

# Studies of Performances by the Interchanging of the Sequence of the Photomodified Layer in the Thin Film Composite (TFC) Membrane

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**ABSTRACT:** UV-initiated photomodification by a hydrophilic functional moiety (i.e., acrylic acid) was performed in and on a polypiperazineamide thin-film composite membrane. The sequence of the bilayers (i.e., acrylic acid and polypiperazineamide) was altered on a polysulfone membrane. The size exclusion order through the membranes was Atrazine > Simazine > 2,4,6-Trichlorophenol > 2,4-Dichlorophenol according to the molecular size, which was calculated by the quantum mechanical approach. Apart from the molecular size, the polarity and hydrophobicity of the mole-

cules also influenced the separation. The performance of the membranes is based on size exclusion. The membrane with an inner layer of acrylic acid showed more blocking effect than the membrane with the same layer on the top of polypiperazineamide membrane and the unmodified polypiperazineamide membrane. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2611–2616, 2008

**Key words:** composites; graft copolymers; membranes; modification; radiation

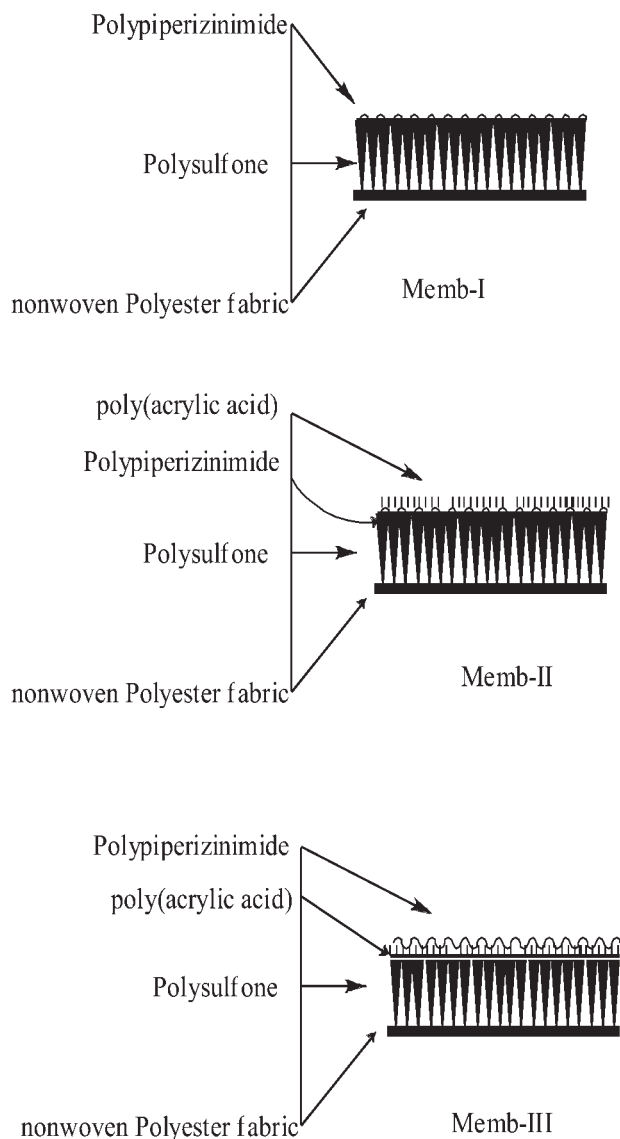
## INTRODUCTION

Membrane separation is one of the most advanced filtration technologies and is attractive to separation scientists because of its diversified potential in different areas. In water processing, the applications of membranes are well understood from the literature. From recent decades, the consciousness regarding the intake of pesticides/water pollutants through water has grown up, and the removal of these by different techniques (viz., ozone/UV irradiation/H<sub>2</sub>O<sub>2</sub>, activated carbon filtration, membrane filtration) has been tested.<sup>1,2</sup> It has been observed that the membrane filtration technique is one potential techniques for removing pesticides from water. In this area, the recent thrust has been on thin-film composite membranes because of their unique applicability. Many researchers have reported the remediations of pesticides through different commercial membranes,<sup>1,3–5</sup> but the chemistry of the membranes was undisclosed. In an earlier study,<sup>6</sup> we succeeded in establishing some correlation of pesticide removal performance with membrane chemistry. In this

