

# Novel, Positively Charged Membrane from a Blending, Crosslinking, and Coagulation Procedure

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**ABSTRACT:** A novel, positively charged membrane was prepared through a blending, crosslinking, and coagulation procedure in which poly(*N,N*-dimethylaminoethyl methacrylate) (PDM) and polyacrylonitrile (PAN) were used as the functional and substrate component, respectively. Because 1,4-dibromobutane (DBT) was used as the crosslinker and quaternizing agent, PDM was crosslinked and quaternized simultaneously. The effects of PDM content, polymer concentration, and additive dosage of the casting solution on the membrane performances are discussed in detail, and differences between the PAN membrane, PDM/PAN blend

membrane, and crosslinked PDM/PAN blend membrane are also discussed. We also studied the adsorption behaviors of the membranes to a positively charged dye and a negatively charged dye. Environmental scanning electron microscopy observation showed that the resulting positively charged membrane from such a blending, crosslinking, and coagulation procedure possessed a unique and uniform structure. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1847–1854, 2005

**Key words:** blending; crosslinking; membranes

## INTRODUCTION

Most conventional membrane processes are established on the physical sieving mechanism; that is, particles smaller than the size of the membrane pores can penetrate through the membrane, whereas larger ones are captured by the membrane pores. Obviously, when there is a decrease in the particle dimensions, a membrane with an even finer pore size is needed, which will lead to a drop in flux and a rise in operating costs. However, charged membranes, which have fixed charges in the bulk or on the surface, possess an electrostatic interaction effect in addition to the sieving filtration mechanism. Therefore, it is possible to separate finer particles with a membrane with larger pores, and species with similar size can be separated from each other. Furthermore, because of the introduction of charged groups, membrane hydrophilicity is enhanced, and as a result, filtration flux is increased. In addition, because of the electrostatic interaction between the fixed charges in the membrane and the mobile charged species in the solution, the osmotic pressure of the solute is lowered, and therefore, membrane filtration can be operated under a relatively low pressure. Moreover, charged membranes possess a good resistance to compaction, chemicals, and bacteria. In conclusion, charged membranes have advanced

tages of water permeation, antifouling, and permselectivity over conventional neutral membranes.

Charged membranes have found applications in many fields, including the separation of protein mixtures, the separation of macromolecules with similar molecular weights but different charging properties,<sup>1</sup> salt production,<sup>2</sup> and the concentration of electrocoating paint rinsing water.<sup>3</sup> In addition, charged membranes are also very important for physical and chemical studies of model systems.<sup>4</sup>

Generally, there are two types of charged membranes: negatively charged and positively charged. Positively charged membranes (PCMs) have been employed to recycle cathodic electrodeposition paint for decades, and more recently, researchers have sought application in the manufacturing of pure water for many suspended particulates, such as bacterial endotoxins and virus that have a negative  $\zeta$  potential, which can be removed by an electrokinetic capture mechanism with a PCM.<sup>5</sup>

Different methods have been adopted to prepare PCMs. Kobayoshi et al. grafted tertiary-amino-group-containing monomers, including diethylaminoethyl methacrylate and vinyl pyridine, onto a porous polypropylene hollow-fiber membrane and subsequently quaternized the grafted membranes with benzyl chloride, which resulted in a PCM with strongly basic anion-exchange groups; this was obtained and used to collect anions in solution.<sup>6</sup> Another popular strategy for the preparation of PCMs is the phase inversion of a solution of a copolymer containing quaternized ammonium groups in a coagulation

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bath.<sup>2</sup> Miyama and Tanaka photochemically synthesized and quaternized polyacrylonitrile (PAN)-*g*-poly(*N,N*-dimethylaminoethyl methacrylate) (PDM) and prepared PCMs from the quaternized graft copolymer with the phase inversion method.<sup>7</sup>

In addition, chitosan, which is a unique basic polysaccharide, was also used to prepare PCMs,<sup>8</sup> for chitosan turns positively charged at pH values below its  $pK_a$  value of 6.3. However, a chitosan-based charged membrane may lose its charge at high pH because it depends on the basicity of an amine to acquire a charge in aqueous media.<sup>9</sup>

In this study, we developed a new method for preparing PCMs. In contrast to the copolymerization of acrylonitrile and dimethylaminoethyl methacrylate,<sup>7</sup> we first blended PAN and PDM in a solvent and subsequently crosslinked and quaternized PDM at the same time with a difunctional quaternizing agent. The PCM was obtained after the coagulation of the crosslinked system in water.

