

# Preparation of Novel Membrane from Dianhydride-Modified Polystyrene with Controlled Pore Size on Micro- and Macrolevels

S. CHATTERJEE GANGULY, B. C. BHATTACHARYYA

Department of Chemical Engineering, Indian Institute of Technology, Kharagpur 721302, India

Received 28 April 1997; accepted 5 October 1997

**ABSTRACT:** A technique has been developed to prepare crosslinked, porous membrane from a chemical modification of polystyrene. Polystyrene was chemically modified by crosslinking with pyromellitic dianhydride in nitrobenzene using a Friedel–Crafts acylation reaction in the presence of  $\text{AlCl}_3$  at  $100^\circ\text{C}$ . Solid-state cross polarization/magic angle spinning NMR of powdered membrane was reported. TGA of the membrane was verified in air and in nitrogen. The morphologies of the membranes were analyzed.

© 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 709–717, 1998

## INTRODUCTION

This study is a continuation of previously published work<sup>1–4</sup> of the author in which the syntheses of polystyrene pyromellitic dianhydride (PSPMDA) and the corresponding sulfonic acid resin were reported (PSPMDAS). We studied the possibility of technology transfer of the process in terms of process design, mechanical design of selected equipment, and an estimate of cost.<sup>5</sup> This article reports the novel procedure of membrane fabrication from PSPMDA.

With the advancement of science and technology, there are increasing demands for quality polymeric membranes for their important commercial roles in a variety of separations in the chemical, food, pharmaceutical, and biotechnology industries. High performance membranes from high performance polymers are sought.

The limitations of conventional cellulose membranes in terms of chemical and biological attack, hydrolysis of the acetyl group in an alkaline medium, short life, low thermal stability, and pore compaction has reduced the other advantages.

Polymeric membranes have been prepared from polyamides, polyimides, etc. Most of these membranes are formed through a phase-separation process (i.e., melt extrusion or coagulation of polymer solution by a nonsolvent), a process often designed as phase inversion. A considerable body of knowledge has yet to be unraveled to exploit the mode of polymer aggregation resulting from the host of interactions that prevail among solvents and nonsolvents and the macromolecules themselves. Membrane fabrications are not possible during synthesis of a polymer from monomer using the condensation reaction.

Those processes cannot give a high-performance, high-strength membrane because the binding forces between the coagulants are very weak and little is known about the intricate relationships among the physicochemical parameters that control the formation of the micro- and macromorphologies of most dense and porous membranes.

Recently, Fujita and Soane<sup>6</sup> prepared asymmetric polystyrene (PS) based membranes by radiation polymerization of PS with divinyl benzene (DVB). They performed a copolymerization crosslinking reaction between styrene and DVB and presented a nonsolvent system and made hole artificially.

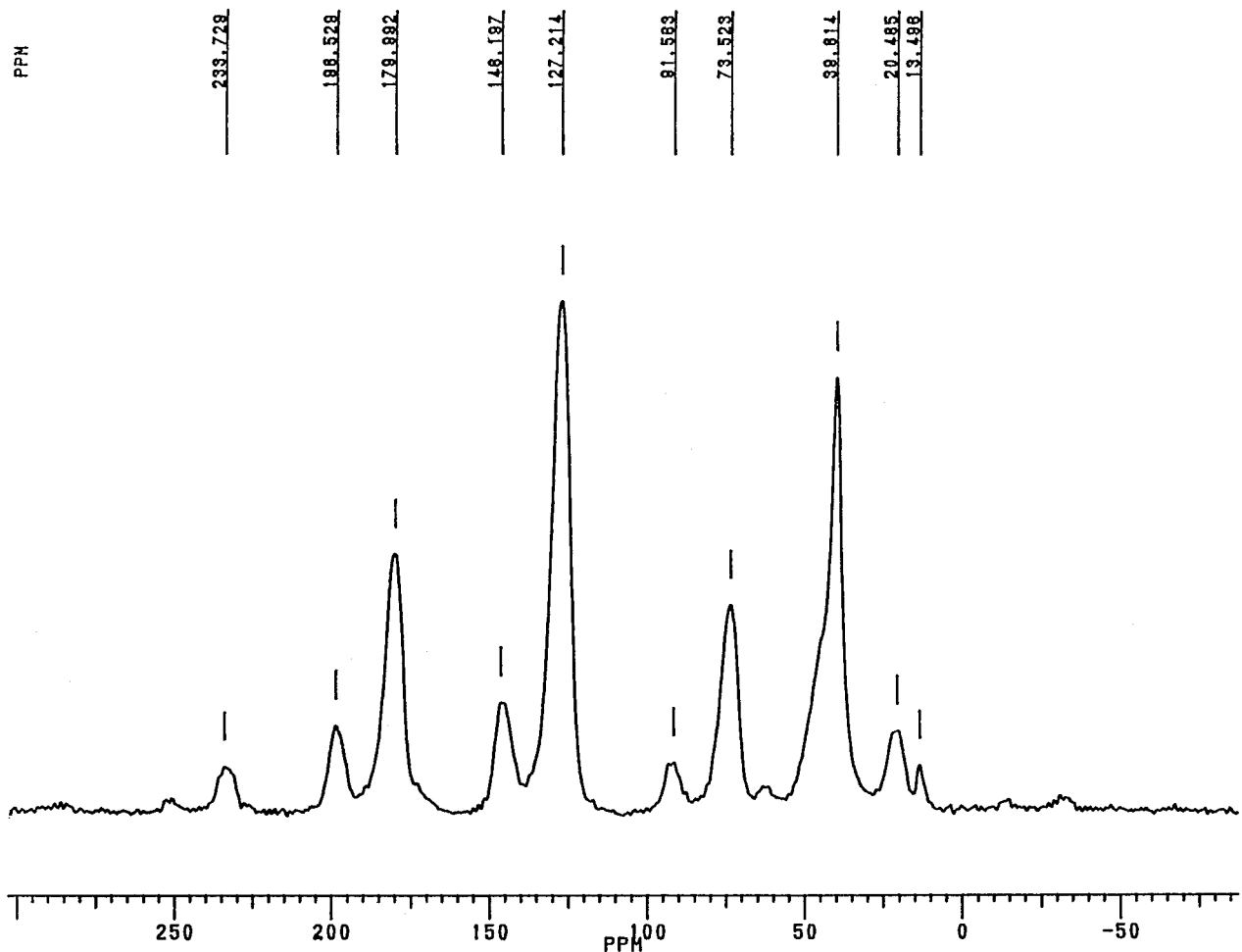
It has been observed that PSDVB based copoly-