investigation, we highlighted the effect of surface modification to the thin-film composite membrane with regard to the separation performances of the pesticide molecules. It is a simple method to obtain tailor-made membranes with specific properties, and this can be conveniently implemented by the modification of the polymer membrane either by radiation or the incorporation of a suitable monomer into it.<sup>7</sup> The modification targeted at the improvement of separation performances was the subject of our research. Several techniques can be used to impart specific properties of the membranes. These include (1) the radiation technique; (2) glow-discharge, low-temperature plasma treatments; (3) the redox reaction, and (4) the light-induced technique. Apart from the simplicity in setup and operation, the light-induced technique is preferred in terms of low monomer residue and the reduction of emissions of volatile organic compounds. The sequence of the modified acrylic acid and polyamide layer [due to the interfacial polymerization of piperazine and trimesoyl chloride (TMC)] was altered over the polysulfone membrane, and we targeted performances with regard to the separation of the organics [atrazine, simazine, 2,4,6-trichlorophenol (2,4,6-TCP), and 2,4-dichlorophenol (2,4-DCP)]. The schematic presentation of the three different types of membranes is in Figure 1.

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**Figure 1** Schematic presentation of three membranes (Memb-I, Memb-II, and Memb-III).

## EXPERIMENTAL

### Materials

Polysulfone (Udel P-3500, Solvay Advanced Polymers, Alpharetta, GA), dimethylformamide (DMF; Qualigen, Mumbai, India), and sodium lauryl sulfate were used to prepare the asymmetric membrane. Piperazine (Loba, Mumbai, India) and TMC (Lancaster, PA) were used for the preparation of the thin-film composite membranes. Acrylic acid (SRL, Mumbai, India) was used as a monomer to modify the membrane surface.

Atrazine, simazine (Sigma Chemicals, USA), 2,4,6-TCP, and 2,4-DCP (Loba) were used for the performance testing. Glucose (Glaxo, Mumbai, India), Sucrose (SD Fine Chemicals, Mumbai, India) were used for the performance testing of the membranes to

determine the molecular weight cutoff. Reverse-osmosis-treated water was used in the experiment.

We fitted the membranes on a glass tray and irradiated them by keeping 5-cm distances from UV lamp (Philips HPR-125 watt, Turnhout, Belgium) at ambient temperature and under a nitrogen atmosphere. The lamp generated 300–400-nm and 171-W/m<sup>2</sup> light. The photoirradiation setup is displayed in Figure 2. The radiation density flux on all of the surface areas of the membrane was assumed to be constant in each run. The total setup was in a closed wooden box.

For permeability measurements, a laboratory-made pressure cell was used. The experimental setup was sketched elsewhere.<sup>6</sup> The permeability was tested at 1.4 MPa. The sizes of membranes were kept at  $1.52 \times 10^{-3} \text{ m}^2$ .

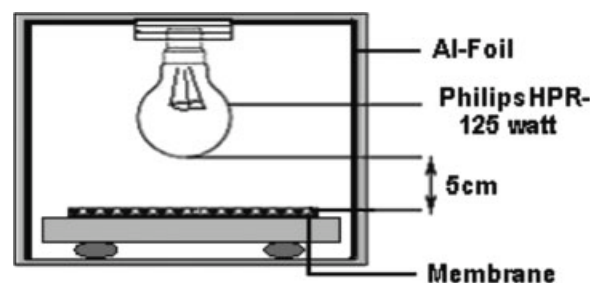
### Preparation of the membranes

#### Preparation of the polysulfone membranes

A homogeneous solution of the membrane-forming polysulfone in DMF (15% w/w) was prepared by continuous stirring overnight. The DMF solution was preferred to prepare the homogeneous solution as the dissolution was slow. The solutions were cast on a polyester nonwoven (1 m in width), with the thickness controlled, and dipped into a gelation bath [composition: water (700 L) and sodium lauryl sulfate (0.1%)] with a prototype casting machine. To complete the wet-phase inversion, the membranes were kept in the gelation bath for at least 3 h. Then, they were washed (with water) and dried at room temperature.

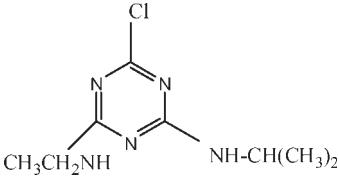
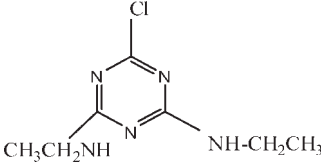
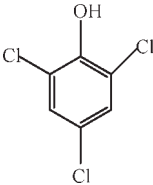
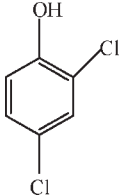
#### Preparation of the thin-film composite membranes