## EXPERIMENTAL

### Reagents

*N,N*-Dimethylaminoethyl methacrylate (DM; Wuxi Xinyu Chemical Engineering Co., Ltd., Wuxi, China) was purified by distillation *in vacuo*. Azobisisobutyronitrile (North China Center for Special Chemicals, Tianjin, China), the initiator for the polymerization of DM, and 1,4-dibromobutane (DBT; Shanghai No. 3 Chemical Reagents Plant, Shanghai, China), the crosslinker for PDM, were used with further purification. PAN containing 0.5–1% sodium methylallyl sulfonate (MAS) segments (number-average molecular weight =  $3 \times 10^4$ ; Qinhuangdao Acrylon Plant, Qinhuangdao, China), polyvinylpyrrolidone (PVP; K30, BASF), and *N,N*-dimethylacetamide (DMAc; Hebei Chemical Engineering Academe, Shijiazhuang, China) were used as received. The two dyes, orange II and basic red I, were both purchased from Tianjin No. 3 Dyestuff Plant (Tianjin, China) and were used as received.

### Bulk polymerization of DM

A certain amount of distilled DM and 1 wt % initiator (azobisisobutyronitrile) were introduced into a vessel and deaerated with  $N_2$  for several minutes. Then, the vessel was transferred into a water bath controlled at 60°C for polymerization. Three days later, the polymerized product was taken out and cut into chips and was then treated at 80°C in a vacuum oven for 12 h to remove the residual monomer.

### FTIR confirmation of the crosslinked PDM

After a small amount of PDM chips was completely dissolved in ethanol, an excess of DBT (the

crosslinker) was dropped into the solution under vigorous magnetic agitation. The mixture was kept at room temperature for several days until it completely solidified as a block. It was then taken out and ground into powder and washed with copious amounts of ethanol to remove the residual DBT and dried at 60°C for 6 h in a vacuum oven. The final obtained crosslinked PDM and the nascent PDM were then scanned with an FTIR spectrometer (Magna-560, Nicolet), respectively.

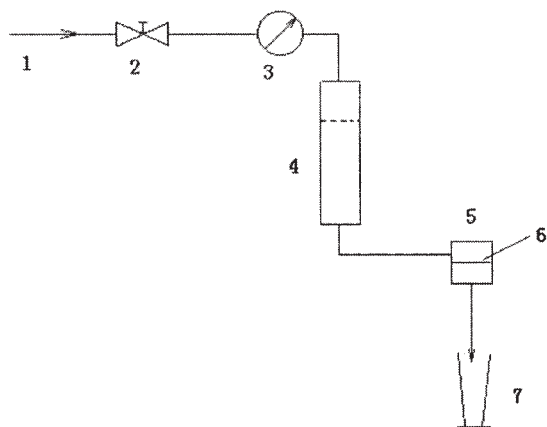
### Preparation of PCMs

Previously dried PDM, PAN, and PVP with desired weight ratios were mixed in DMAc at 50–60°C under agitation for 2–3 days, and a clear and homogeneous solution was obtained. The solution was then transferred into a temperature-controlled water bath at 30°C, and a certain amount of DBT (dissolved in DMAc for the sake of a good diffusion in the blend solution) was added dropwise into the solution slowly under vigorous agitation. The solution was continually agitated for at least 30 min to facilitate the crosslinking reaction, which was then defoamed by vacuum rapidly and thereafter kept in the 30°C water bath. After the crosslinking reaction had proceeded for 2 h (counting from the introduction of DBT), the final obtained cast solution was spread onto a glass plate with a pair of spacers, and the glass plate was immediately immersed into a coagulation water bath at 25°C. To coagulate the membrane completely, the membrane was kept in the coagulation bath overnight and was then washed with an excess of water to remove the solvent, DMAc, and the additive, PVP. To compare the membrane performances, a PAN membrane and a PDM/PAN blend membrane were also prepared through the same wet phase-conversion method described previously but without the crosslinking procedure.