Correspondence to: S. Ganguly, 357A Invermay Road, Mowbray 7248, Tasmania, Australia.

*Journal of Applied Polymer Science*, Vol. 69, 709–717 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/040709-09



**Figure 1**  $^{13}\text{C}$  CP/MAS spectra of PSPMDA synthesized in nitrobenzene and 1,2-dichloroethane solvent.

mers are characterized by an inhomogeneous pore structure<sup>7</sup> due to the different reaction rates of the copolymers. The inhomogeneous pore structure of the copolymers is allegedly responsible for their low osmotic ability and insufficient permeability to large ions. This is also an undesirable feature for membrane fabrication, because wide pore size distribution in a microlabel may affect separation processes.

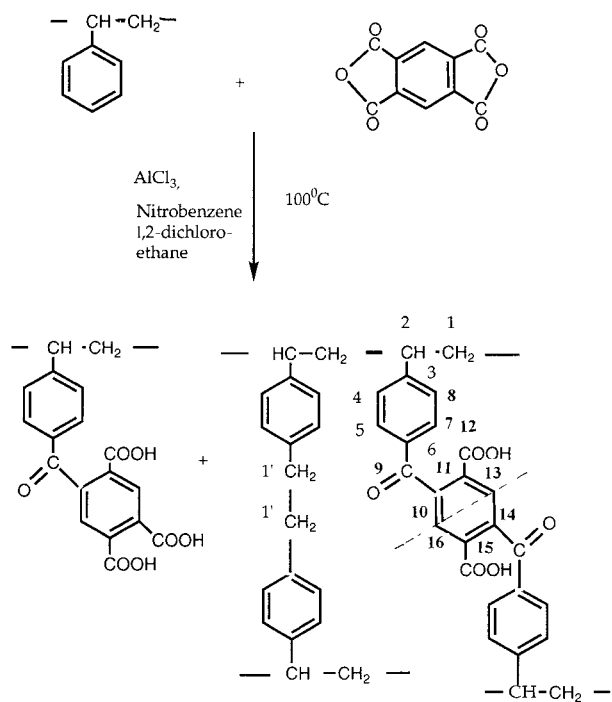
We propose a novel technique of membrane fabrication from chemically crosslinked PS with macronet isoporous structures. We exploited the easy and controlled reaction procedure of copolymerization crosslinking of the Friedel–Crafts acylation reaction during membrane fabrication. This process is entirely different from coagulation or phase separation processes. Crosslinking of PS was done by dianhydride (D) during casting conditions, and the thin films were subsequently water quenched to give a characteristic structure.

The structure was termed a macronet isoporous structure.<sup>7</sup> Due to the high crosslinked structure, egression of one solvent by ingress of another will take place through the mesh of the network<sup>8</sup> at specific ionic or physiological conditions due to a selective network response to the environment by swelling or deswelling, depending on the ionization of the fixed groups. Unlike other processes, the morphology of the membrane will be dominated by well-organized chemical crosslinking at the microlevel. Subsequently, the process will allow efficient recycling of PS foams generally used for packing materials.

