Structure and Properties of Microporous Membranes Prepared by Applying Phase Separation during Polymerization

YUKIO MIZUTANI and MASAKATSU NISHIMURA, *Research and Development Division, Tokuyama Soda Co., Ltd., Tokuyama City, Yamaguchi Prefecture, 745, Japan*

Synopsis

Porous membranes of poly(vinyl chloride) were obtained from cation exchange membranes prepared by the soaking and paste method, by selective decomposition of the cation exchange resin component. The structure and properties of the membranes as filters were investigated by scanning electron microscopy, infrared analysis, water permeability measurement, and determination of rejections for some solutes and dispersers with widely differing sizes. They completely rejected two kinds of bacteria and polymer particles with a diameter of about 0.1 μm. The rejection of hemoglobin ranged from 90 to 100%, depending upon the preparative conditions. Heat treatment of the cation exchange membranes increased water permeability of the resulting PVC porous membranes and decreased hemoglobin rejection in varying degrees, depending upon the treatment temperature.

INTRODUCTION

Recently, membrane microfiltration (MF) and ultrafiltration (UF) have gained increasing prominence as simple and convenient processes for concentrating, purifying, and fractionating solutions containing colloids or solutes of large molecular weights.[1,2] These processes are performed under vacuum or at low pressure. Advances in these techniques are attributable to the development of characteristically structured microporous membranes with high solute retention efficiencies and high solvent permeation rates. They are prepared by polysalt formation process,[3-5] phase inversion process,[6] particle-track etching process,[7] and other processes.[8]

As reported in previous articles,[9,10] the cation exchange membranes prepared by the paste method[11-13] have a microheterogeneity: The cation exchange resin component (R resin), sulfonated styrene (St)–divinylbenzene (DVB) copolymer, is finely distributed in poly(vinyl chloride) (PVC). This microheterogeneity is due to the phase separation of the St–DVB copolymer from PVC gel phase during the polymerization step. Thus, the selective removal of the R resin from the cation exchange membranes according to hydrogen peroxide treatment[10] gives PVC microporous membranes. PVC microporous membranes should likewise be obtained from cation exchange membranes prepared by the soaking method[14,15] involving also the copolymerization of St and DVB in PVC gel phase. There have been no reports concerning such methods for preparing porous membranes.

The present work was initiated to study the applicability of PVC porous membranes prepared by the above method to MF or UF. Their structural features and some fundamental properties as filters were investigated by scanning

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electron microscopy, infrared analysis, water permeability measurement, and determination of rejection characteristics. Heat treatment of a cation exchange membrane was also carried out to alter the properties of the resulting PVC porous membrane.

EXPERIMENTAL

Cation Exchange Membranes

Table I shows some characteristics of the cation exchange membranes used (PM, SMA, SMB) which were measured by the usual methods.[16,17] The PM membrane and both the SMA and SMB membranes were prepared by the paste method and by the soaking method, respectively.

PM Membrane

The paste, consisting mainly of St, commercial DVB (55%), benzoyl peroxide (BPO), and PVC powder in a weight ratio of 90:10:1:45, was coated on a PVC cloth. The resultant composite was wrapped with a cellophane (regenerated cellulose) film and then heated in an autoclave at 105°C for 4 hr. The base membrane thus obtained was sulfonated in conc. H_2SO_4 at 60°C for 16 hr.

SMA and SMB Membranes

A sheet of PVC 0.1 mm thick (Swallon from Hiroshima Kasei Co., Ltd.) was immersed in a mixed solution of St, commercial DVB, BPO, and dioxane in the weight ratio of 90:10:1:25 for 2 hr. The immersion temperature was 40°C for SMA and 50°C for SMB. The heat polymerization of the monomers imbibed by the PVC sheet and the sulfonation of the resultant base membrane were carried out as described above for the PM membrane.

Hydrogen Peroxide Treatment

Cation exchange membranes of the H^+ form were converted to the Fe^{3+} form in a large excess of $0.1N$ $FeCl_3$ solution. After washing with deionized water, they were treated with 5% hydrogen peroxide solution at room temperature for 100 min.

TABLE I
Characteristics of the Cation Exchange Membranes

Membrane	Thickness, mm	Capacity, mequiv/g dry membrane	Water content, g H_2O/g dry membrane
PM	0.13	2.72	0.46
SMA	0.16	3.08	0.63
SMB	0.16	3.34	0.68

Infrared Analysis

The infrared spectra of both the cation exchange membranes and the porous membranes were taken by the KBr method with a recording spectrophotometer (EPI G3 from Hitachi Ltd.) in the range of 4000 to 600 cm^{-1}. The sample powders were prepared by scraping the dried membranes with a razor blade.