### Filtration tests

All of the filtration tests were carried out under 0.1 MPa of pressure at 25°C after a precompaction step at 0.3 MPa for 30 min. For the measurement of flux and rejection, pure water and 0.1% egg albumin aqueous solution conditioned to pH = 10–11 with 0.03% NaOH were used as cycling media. The egg albumin concentrations in the feed and permeate solutions were analyzed with a ultraviolet–visible spectrometer (Shanghai No.3 Analyzing Apparatus Factory, Shijiazhuang, China) at 280 nm. The egg albumin rejection ( $R$ ) is defined as

$$R (\%) = (1 - A_p/A_f) \times 100$$



**Figure 1** Experimental apparatus of dye adsorption: (1)  $N_2$ , (2) reducing valve, (3) pressure gauge, (4) feed tank, (5) evaluating cell (the membrane discs were sandwiched in this), (6) membrane sample, and (7) measuring cylinder.

where  $A_p$  and  $A_f$  denote the absorbance of the permeate and feed samples, respectively.

### Dye adsorption

A negatively charged dye, orange II ( $C_{16}H_{11}N_2NaO_4S$ ), and a positively charged dye, basic red I ( $C_{28}H_{31}ClN_2O_3$ ), were used to investigate the charge properties of the resulting three types of membrane on a homemade apparatus (see Fig. 1). A dilute dye aqueous solution (80 mL) was filtered through a membrane disc with a fixed surface area under the driving of 0.1 MPa of  $N_2$ . The dye concentrations in the feed and permeate solutions were analyzed with an ultraviolet-visible spectrometer at 484.4 nm. The dye absorbance ( $A$ ) is defined as

$$A (\%) = (1 - A_p/A_f) \times 100$$

where  $A_p$  and  $A_f$  denote the absorbance of the permeate and feed samples, respectively. The filtration time of each sample was also recorded.

### Environmental scanning electron microscopy (ESEM) observations of the membrane structure

A Phillips XL 30 environmental scanning electron microscope was used to investigate the structure of the cross-section surfaces of different membrane samples. Wet samples were observed directly without any treatment for conventional scanning electron microscopy (CSEM) observation.

## RESULTS AND DISCUSSION

PDM is a water-soluble polymer, and it cannot form a porous membrane through the wet phase-inversion procedure by itself. In this work, we overcame the problem

by first blending it with another polymer with good membrane-forming properties and then crosslinking the PDM chains before coagulation in water.

Above all, we examined the miscibility of PDM with some other widely used polymeric membrane materials, including PAN, polyvinylidene fluoride, and polysulfone, in different solvents, such as DMF, DMAc, and dimethyl sulfoxide. PDM and PAN formed a macroscopically stable and homogeneous solution in DMAc.

### Crosslinking and quaternization of PDM with DBT

There is an active tertiary amide group in each repeating unit of the PDM macromolecule. Halogenated alkane can readily react with the tertiary amide groups and lead to the formation quaternized ammonium, which is positively charged. However, PDM quaternized with monohalogen-substituted alkanes tends to swell or even dissolve in water. Therefore, they cannot be used directly to prepare PCM applied in a water environment. In this study, a dihalogen-substituted alkane, DBT, was selected to quaternize the tertiary amine groups and to crosslink the PDM chains at the same time. On the condition that the quaternizing reaction happened simultaneously on two tertiary amine groups in different PDM chains, the crosslinking reaction occurred. The scheme of the structure of the crosslinked PDM is shown in Figure 2.

There were four possibilities in the interaction between DBT and PDM:

- Intermolecular crosslinking.
- Intramolecular crosslinking.
- The reaction of one DBT molecule just with one tertiary amine.
- Some tertiary amine groups remaining unreacted.

a, b, and c are all quaternization reactions and enhance the positively charging property of the membrane, but only 1 is helpful for the insolubility of PDM. The formation of a solidified block after the mixture of PDM and DBT for several days at room temperature implied the success of the crosslinking of PDM with DBT. Also, the final obtained PCM could not be dissolved completely in DMAc, whereas the PAN and PDM/PAN blend membranes disappeared rapidly in DMAc, suggesting the accomplishment of the crosslinking of PDM with DBT.