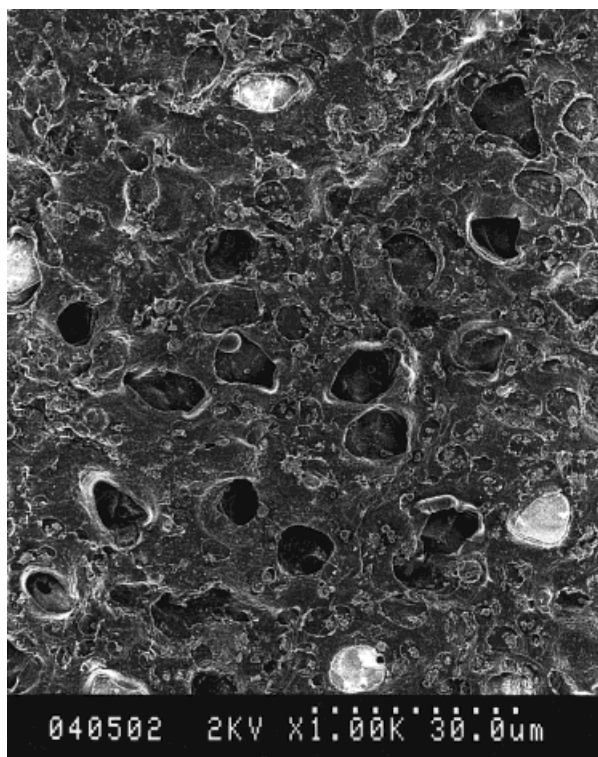
## EXPERIMENTAL

### Materials

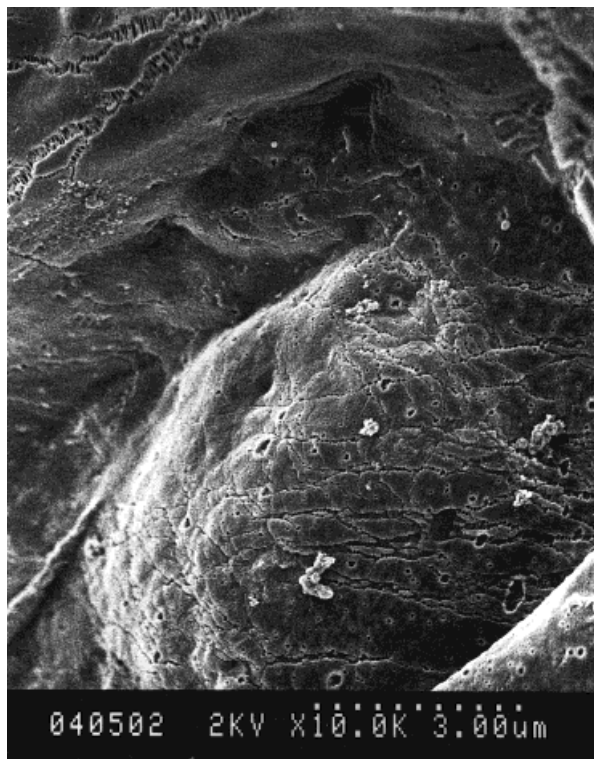
The following materials were used for the synthesis of PSPMDA condensate: pyromellitic dianhy-



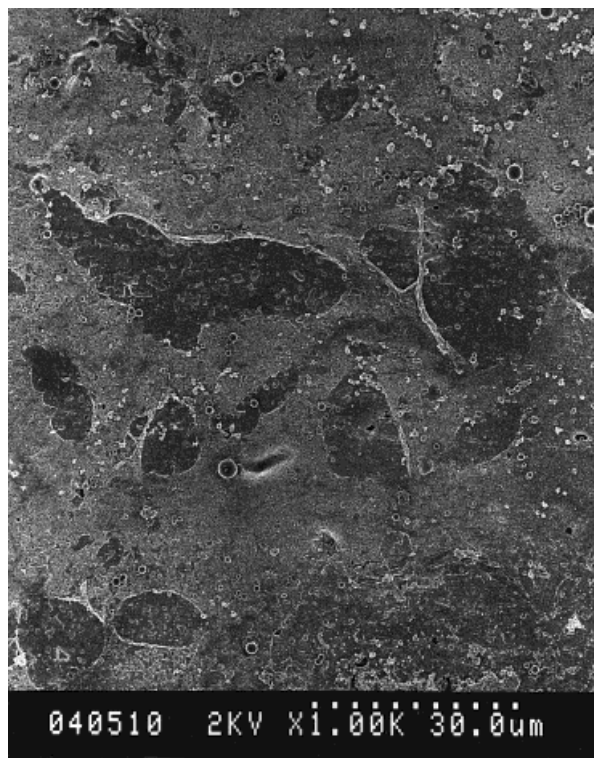
**Scheme 1**



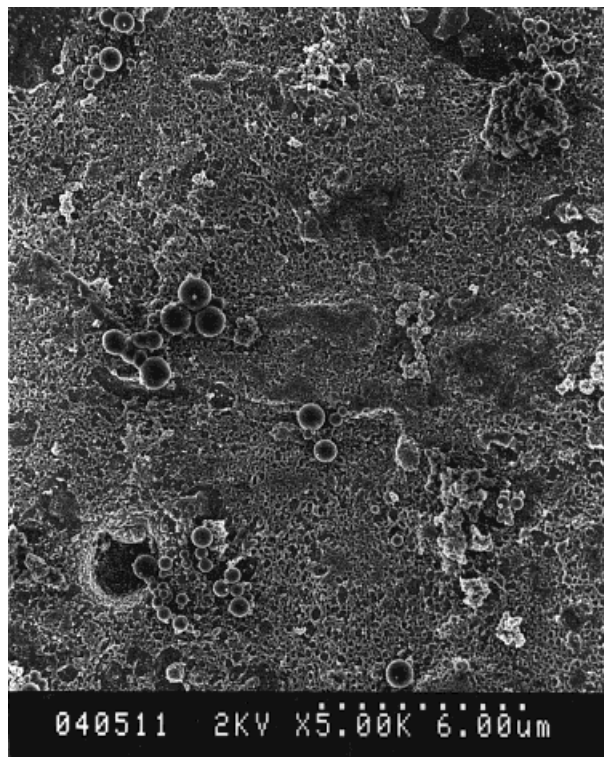
**Figure 2** Morphology of the top surface of PSPMDA film prepared from nitrobenzene and 1,2-dichloroethane at low magnification. Original magnification  $\times 1000$ .



**Figure 3** Morphology of top surface of PSPMDA film prepared from nitrobenzene and 1,2-dichloroethane at high magnification.



**Figure 4** Morphology of bottom surface of PSPMDA film prepared from nitrobenzene and 1,2-dichloroethane at low magnification. Original magnification  $\times 1,000$ .



**Figure 5** Morphology of bottom surface of PSPMDA film prepared from nitrobenzene and 1,2-dichloroethane at high magnification. Original magnification  $\times 5,000$ .