The polyamide composite membranes were prepared by the interfacial polymerization of piperazine and TMC on the surface of the asymmetric polysulfone membranes. First, the polysulfone membranes were coated with a 2 wt % aqueous solution of piperazine; the excess amount of piperazine solution of water remaining on its surface was removed and then



**Figure 2** Schematic presentation of the photoirradiation setup.

TABLE I  
Chemical Structures and Some Characteristic Data of the Solutes

Solute organic	Chemical structure	Molecular weight	Molecular volume ( $\text{\AA}^3$ )	Dipole moment (D)	$\log P$
Atrazine		215.7	212.93	3.44	2.61
Simazine		201.7	194.4	3.56	2.18
2,4,6-TCP		197.5	170.3	1.072	3.69
2,4-DCP		163	153	2.164	2.92

immersed into a 0.1 wt % TMC solution (in hexane) for the interfacial polymerization, after which it was cured at 85–90°C. As the high unfavorable partition coefficient for acid chloride limited its availability in the aqueous phase, the interfacial polymerization reaction occurred in the organic (hexane) side; thus, the coating was followed by dipping in piperazine solution at first and afterward in TMC.

#### Modification of the thin-film composite membrane

The polysulfone membrane was modified by the dipping of the membranes in acrylic acid of different concentrations (2 and 5%) for 15 min and photoirradiation for a 10-min duration. The interfacial polymerization of piperazine and TMC (as described) was done on the acrylic acid modified polysulfone membrane.

Similarly, the thin-film composite membranes were photomodified by following same procedure, that is, by the dipping of the membranes in acrylic acid (2 and 5%) for 15 min and photoexposure for

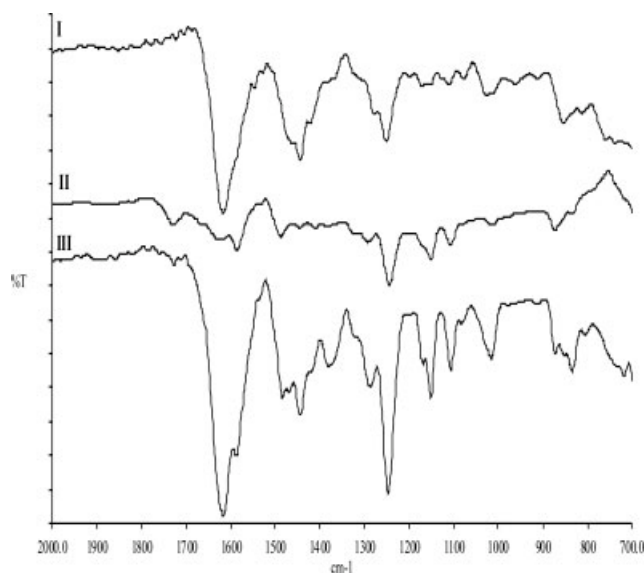
10 min. The three types of membranes (modified and unmodified) are schematically presented in Figure 1.

#### Preparation of the pesticides solutions

The pesticide organics were dissolved in methanol solutions (300 mg/L). An appropriate amount of methanol solution was kept in open conditions to evaporate, and the residues were dissolved into reverse-osmosis-treated water. The final concentration was 20 mg/L for the selected pesticides.

#### Analysis

To confirm the presence of acrylic acid over the membrane, attenuated total reflection (ATR) infrared spectroscopy (with a PerkinElmer (Norwalk, CT) Spectrum GX with a resolution of  $\pm 4 \text{ cm}^{-1}$  and an incident angle of 45°) of the surface layer of the modified and unmodified membrane was done. The membranes were also visually characterized by scanning electron microscopy (Leo, 1430UP, Oxford Instruments, UK).



**Figure 3** FTIR-ATR spectra of unmodified and modified membranes (Memb-I, Memb-IIa, and Memb-IIIa).

The pesticide organics concentrations were analyzed with high-performance liquid chromatography (HPLC-GPC Waters, 2695 separation module, reverse phase), with the direct injection mode under the following conditions: Nucleosil C18 (Supelco) 4.6 mm  $\times$  250 mm  $\times$  5  $\mu$ m column, acetonitrile/water (80 : 20) mobile phase, 0.125% acetic acid, 1.0 mL/min flow, 2996 photodiode array detector ( $\chi_{\text{max}}$  (absorption maxima) = 280 nm), 30°C temperature, and 20  $\mu$ L injection volume. For the glucose and sucrose solutions (2414 RI (refractive index) detector HPLC mode), the following conditions were maintained: Supelcogel C610H, 30 cm  $\times$  7.8 mm column, 0.5 mL/min flow, 30°C temperature, 0.1%  $\text{H}_3\text{PO}_4$  eluent in water, and 60  $\mu$ L injection volume.