Figure 3 shows the FTIR spectra of nascent PDM and crosslinked PDM. Three new peaks appeared at 3423.0, 2065.0, and 1634.9  $cm^{-1}$  on the spectrum of the crosslinked PDM. The former two were due to the adsorbed water in the sample, whereas the peak at

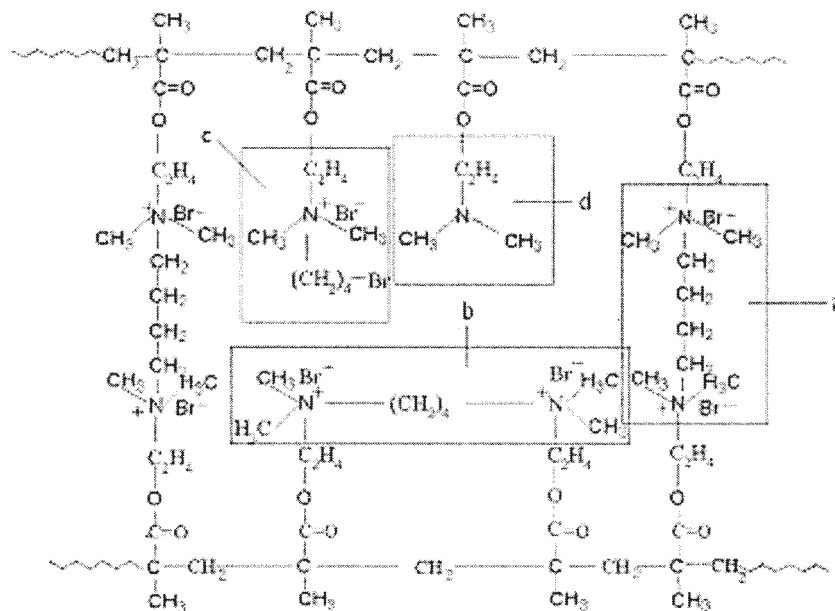


Figure 2 Schematic illustration of the structure of the crosslinked PDM.

$1634.9\text{ cm}^{-1}$  was assigned to the quaternized ammonium groups in the crosslinked sample.<sup>10</sup>

### PDM/PAN blend membranes

#### PDM content

A series of PDM/PAN blend membranes were prepared by the alteration of the PDM content in the casting solution with the polymer concentration (defined as the percentage of the total weight of PDM and PAN to the weight of solvent) kept constant at 10% and the additive dosage (the percentage of the weight of the additive, PVP, to the total weight of PDM+PAN) kept constant at 20%.

Generally, membrane flux and rejection change toward opposite directions when preparation conditions were altered; however, as shown in Figure 4, flux and

rejection decreased simultaneously with increasing PDM content. The main reason perhaps was due to the application of different cycling media in the measurement of flux and rejection. In the determination of membrane rejection, 0.03% NaOH was used to adjust the pH to 10–11 to avoid the absorption and deposition of egg albumin on the membrane surface. However, the pH of the solution affects the swelling behavior of PDM strongly: the ionization of the tertiary amine groups is much easier at a lower pH, which promotes the swelling of PDM, whereas PDM almost has no tendency to swell when the environmental pH is as high as 10–11. The membrane structure kept the original blending state when the pH was at 10–11, and the miscibility of PDM and PAN deteriorated with increasing PDM content, which resulted in phase sep-

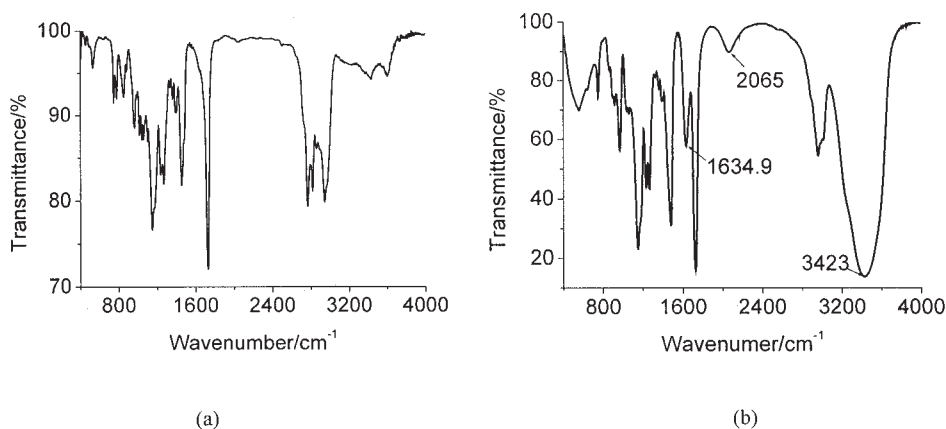
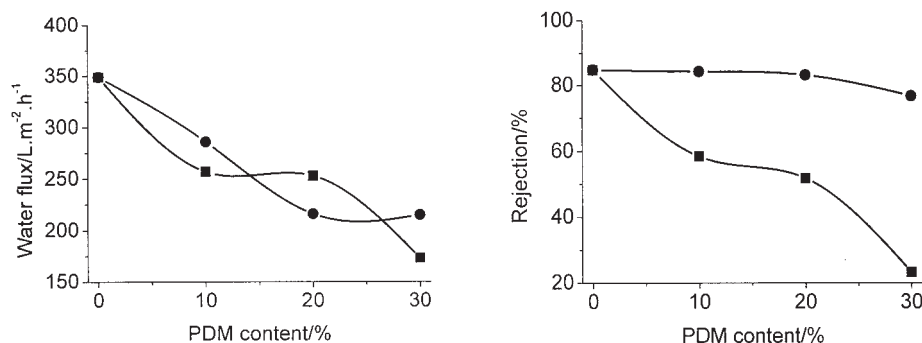