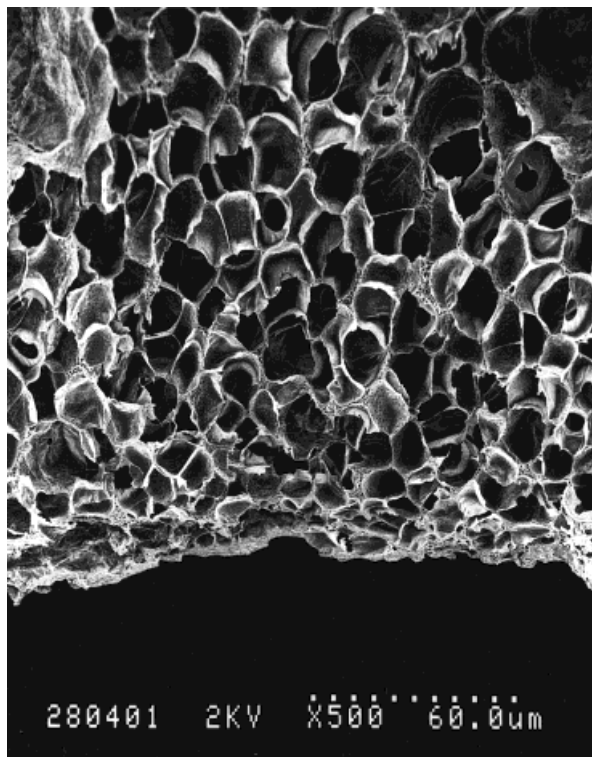
dride (PMDA) from BDH was purified by sublimation under a vacuum and was finally recovered as a white powder. Fresh anhydrous aluminum chloride was used (Aldrich Chemicals). The PS (Chemplex, Melbourne) used has an number-average molecular weight ( $M_n$ ) of about 260,000.

#### Preparation of PSPMDA Film

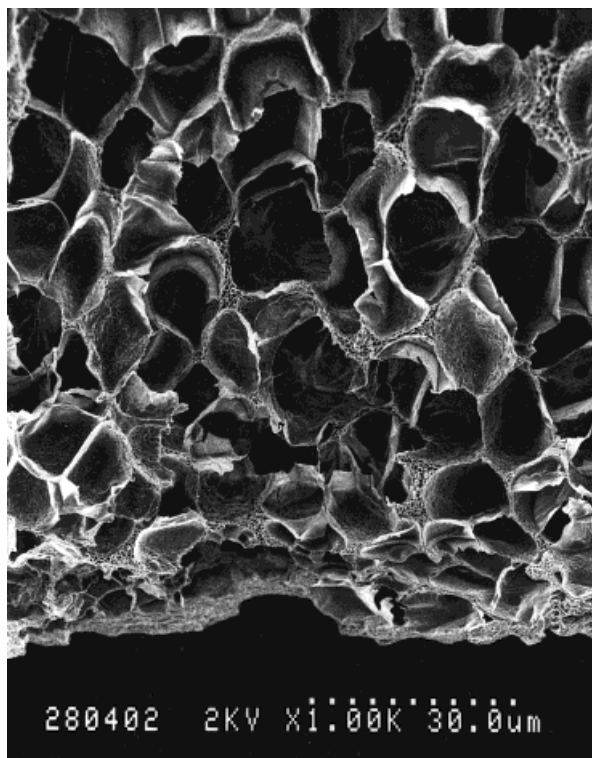
The condensation of PS with PMDA was carried out after minor modification of our former procedure<sup>3</sup> in which 2 g of PS was dissolved in a mixture of 9 mL nitrobenzene and 1 mL of 1,2-dichloroethane. To that mixture was added 0.8 g of PMDA, and it was stirred well using a magnetic stirrer. Then 5 g of  $\text{AlCl}_3$  was added. The solution was kept at  $0^\circ\text{C}$  for 30 min and then filtered through a strainer to remove any undissolved lumps of PMDA or  $\text{AlCl}_3$  particles.

The cast solution was spread on a 10-cm diameter sealed stainless steel mold of 1 mm depth and kept in a water bath at  $100^\circ\text{C}$  for 4 h. A dark colored gel formed. Completion of the reaction was identified by a model reaction in another flask.

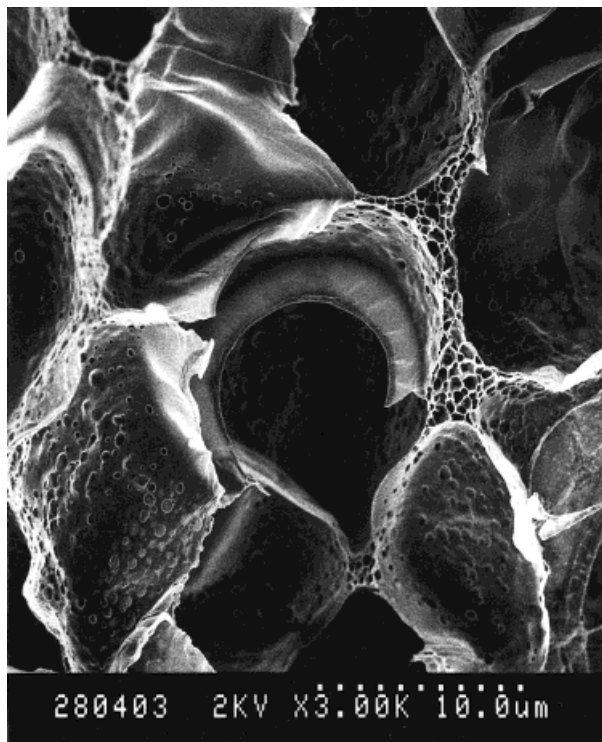
The film was cooled and rinsed with distilled



