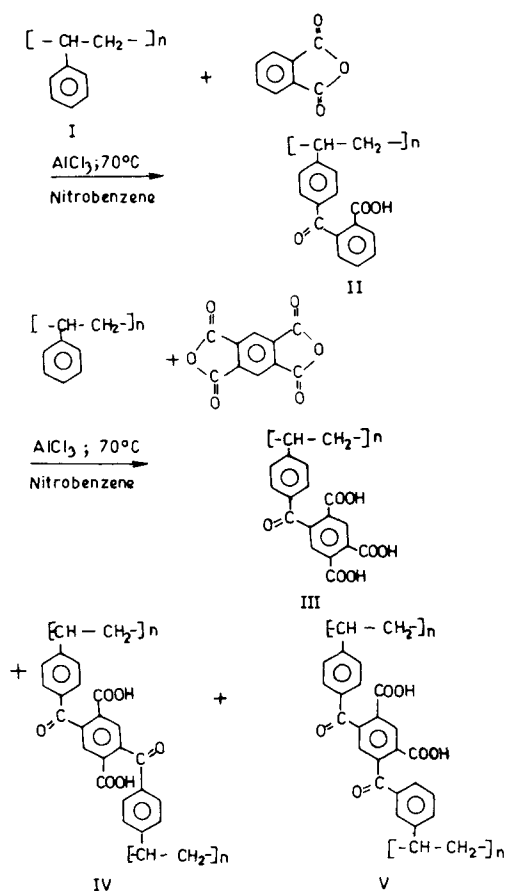
### Materials

Polystyrene ( $\overline{DP} = 480$ ) was supplied by Poly Chem., India, Ltd. Phthalic anhydride (BDH) was purified by sublimation. Pyromellitic dianhydride was obtained from Fluka AG, Buches, Switzerland, and purified by sublimation under vacuum. Aluminium chloride (Riedel) was purified by sublimation following the procedure of Howie and Macmillian.<sup>5</sup> Nitrobenzene (BDH) was distilled, and a middle fraction was collected.

### Synthesis

In a flask, anhydrous powdered  $AlCl_3$  (0.5 g) was slowly added to a shaken solution of PS (0.5 g) in nitrobenzene (5 mL) containing PA (1 g) or PMDA (1 g) at 20°C. The temperature was allowed to rise to 70°C, and the flask was ag-

\* Dedicated to (late) Professor S. R. Palit.



Scheme I.

itated by rotation for 24 h.

The reaction products separated out in nitrobenzene medium. To the cooled mixture was added crushed ice, and the mixture was shaken vigorously and kept for overnight to make the hydrolysis complete. The insoluble mass was filtered off, and washed successively with concentrated HCl, distilled water, and methanol. Finally, the products were refluxed separately with benzene and methanol several times to remove any unreacted PS, PA/PMDA, and nitrobenzene remaining with it. The products, PSPA and PSPMDA, were dried under vacuum at 60–80°C.

## Characterization

### IR Spectra

IR spectra of PSPA and PSPMDA in KBr pellets were recorded on a Perkin-Elmer 237B Grating Spectrophotometer.

*Elemental Analysis*

Carbon and hydrogen were estimated in a Thomas CH-Analyzer, 35.

*Thermal Characteristics*

The TGA of the polymer samples were made both in air and nitrogen with a "Stanton RedCroft TG-750 (U.K.)." DTA of the samples were studied with a MOM derivatograph over temperatures up to 1000°C in air. The heating rate was maintained at 10°C/min in both the instruments.