Figure 3 FTIR spectra of (a) nascent and (b) crosslinked PDM.





**Figure 4** Flux and rejection comparison of (■) uncrosslinked and (●) crosslinked PDM/PAN blend membranes with different PDM contents.

aration and a looser membrane structure. Therefore, there was a drop in rejection with increasing PDM content. During the measurement of flux, pure water (pH = 5.8, which is smaller than 7 because of the dissolution of CO<sub>2</sub> from the atmosphere) was used, and PDM swelled to a higher degree because of the lower pH value, and there was a shrinkage in the original membrane pore sizes, which led to a decrease in the membrane flux.

#### Polymer concentration and additive dosage

The effects of polymer concentration and additive dosage on the membrane performances are shown in Figures 5 and 6. The composition of their cast solutions was the same as those of the crosslinked counterparts just without the addition of DBT and can be found in the sections on Polymer Concentration and Additive Dosage.

Similar to many other studies, flux decreased and rejection increased with increasing polymer concentration and decreasing additive dosage, which was due to the denser membrane structure, which resulted from a higher polymer concentration and/or a lower additive dosage.

From the investigation of the performances of the PDM/PAN blend membrane, we could see that blend membrane without crosslinking could not be used in

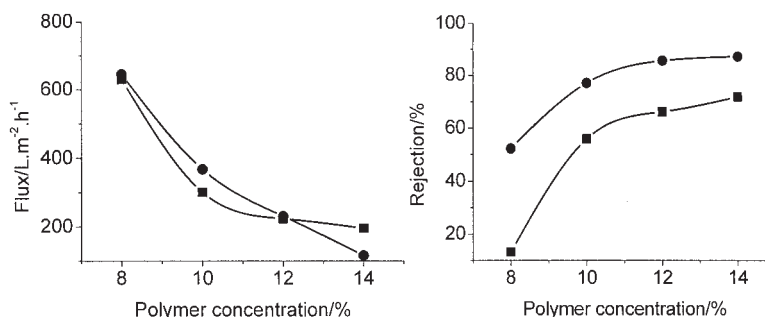
practice for the introduction of PDM; it just slightly enhanced the positively charging properties (see section on Comparison of Dye Adsorption Behaviors) and reduced the flux and rejection tremendously. Furthermore, PDM leaked out gradually from the blend membrane when used in a water environment and the membrane properties further deteriorated. As a result, there was an urgent need to crosslink the PDM/PAN blend membrane.

However, there still existed another problem: at what time to undertake the crosslinking of the PDM chains—before or after the coagulation of the cast solution? We preferred the former because if the crosslinking reaction were carried out after the formation of the PDM/PAN blend membrane, the PDM component in the blend would have been partially leached out during the processing of coagulation and rinse. Also, the crosslinking reaction after coagulation was heterogeneous, which perhaps could not result in a high enough crosslinking degree and enough positive charges in the membrane.