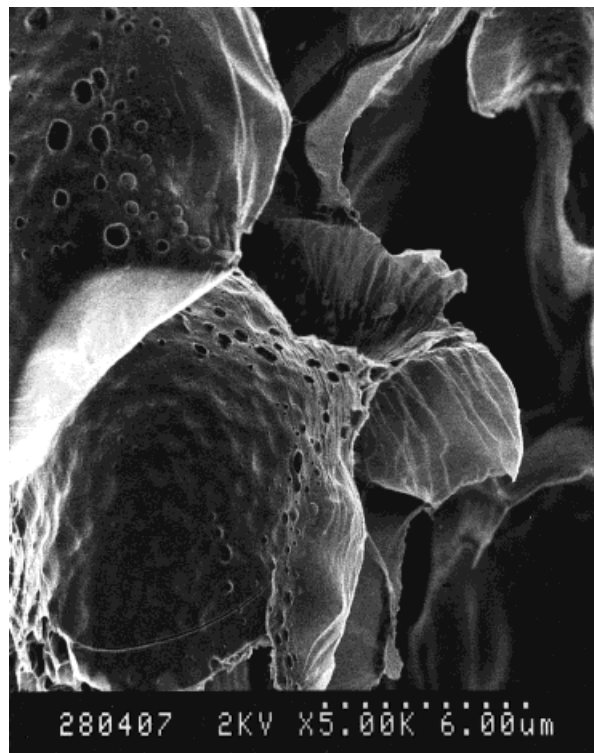
**Figure 6** Side view of PSPMDA film prepared from nitrobenzene and 1,2-dichloroethane at low magnification. Original magnification  $\times 500$ .



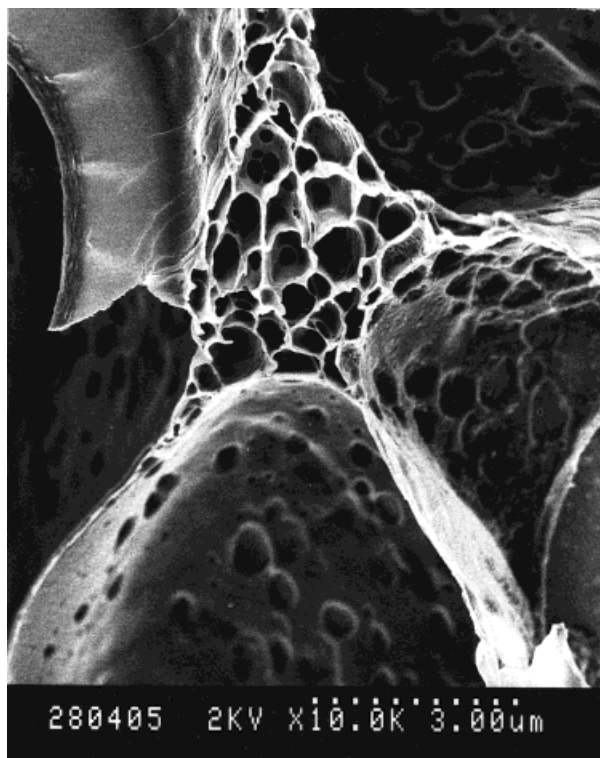
**Figure 7** Side view of PSPMDA film prepared from nitrobenzene and 1,2-dichloroethane at low magnification. Original magnification  $\times 1,000$ .



**Figure 8** Side view of PSPMDA film prepared from nitrobenzene and 1,2-dichloroethane at high magnification. Original magnification  $\times 3,000$ .



**Figure 10** Side view of PSPMDA film prepared from nitrobenzene and 1,2-dichloroethane. Original magnification  $\times 5,000$ .



**Figure 9** Side view of PSPMDA film prepared from nitrobenzene and 1,2-dichloroethane at high magnification. Original magnification  $\times 10,000$ .

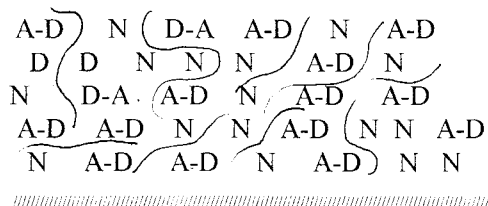
water in the presence of dilute hydrochloric acid. The color changed to white due to the hydrolysis of the polymer- $\text{AlCl}_2$  complex into polymer-COOH and  $\text{AlCl}_3$ . The films were immersed in methanol and benzene solvent, respectively, and finally dried under a vacuum for 7 days.

## CHARACTERIZATION

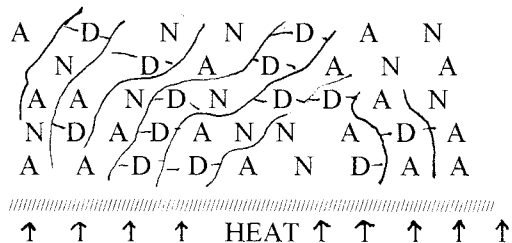
### Scanning Electron Micrographs

PS-PMDA condensate prepared in nitrobenzene and 1,2-dichloroethane media were processed for observation under a scanning electron microscope. Samples were dried in a vacuum at  $60^\circ\text{C}$  to a constant weight. Test pieces were cut by a knife to view the structure under a microscope. All SEM samples were imaged in a Hitachi S900 FESEM in which an "in-lens" type field emission SEM with ultraresolution was used. A Dynavac Xenosput 2000 sputter coater was used to coat samples with chromium, giving a coating thickness of 2–4 nm.