Theoretical methods to determine the structural parameters

The main rejection mechanism depends on size exclusion, so the first and foremost condition to reject organics by the membrane is their size. Although membrane molecular weight cutoff apparently signifies the size of the organics that will be rejected, it is better to consider the volume of experi-

mented organics. The semiempirical Austin model 1 (AM1) method was used to calculate the molecular volume and dipole-moment data.<sup>8–10</sup>

First, the stable conformers were predicted at the AM1 level of theory, and then, the molecular volume and dipole moment were calculated. The AM1-calculated results along with their simple chemical structures are depicted in Table I.

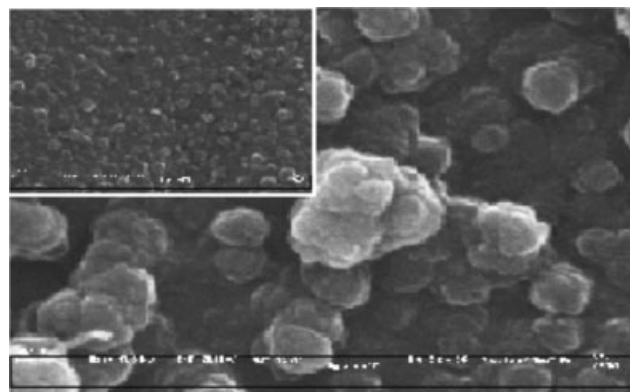
## RESULTS AND DISCUSSION

Fourier transform infrared (FTIR)-ATR studies proved the acrylic acid incorporation on the polysulfone membranes and on the thin-film composite membranes. The 1725–1729- $\text{cm}^{-1}$  peak was the evidence of  $-\text{COOH}$  groups on the membrane. The peak intensity of the  $-\text{COOH}$  group was higher for Memb-II than for Memb-III. The  $-\text{COOH}$  peak was less intensified (for Memb-III) due to the polyamide layer over it (Fig. 3). The  $-\text{CONH}-$  peak intensity (1617  $\text{cm}^{-1}$ ) was higher for Memb-III due to the incorporation of acrylic acid over the polysulfone layer; the piperazine absorption was higher, as the wettability of acrylic acid-g-polysulfone was more evidenced from the lower contact angle with respect to unmodified polysulfone.<sup>7</sup> Table II features the weight differences (with respect to the thin film composite (TFC) membrane, Memb-I) with the compositions of different membranes. The table shows that the increases in weight of Memb-II and Memb-III with respect to Memb-I were due to the incorporation of acrylic acid. Thus, Memb-III had an appreciably higher weight difference compared to Memb-II as the attachment of acrylic acid was more facile with the polysulfone membrane. The increase in weight also depended on the acrylic acid concentration in both the cases for Memb-II and Memb-III.

The incorporation of acrylic acid on the thin-film composite membrane was evidenced from the microscopic photograph (Fig. 4). The micrograph of Memb-I is embedded in the figure. The characteristic features of Memb-II proved the existence of the incorporation of acrylic acid on the thin-film composite membrane. However, for Memb-III, the top surface was similar to that of Memb-I.

**TABLE II**  
Weight Difference Data and Layer Compositions in the Order of Modification of the Membranes

Membrane	Composition (order-wise)	Weight difference ( $\times 10^4$ g/cm <sup>2</sup> )
Memb-I	Polysulfone + polypiperizinimide	—
Memb-IIa	Polysulfone + polypiperizinimide + acrylic acid (2%)	0.67
Memb-IIb	Polysulfone + polypiperizinimide + acrylic acid (5%)	1.02
Memb-IIIa	Polysulfone + acrylic acid (2%) + polypiperizinimide	0.7
Memb-IIIb	Polysulfone + acrylic acid (5%) + polypiperizinimide	2.04



**Figure 4** Scanning electron micrographs of membranes [the photo of Memb-I (unmodified) is embedded in Memb-II photograph].

Although molecular weight data apparently corresponds to molecular volume order in terms of size exclusion, it was properly correlated with the volume data. Table I lists the molecular volume and weight data along with dipole moment data of the pesticides, as calculated from semiquantum mechanical approach. An interesting point to note is that although the molecular weights of simazine and 2,4,6-TCP were similar or had little difference, their volumes had marked differences. The dipole moment data shows that among the four pesticides, simazine had the highest dipole moment.