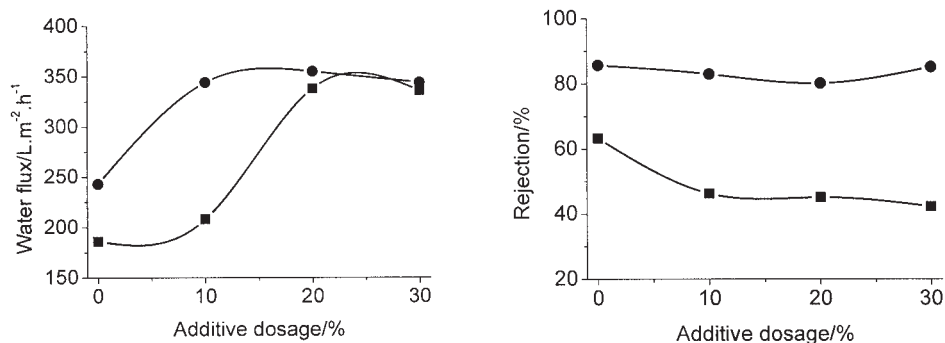
#### Crosslinked membrane and comparison with the uncrosslinked blend membrane

##### PDM content

A series of crosslinked blend membranes were prepared by the alteration of the PDM content while the



**Figure 5** Flux and rejection comparison of (■) uncrosslinked and (●) crosslinked PDM/PAN blend membranes with different polymer concentrations.



**Figure 6** Flux and rejection comparison of (■) uncrosslinked and (●) crosslinked PDM/PAN blend membranes with different additive dosages.

polymer concentration was fixed at 10%, the additive dosage at 20%, the crosslinking ratio (ratio of the number of bromine atoms in the added crosslinker, DBT, to the number of tertiary amine groups in PDM) at 1, and the time for crosslinking at 2 h. Just like the uncrosslinked blend membrane, the flux and rejection of the crosslinked membrane decreased simultaneously with increasing PDM content, which still resulted from the difference in the media in the measurement of flux and rejection. Because those membranes had just crosslinked for 2 h at room temperature, their crosslinking degree was still at a lower level, and they still had a tendency to swell to some extent in low pH systems. However, because of the entangling and binding of the PDM crosslinking network, the phase separation of the PDM/PAN blend was restrained. Therefore, as shown in Figure 4, the decrease in the flux and rejection of the crosslinked membranes was slighter compared with that of the uncrosslinked ones.

#### Polymer concentration

Crosslinked membranes with various polymer concentrations and the same PDM content (20%), additive dosage (20%), crosslinking ratio (1), and crosslinking time (2 h) were prepared, and their performances were evaluated. Similar to the uncrosslinked membranes, the flux of the crosslinked membranes decreased when the rejection increased with increasing polymer concentration.

However, because the increase in polymer concentration meant that the content of PAN and PDM in the cast solution increased at the same time, the increase in the PDM content led to a denser membrane structure after crosslinking. Therefore, there was a larger drop in the flux of crosslinked membranes compared with that of the uncrosslinked membranes (see Fig. 5). As to the rejection, because the crosslinked membranes already had a higher rejection at a lower polymer concentration than the uncrosslinked ones, their

increase in rejection was slighter than that of the uncrosslinked membranes.

#### Additive dosage

A number of crosslinked blend membranes were prepared by alteration of the additive dosage with other parameters fixed (PDM content = 20%, polymer concentration = 10%, crosslinking ratio = 1, and time for crosslinking = 2 h).

There was also a similar tendency of the change in the flux and rejection with increasing additive dosage: the flux increased, whereas the rejection decreased, and it was still caused by the weaker interaction between the polymer chains and the looser membrane structure resulting from the introduction of the additive molecules in the cast solution. However, because the refraining of the crosslinking polymer network reduced the loosening effect of the additive, the scope of the increase in the flux and the decrease in the rejection of the crosslinked membranes was slighter compared with the uncrosslinked membranes (see Fig. 6).

#### Comparison of dye adsorption behaviors

The absorption behaviors of the negatively charged dye (orange II) and the positively charged dye (basic red I) to the three types of membranes, PAN (A), PAN/PDM (B), and crosslinked PAN/PDM (C), were studied, respectively. The experimental data are shown in Table I.