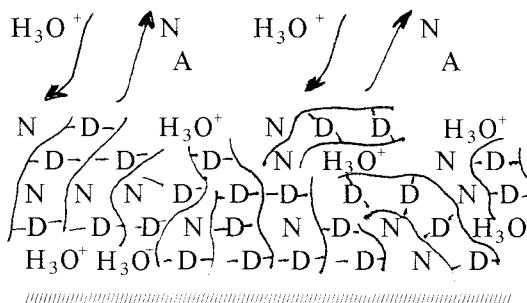
- 1) Casting step-Friedel Crafts interaction between  $\text{AlCl}_3$  and dianhydride at  $-2^\circ\text{C}$  for 30 min.



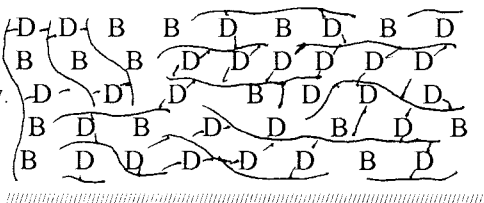
- 2) Exposure to heat at  $100^\circ\text{C}$ . Time will be decided by experimental results. Crosslinking via D will give micronet structure. Which will be swelled in nitrobenzene.



- 3) Hydrolysis and removal of  $\text{AlCl}_3$  and nitrobenzene (partly) resulting in phase separation and white swelled film.



- 4) Nitrobenzene, unreacted dianhydride unreacted PS, will be removed by water, ethanol and benzene respectively.



Stainless steel surface with silicon (//////////), polystyrene ( ~ ), D- dianhydride, N- nitrobenzene, A-  $\text{AlCl}_3$ ,  $\text{H}_3\text{O}^+$  - ice cold acidic water, B-benzene.

**Figure 11** Schematic of the proposed membrane formation mechanism.

### Solid-State $^{13}\text{C}$ -NMR Cross Polarization/Magic Angle Spinning (CP/MAS)

Solid state  $^{13}\text{C}$ -NMR CP/MAS spectra were recorded on a Bruker MSL 300s spectrometer operating at 75.47 MHz. Samples of 300 mg of the polymer were packed in 7-mm o.d. Zirconia rotors and subjected to MAS at 4 kHz. Spectra were acquired using single contact CP conditions with the following parameters. The  $^{13}\text{C}$  pulse times were 5.8–6.0  $\mu\text{s}$  (decoupler field strength, 50–60 kHz), contact time 1 ms, and recycle times 3–5 s.  $^{13}\text{C}$  chemical shifts are reported relative to adamantane ( $\delta\text{C} = 37.8$  ppm) as an external standard.

### Thermal Characteristics

The DTA and TGA of the membrane was studied in air and nitrogen with a DuPont 2100 model up to  $800^\circ\text{C}$ . In both the cases the heating rate was  $10^\circ\text{C}/\text{min}$ .

### RESULTS AND DISCUSSION

The membrane is insoluble in all solvents and swells in benzene, toluene, etc. In the swollen condition, the membrane is soft and rubberlike. For