*Evaluation of Ion-Exchange Capacity*

The total ion-exchange capacity of PSPA and PSPMDA was measured by recommended procedures.<sup>6-8</sup>

*pH-Metric Titration*

pH-Metric titration characteristics of the PSPA and PSPMDA were determined by adding incremental quantities of NaOH solution (0.1N) to different mixtures containing a known weight of PSPA or PSPMDA 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 in each case. The capacities were evaluated after the attainment of a constant pH (after ~24 h).<sup>6,7</sup>

**RESULTS AND DISCUSSION****General Characteristics of PSPA and PSPMDA**

After purification, PSPA and PSPMDA were recovered as white and greyish flaky products, respectively. Both of them are insoluble in organic solvents including aliphatic and aromatic hydrocarbons in which PS is freely soluble.

**Elemental Analysis**

Table I compiles the elemental analysis data based on the suggested structures of PSPA (II) and PSPMDA (III-IV).

TABLE I  
Elemental Analysis Data

Compound	Tentative structure	% C	% H	% O
PS	I <sup>a</sup>	92.00	8.13	—
PSPA	II <sup>b</sup>	60.07	6.77	33.16 <sup>e</sup>
PSPMDA	III <sup>c</sup>	68.75	6.35	24.90 <sup>e</sup>
PSPMDA	IV or V <sup>d</sup>	68.75	6.35	24.90 <sup>e</sup>

<sup>a</sup> Calcd: C, 92.30%; H, 7.69%.

<sup>b</sup> Calcd: C, 76.19%; H, 4.76%; O, 19.04%.

<sup>c</sup> Calcd: C, 63.52%; H, 3.52%; O, 32.94%.

<sup>d</sup> Calcd: C, 73.33%; H, 4.22%; O, 22.53%.

<sup>e</sup> On the assumption that only oxygen atoms have been introduced in the structure.

The decrease in the weight percentage of carbon in II, and III–IV relative to that in I, is consistent with the incorporation of oxygen atom under the present experimental conditions in the skeleton of modified polymer. However, for II, the calculated percentage of oxygen is seen to fall short of the experimental value, the exact reason for which is obscure. For PSPMDA, all three structures suggested are probably present, and discrepancies between the theoretical and experimental values should rather be regarded in this light.

### IR Characteristics

Further evidence for the incorporation of PA or PMDA in the polystyrene is provided by the IR spectra (Fig. 1) of both PSPA (A) and PSPMDA (B) which are found to possess bands typical of aromatic carboxylic acid at  $1700\text{ cm}^{-1}$ , aromatic C=C stretching bands at  $1600\text{ cm}^{-1}$ , and the band  $1670\text{ cm}^{-1}$  due to the diaryl ketone moiety.

### Ion-Exchange and pH Characteristics

Structures II–V imply that the modified polymers would be expected to behave as weak acid resins with —COOH ionogenic groups, and, accordingly, they should exhibit ion-exchange capacity. In fact, both PSPA and PSPMDA possess total capacities of 0.96 meq/g and 1.6 meq/g, respectively.

The pH metric titration behaviour of PSPA and PSPMDA (Fig. 2) also corroborates the incorporation of —COOH acid moieties in the structure. On the basis of the proposed structures, PSPA should be expected to behave as a monofunctional weak acid, and PSPMDA as a polyfunctional weak acid. These expectations are amply borne out by the pH-metric titration data (Fig. 2) re-

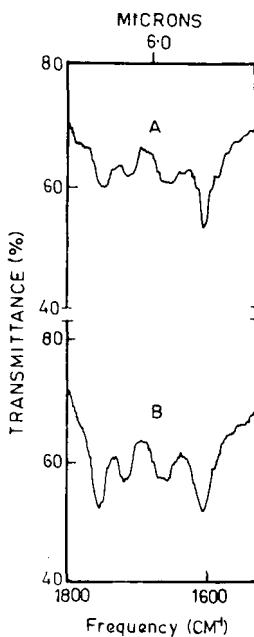


Fig. 1. Infrared spectra of (A) PSPA and (B) PSPMDA.