Table III features the remediation performances in pesticide removal from water. In all of the membranes, the rejection order Atrazine > Simazine > 2,4,6-TCP > 2,4-DCP proved the size exclusion mechanism as following the order from Table I (molecular volume and molecular weight data). The flux decreased to less than half for Memb-III compared to Memb-I. The separation performances increased with the acrylic acid content over the membrane (Table II and III). Moreover, the blocking effect was more pronounced for Memb-III with respect to Memb-II and Memb-I, which meant that the rejection performances of the membranes in which acrylic acid was in the inner layer was higher than those of the membranes where acrylic acid was in the top layer. The weight difference data (Table II) also showed that Memb-III had more weight with respect

to Memb-II, as the acrylic acid grafting of polysulfone was more feasible than over the polyamide membrane. This was because of their (polysulfone and acrylic acid) photosensitive nature. The detailed mechanism of acrylic acid attachment was described in the literature.<sup>7</sup> Similar results were also observed in the case of the permeation of glucose and sucrose (low molecular weight) through them. The molecular volumes of glucose and sucrose were 190 ( $\alpha$ -pyranose) and 279 Å<sup>3</sup>, as calculated from the quantum mechanical approach. The retention of sucrose was higher than that of glucose, as expected (from the molecular weight and molecular volume points of view). The performance behavior depended on the increase in grafting.

Apart from the molecular weight and volume, the partition coefficient and dipole moment acted as synergy in the separation mechanism. The log  $P$  ( $n$ -octanol/water partition co-efficient) is defined as  $\log P = \log (C_0/C_w)$ , where  $C_0$  and  $C_w$  are the concentrations of solute in the  $n$ -octanol and water layers.<sup>3</sup> The rejection was positively correlated with the log  $P$  value. The log  $P$  value has been listed for all of the pesticides in the literature.<sup>11,12</sup> A higher log  $P$  value indicates that pesticides prefer the organic phase instead of the aqueous one. Hence, it tends to keep away from membranes that are hydrophilic while in operation. Atrazine rejection was higher than simazine. Similar results were also observed in the case of 2,4,6-TCP and 2,4-DCP. Although 2,4,6-TCP had the highest log  $P$  among the four pesticides in the experiment, the size exclusion factor was the prime one to consider. Thus, the rejection followed the molecular volume.

Because all of the membranes were of negative charge due to the presence of residual  $-\text{COOH}$  in polyamide or added  $-\text{COOH}$  groups from acrylic acid, the permeation of relatively polar simazine was also favored with respect to atrazine, as there was electrostatic attraction operating between the membrane and polar molecules.<sup>1,13</sup> These results were also explained for 2,4-DCP, where lower molecular volume and higher polarity resulted in lower rejection compared to 2,4,6-TCP. However, for all cases, the size exclusion factor was the major factor to consider and, thus, the order followed, although the dipole moment of 2,4-DCP was less than that of

**TABLE III**  
Separation Performances of All Three Membranes

Membrane	Flux ( $\text{L m}^{-2} \text{d}^{-1}$ )	2,4-DCP	2,4,6-TCP	Simazine	Atrazine	Glucose	Sucrose
Memb-I	1137	62.6	67.9	74.81	81.8	71.2	82.7
Memb-IIa	1191	67.3	73.9	76.36	82.7	71.7	87.4
Memb-IIb	1028.6	69.1	76.9	78.9	88.1	76.2	89.5
Memb-IIIa	505	69.8	89.2	87.4	95.1	87.2	95.3
Memb-IIIb	473.7	70.5	91.9	87.7	96.08	88.4	95.4

simazine/atrazine. The blocking effect was more pronounced for Memb-III than for Memb-II and Memb-I for these molecules.

### CONCLUSIONS

This study dealt with the preparation and modification of polypiperizinamide-based thin-film composite membranes. The sequence of the acrylic acid and polypiperazineamide layer was altered. The study led us to the following conclusions:

1. FTIR-ATR and scanning electron microscopy studies proved that acrylic acid incorporation on the membrane through the photoirradiation technique. The weight difference also suggested that the weight difference of Memb-III was more than that of Memb-II. The weight increase also varied with acrylic acid concentration.
2. The separation of organics followed the order Atrazine > Simazine > 2,4,6-TCP > 2,4-DCP on the basis of preferred size exclusion. Apart from this, the lower the log *P* value and the higher polarity factor also decreased simazine rejection compared to atrazine, 2,4,6-TCP, and 2,4-DCP.
3. The rejection performances of the acrylic acid photomodified thin-film composite membranes were higher compared to that of the unmodified membrane.

4. The blocking effect of the Memb-III membranes was higher than those of Memb-II and the unmodified thin-film composite membrane (Memb-I).

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