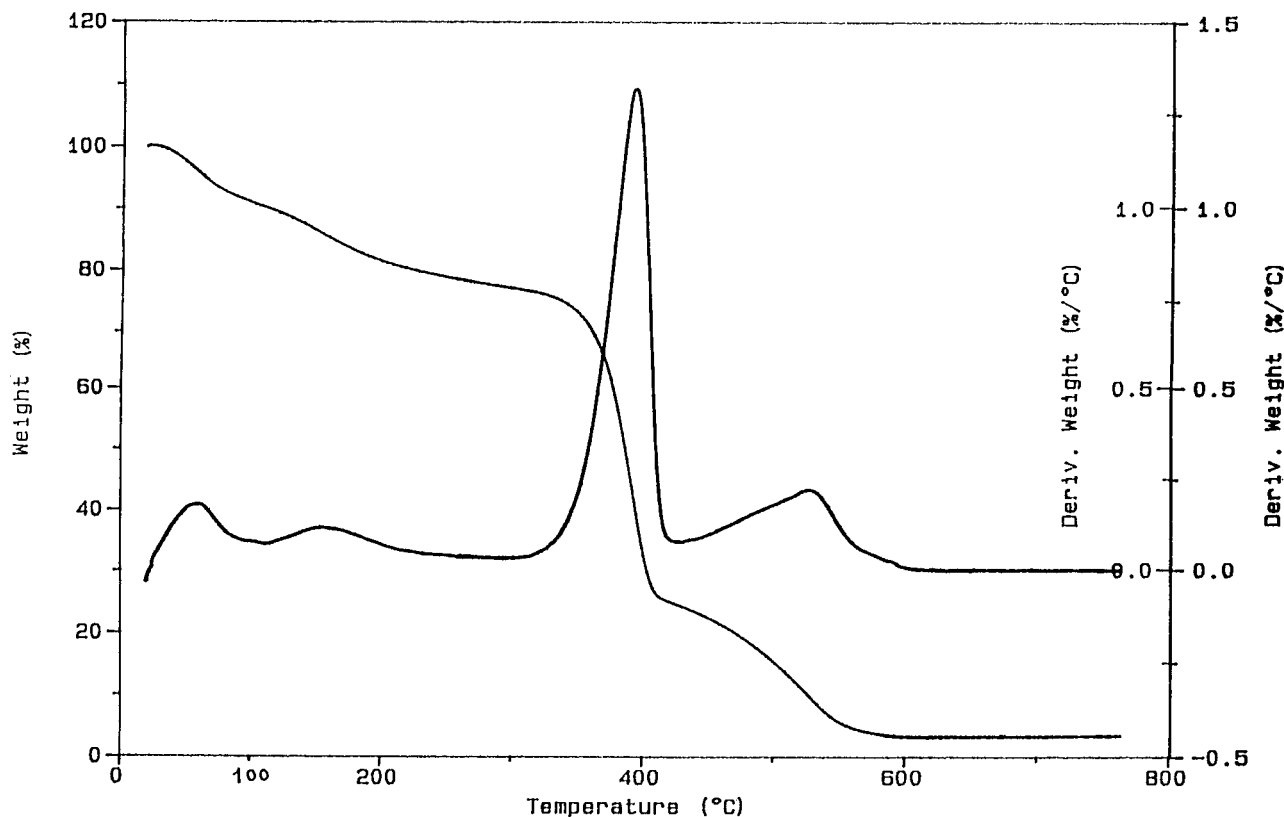


Figure 12 TGA curve of PSPMDA film with first derivative in air.

casting of a membrane, a stainless steel mold greased with silicon oil is ideal.

$\text{AlCl}_3$  has a significant role in membrane fabrication at  $100^\circ\text{C}$ , and an appropriate amount of  $\text{AlCl}_3$  reduces the gelation time significantly.

A mixture of nitrobenzene and dichloromethane (9 : 1) gave the film texture. Other factors for the present synthesis were studied in detail in earlier publications.<sup>1-3</sup>

#### Solid-State $^{13}\text{C}$ -NMR CP/MAS

Solid-state  $^{13}\text{C}$  CP/MAS allowed the investigation of the powdered form of the insoluble membrane (Fig. 1).

Scheme 1 illustrates the present reaction. The crosslinked polymer has a line of symmetry. We consider the upper part for  $^{13}\text{C}$ -NMR discussion. Each different carbon atom produces a different signal. Because of molecular symmetry, C4 and C8 are equivalent, as are C5 and C7; therefore, we expect two spectra of high intensity. In fact, the only broad spectrum of very high intensity, which appears at the aromatic region of  $\delta 127.21$ , might be the combined signals of C4, C5, C7, and C8.

The non-proton-bearing carbon give lower intensity signals.<sup>9</sup> So, non-proton-bearing C3 appears at 91.5 ppm, and C6 and C10 (closed to  $\text{C}=\text{O}$ ) appears at the high field of 148.1 ppm. Non proton bearing C11 (adjacent to  $-\text{COOH}$  group) is expected to appear at high field. On the other hand, proton-bearing C16, which is conjugated with the  $-\text{C}=\text{O}$  group is expected to be in a chemical shift position higher than the base value for aromatics. A moderate intensity peak at 179.99 ppm is presumably the overlap spectra of C11 and C16.

The low intensity peaks for carbonyl functional group C9 were at 233.72 ppm; the carboxyl functional group C12 at 196.52 ppm is also justified.

The medium peak at 73.52 ppm represents the presence of alkyl halide, which may be due to unreacted dichloroethane entrapped in a crosslinked moiety or it may be from a partial Friedel-Crafts alkylation reaction.

There are chemical shifts for an "aliphatic backbone" at 39.81 ppm; the sharp signal represents the tertiary carbon C2. The secondary carbon C1 appears at 20.46 ppm and C1' at 19.49 ppm.