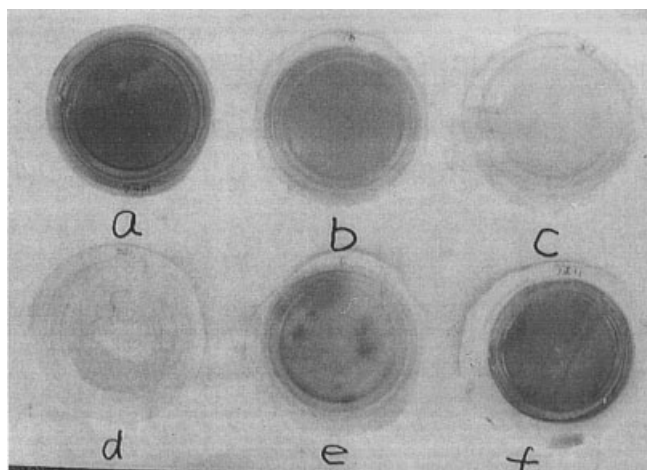
As shown in Table I, membrane C, that is, the crosslinked PAN/PDM blend membrane, absorbed the negatively charged orange II strongly, although it showed little affinity to the positively charged basic red I. This was due to the generation of a large amount of positively fixed charges in the membrane after crosslinking, that is, quaternization, which had strong interactions with charged dye molecules. On the contrary, the PAN membrane showed a strong affinity to positively charged basic red I but repulsed the nega-

**TABLE I**  
**Dye Adsorption Behavior of Membranes A, B, and C**

Membrane	Negatively charged orange II		Positively charged basic red I	
	Dye absorbance (%)	Filtration time (s)	Dye absorbance (%)	Filtration time (s)
A	7.9	1620	70.5	1730
B	88.0	1920	29.1	1635
C	95.8	480	19.3	1235

tively charged orange II for its negatively charged MAS segments. There existed weak positively charged tertiary amine groups in the PDM component and negatively charged MAS segments at the same time in the uncrosslinked blend membrane; their coordination effect led to a weak affinity to both charged dyes for the uncrosslinked blend membrane.

The discrepancy in the charging properties of the three types of membranes was also found easily from their color change after dye filtration. All of the membranes were white or slight yellow before dye filtration, but after that, their color changed greatly because of the adsorption of dye (Fig. 7). The dark red of the membrane in Figure 7(a) and the nearly white surface of the membrane in Figure 7(d) indicated the negatively charging properties of the PAN membrane, whereas the clear color of the membrane in Figure 7(c) and the yellow color of the membrane in Figure 7(f) revealed the positively charging properties of the crosslinked blend membrane, and the slight red of the membrane in Figure 7(b) and the slight yellow of the membrane in Figure 7(e) showed that the charging properties of the uncrosslinked blend membrane was between the two former membranes.



**Figure 7** Comparison of membranes after dye filtration: (a,d) PAN membrane, (b,e) PAN/PDM blend membrane, (c,f) crosslinked PAN/PDM blend membrane. Membranes a, b, and c were filtered with positively charged basic red I, whereas membranes d, e, and f were filtered with negatively charged orange II.