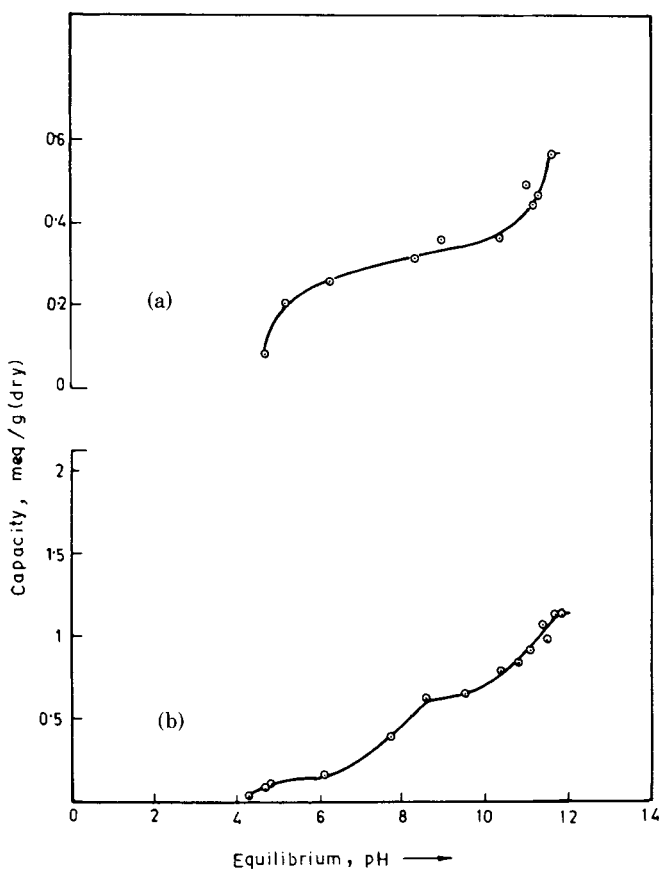


Fig. 2. Capacity vs. equilibrium pH curves: (a) PSPA and (b) PSPMDA.

vealing a single inflection,  $pK_1 = 6.85$  for PSPA, and two inflections,  $pK_1 = 7.05$  and  $pK_2 = 10.6$ , for PSPMDA, as calculated by the procedure of Helfferich.<sup>8</sup> The literature data<sup>8</sup> for  $pK$  of  $-\text{COOH}$  acid are in the range 4–6. The observed  $pK$  values tend to be somewhat higher than usual, which is not unlikely since intermolecular as well as intramolecular H-bonding<sup>3</sup> and the position (o, m, and p) of the  $-\text{COOH}$  groups in the structure will affect the apparent  $pK$  value.

### Thermal Characteristics

Figures 3(a) and 3(b) compare the thermograms of PS, PSPA, and PSPMDA in nitrogen and in air, respectively. It is clear that the original thermal stability of PS has been considerably improved after substitution by PA or PMDA moieties, the effect being more in the latter case. Thus PS appears to degrade 100% in air at  $400^\circ\text{C}$ , whereas PSPMDA does so at ca.,  $680^\circ\text{C}$ . Interestingly, PSPA remains somewhat less thermally stable than PS up to  $350\text{--}360^\circ\text{C}$ , and thereafter the stability is enhanced, in the polymer ultimately showing a limiting degradation of ca., 90% at  $550^\circ\text{C}$  onward.

In nitrogen atmosphere, however, the general trend in the thermal stability continues to be the same as in air except that all the three polymers exhibit, in general, higher stability in nitrogen atmosphere.