Figures 2 and 3 illustrate the top surface (i.e.,

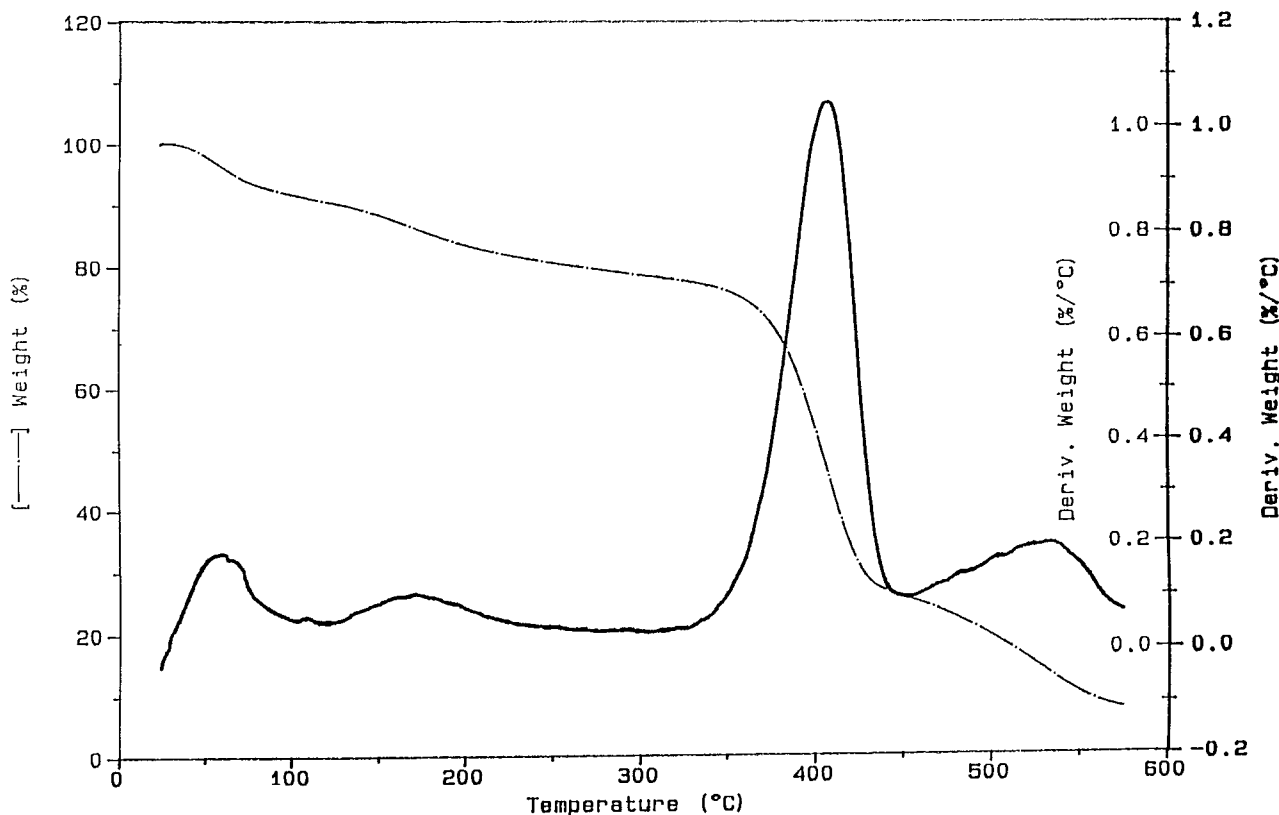


Figure 13 TGA curve of PSPMDA film with first derivative in nitrogen.

air-solution interface) and bottom surface (i.e., solution-steel for membrane) (Figs. 4, 5). It is obvious from micrographs of the solution side (Figure 2) that quenching of the solvents, as well as the hydrolysis of polymer- $\text{AlCl}_2$ , leaves pores of  $2\text{-}\mu\text{m}$  diameter. The enlargement in Figure 3 shows the interior of those pores. The mold side exhibits several macroscopic defects (pinholes). The enlargement in Figure 4 shows many changes that were observed.

The cross-section morphology is spectacular. The membrane is generally viewed as a honeycomb structure as shown in Figures 6 and 7. The pore size is approximately  $6\ \mu\text{m}$ . It appears that the mean diameter of the pores increases from the surface. The magnification in Figs. 8 and 9 shows the interior of the large holes. The walls of those cavities and boundaries are also porous. The average pore size is  $0.6\ \mu\text{m}$ . Figure 10 shows covered and uncovered holes side by side.

Based on our technique of membrane fabrication and the feature of the above morphology, a possible mechanism has been proposed that is presented in Figure 11.

During copolymerization crosslinking due to

the Friedel-Crafts reaction, a D isoporous network structure developed. The network polymer- $\text{AlCl}_2$  in the form of dark color complex hydrolyzes to polymer-COOH. Ingression of water and egression of nitrobenzene and unreacted PMDA leaves macro- and micropores. Finally, the membrane was immersed in ethanol and benzene for a long time to remove nitrobenzene and any unreacted PS.

#### Thermal Characteristics

Figures 12 and 13 show the TGA curves along with the first derivatives in air and nitrogen atmospheres. The original thermal stability of PS improved considerably as reported earlier.<sup>3</sup> Both the TGA curves (air and nitrogen) revealed a weight loss of ca. 20% at  $350^\circ\text{C}$ ; in our former work<sup>3</sup> a 10% weight loss was observed at  $321^\circ\text{C}$ . In general, removal of impurities or solvents of low molecular weight entrapped in the highly cross-linked PSPMDA occurs around this temperature range. Presumably, the highly porous structure developed due to the use of the mixture of nitrobenzene and dichloroethane as the solvent. A



sharp weight loss of 60% was observed in the temperature range of 350–400°C in air and at 350–450°C in nitrogen. Another 18% weight loss took place around 550°C. A sharp exothermic peak was observed in the first derivative 60% weight loss. A small exothermic hump was noted at 400–600°C in air and at 450–560°C in nitrogen. In our previous work a small exothermic peak appeared at 390°C and a sharp exothermic peak appeared at 450°C.

The above data is encouraging for the transfer of the process of chemical modification of PS into a useful finished product as a membrane. The cost for the product as estimated in 1984 was \$8.126/kg<sup>5</sup>. Recycling of PS foams will make it cheaper. A membrane of this type may be employed for the removal of toxic contaminants from waste- or polluted water.<sup>9</sup> <sup>13</sup>C CP/MAS NMR can be compared to identify those toxic chemicals from the present type of membrane.

## REFERENCES

1. S. Chatterjee and M. Biswas, *J. Appl. Polym. Sci.*, **44**, 619 (1992).
2. S. Chatterjee and B. Bhattacharyya, *J. Appl. Polym. Sci.*, **33**, 2769 (1987).
3. M. Biswas and S. Chatterjee, *J. Appl. Polym. Sci.*, **27**, 3851 (1982).
4. M. Biswas and S. Chatterjee, *J. Appl. Polym. Sci.*, **27**, 4645 (1982).
5. M. Chakrabarti, thesis, I.I.T, Kharagpur, India, 1986, p. 83.
6. S. M. Fujita and D. S. Soane, *Polym. Eng. Sci.*, **28**, 341 (1988).
7. V. A. Davankov and M. P. Tsyurupa, *Angew. Macromol. Chem.*, **91**, 127 (1980).
8. D. Hariharan and N. A. Peppas, *J. Membr. Sci.*, **78**, 1 (1983).
9. W. Kemp, *Organic Spectroscopy*, ELBS/Macmillan, 2nd ed., New York, 1987, p. 85.
10. I. M. Huxan, B. Rowatt, D. C. Sherrington, and T. L. Sherrington, *Polymer*, **33**, 2768 (1992).