### ESEM observation of the membrane structure

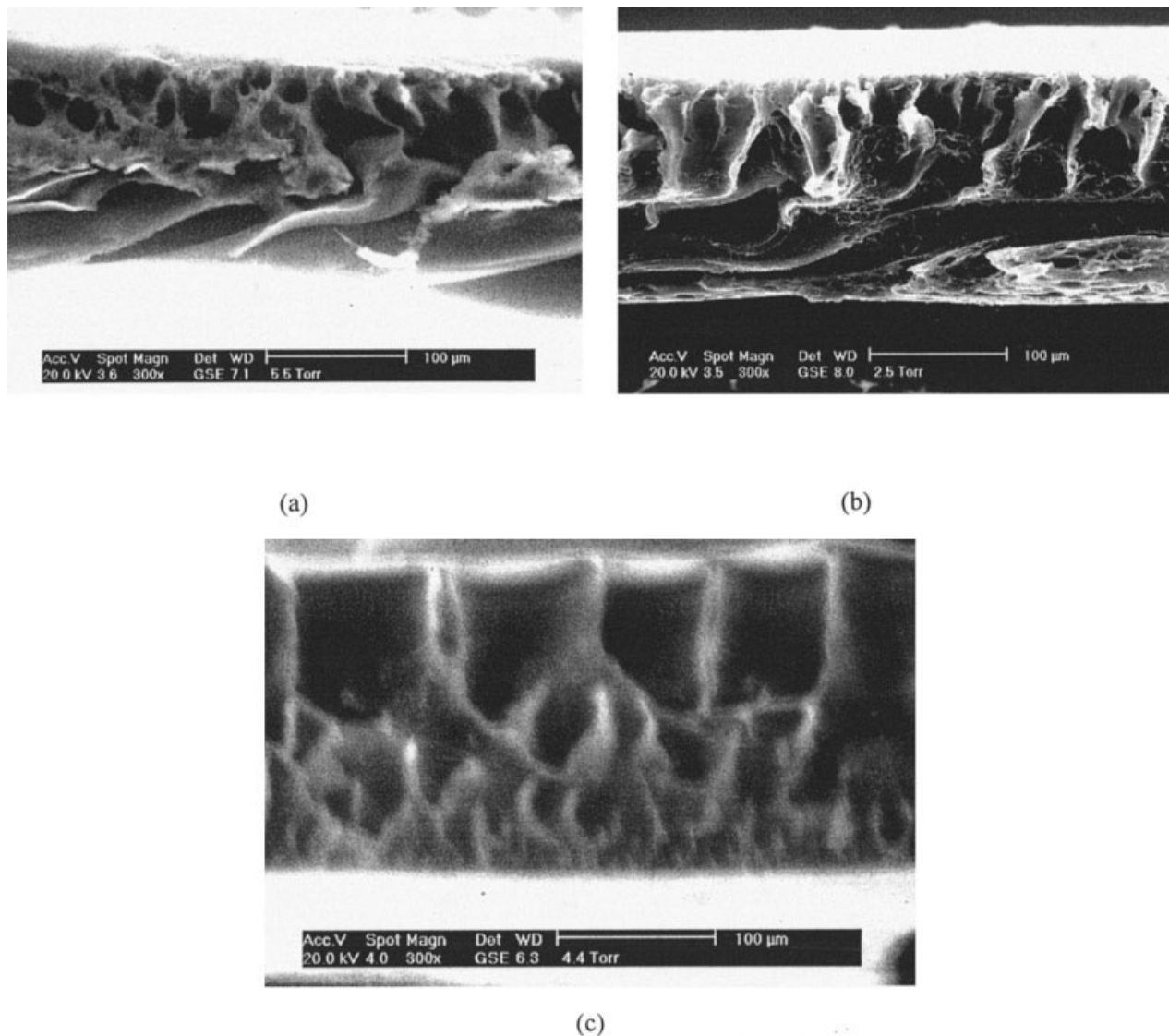
CSEM is widely used to observe membrane structure; however, wet membrane samples must undergo a series of treatment including dehydration and coating that possibly damage the fine structure of samples. ESEM, developed in the mid-1980s, overcame the limits of CSEM; it can provide second electron images with high resolution in any gas atmosphere with pressure as high as 50 Torr and a temperature as high as 1500°C. It does not require high vacuum for the sample environment and still retains all the advantages of CSEM. In other words, wet, dirty, and nonconductive samples can be directly observed under ESEM without any pretreatment.

As shown in Figure 8, there existed notable differences in the morphology of the three types of membranes. The uncrosslinked PDM/PAN blend membrane presented a gel-like morphology under ESEM because of the swelling of the PDM component in the water vapor atmosphere in the sample chamber of the ESEM, but there was no obvious swelling in the crosslinked blend membrane and the PAN single-component membrane because of the restraint of the crosslinked polymer network and the absence of the PDM component, respectively.

There were many large cavities in all three types of membranes, but the cavities in the crosslinked membrane were much more uniform than those in the other two. This also resulted from the restraint of the crosslinked network to the process of coagulation. The mechanism of the formation of the special uniform structure of the crosslinked blend membrane is now under investigation and will be reported later.

### CONCLUSIONS

PDM, the functional component, and PAN, the substrate component, were first blended in DMAc, and a homogeneous clear solution was obtained. Then, DBT was added to the solution to crosslink and quaternize PDM simultaneously, and the crosslinked system was subsequently coagulated in water, which resulted in a PCM. FTIR spectroscopy confirmed the occurrence of the quaternization. The



**Figure 8** Cross-section surface ESEM images of the (a) PAN membrane, (b) PDM/PAN blend membrane, and (c) crosslinked PDM/PAN blend membrane.

crosslinked membrane was much better than the blend membrane without crosslinking in performances, although the flux and rejection of both membranes were dependent on PDM content, polymer concentration, additive dosage, and other factors. The strong adsorption to the negatively charged dye and the slight affinity to the positively charged dye of the crosslinked blend membrane implied its positively charging property. ESEM observation found the crosslinked blend membrane had a highly uniform structure due to the restraint of the crosslinked PDM network to the coagulation procedure, which differed markedly to that of the PAN membrane and the uncrosslinked blend membrane.

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