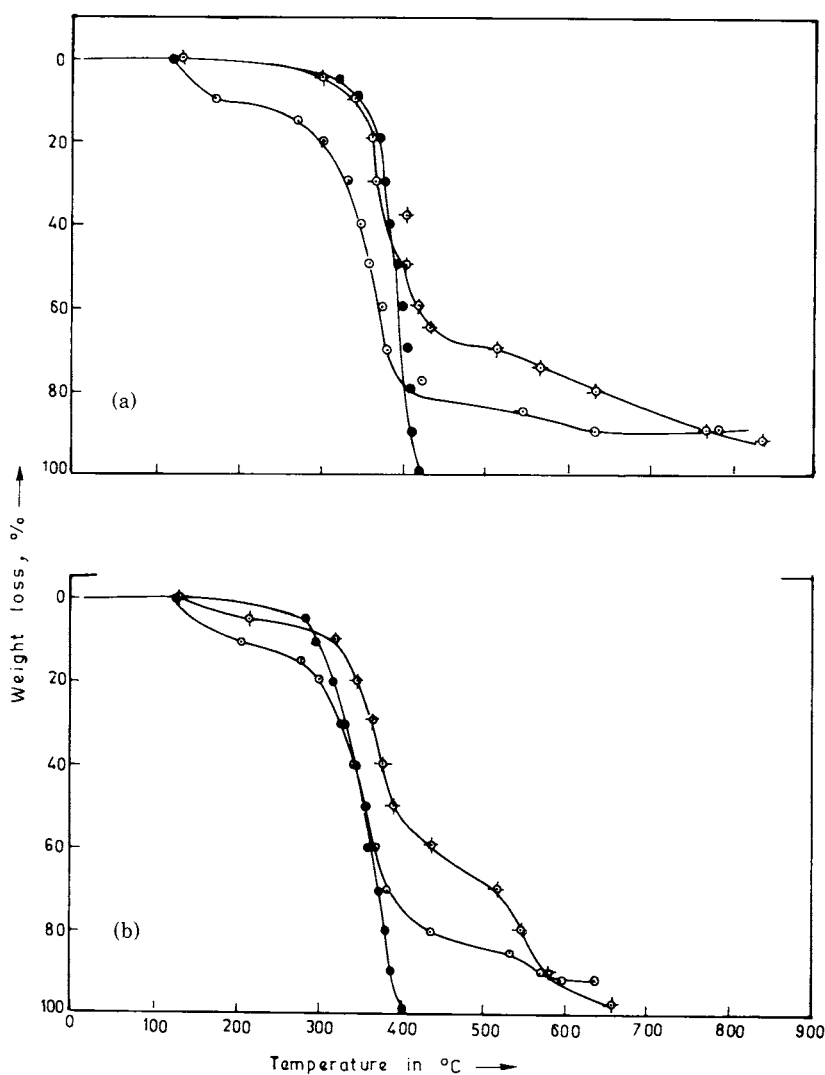


Fig. 3. TG curves: (a) in nitrogen; (b) in air; (●) PS; (○) PSPA; (-○-) PSPMDA.

The above trend in the order of thermal stability appears to be perfectly consistent with the proposed structure (Scheme I) for the substituted product. II suggests that PS undergoes condensation through the *p*-position of the benzene ring with phthalic anhydride forming poly(4-vinyl, 2'-carboxy benzophenone).

TABLE II  
Comparative Studies of DTA Peaks

Polymer	DTA peak
PS	Exotherm begins at 240°C Sharp endothermic peak at 400°C
PSPA	Small exothermic peak at 260°C and 300°C Sharp exothermic peak at 450°C and 580°C
PSPMDA	Broad exothermic peak around 240-320°C Sharp exothermic peak at 440°C and 560°C

It is possible that, at a higher temperature, II may undergo cyclization, which possibly accounts for the enhanced stability related to that of PS. As for the reaction of PS with PMDA, three possibilities may be considered. Structure III represents the case where PS is substituted at the *p*-position, while IV and V indicate that two PS chains are crosslinked through condensation with PMDA molecule. Such interchain crosslinking could be expected also to enhance the stability of PSPMDA.

Table II summarizes the salient DTA data for PS, PSPA, and PSPMDA and clearly reveals some interesting differences in the thermal behavior of the modified and unmodified polystyrene. Apparently, the appearance of exothermic peaks in both PSPA and PSPMDA is consistent with the incorporation of aromatic groups in the polymer, which undergo oxidative degradation under these conditions.

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