Scanning Electron Microscopy

The surface and the cross section of the porous membrane obtained from the SMA membrane were observed by using scanning electron microscope (JSM-50A from Jeol Ltd.). The cross section was obtained by breaking the membrane at liquid nitrogen temperature. The specimens were freeze-dried, fixed on cylindrical copper disks, and then coated with a thin layer of gold by using a vacuum metallizer.

Heat Treatment

Four pieces of the SMA membrane of the H$^+$ form were separately treated in hot waters maintained at 65, 75, 85, and 95°C for 30 min and then quenched rapidly in cold water. They were also submitted to the hydrogen peroxide treatment.

Water Permeability Measurement and Filtration Test

The filtration cell used in the majority of the experiments were made of stainless steel and was similar to that described in an earlier article.[18] The solution reservoir capacity was 90 cm^3, and the effective membrane area was 6.2 cm^2. The pressure was obtained from an external high-pressure nitrogen bomb. A stirrer was set approximately 0.5 mm above the membrane.

A simple vacuum filtration device made of glass was also used. The filtering flask was connected by its side tube to an electric vacuum pump. The effective membrane area was 5 cm^2.

The effect of pressure on the water permeation characteristics of the porous membranes was studied by using the filtration cell without stirring. The pressure was raised stepwise by 1 kg/cm^2 for each measurement of water permeation rate.

Table II shows the colloidal and molecular substances used for the rejection studies and their analytical methods. Filtration experiments were conducted in the following ways.

Acrylic resin particles, hemoglobin, and Congo Red. The solution or the emulsion in the reservoir of the filtration cell was stirred vigorously, and a pressure of 3 kg/cm^2 was applied to it. The first filtrate of 20 ml was discarded. A small volume of filtrate was then collected and analyzed. The rejection of a membrane for a solute or a disperser (R_s) was defined as follows:

$$R_s = 100 \left(1 - \frac{C_f}{C_b}\right) \% \qquad (1)$$

where C_f is the concentration of solute or disperser in the filtrate and C_b is the concentration in the bulk solution.

TABLE II
Substances Used for Rejection Studies and Their Analytical Methods

Sample substance	Size, μm	Concentration or cell population	Analytical method
Coliform bacteria in sewage[a]	$(2–4) \times (0.4–0.7)$	$2.7 \times 10^3/cm^3$	plate count technique[b]
Serratia marcescens in boullion	0.7	$1.3 \times 10^5/cm^3$	plate count technique[c]
Acrylic resin emulsion	about 0.1	1 wt %	turbidimetric analysis
Hemoglobin (bovine), solution	0.003×0.015 (MW = 68,000)	0.1 wt %	absorbance analysis at 410 nm
Congo Red, solution	0.0012 (MW = 696)	0.1 wt %	absorbance analysis at 490 nm

[a] Effluent from the final sedimentation tank in an activated sludge treatment plant for domestic sewage.

[b] Mixing of a known volume of filtrate with desoxycholate medium, incubation (35°C, 20 hr), and then counting of colonies.

[c] Mixing of a known volume of filtrate with nutrient agar medium, incubation (30°C, 48 hr), and then counting of colonies.

Coliform Bacteria, *Serratia marcescens*

The bacterial suspension of 25 ml was filtered through the porous membrane by using a vacuum filtration device previously autoclaved (121°C, 1 atm, 30 min). Then the number of the cells in the filtrate was determined.

RESULTS AND DISCUSSION

Chemical Structure

The hydrogen peroxide treatment of the PM, SMA, and SMB membranes resulted in porous membranes (FPM, FSMA, and FSMB, respectively) with no ion exchangeability and with Cl contents (54.5–55.3%) approximate to the calculated value for PVC (56.8%). The reactive intermediates such as OH· radicals formed by the Fe-catalyzed decomposition of hydrogen peroxide probably caused the scission of the crosslinked polymer chains of the R resin, forming linear polystyrene sulfonates soluble in water.

The three porous membranes had similar infrared spectra. Figure 1 compares the infrared spectrum of the FPM membrane, as example, with that of the original cation exchange membrane (PM). Figure 1(a) indicates that the cation exchange membrane is composed of PVC and sulfonated St–DVB copolymer. On the other hand, the spectrum of the porous membrane [Fig. 1(b)] does not exhibit the absorption bands at 775, 1500, and 1603 cm^{-1} owing to benzene ring and is essentially identical with that of PVC. The porous membrane was somewhat hydrophilic; correspondingly, the spectrum shows broad absorption bands at about 1630 and 3420 cm^{-1} owing to the strongly absorbed water. The treatment of the porous membrane with an aqueous solution of NaOH, followed by rinsing with water and drying, caused a considerable decrease in the intensity of the band at 1720 cm^{-1} and the appearance of a shoulder at about 1580 cm^{-1}. This suggests that PVC undergoes oxidation accompanying the formation of carboxyl groups at its interface with the R resin during the hydrogen peroxide
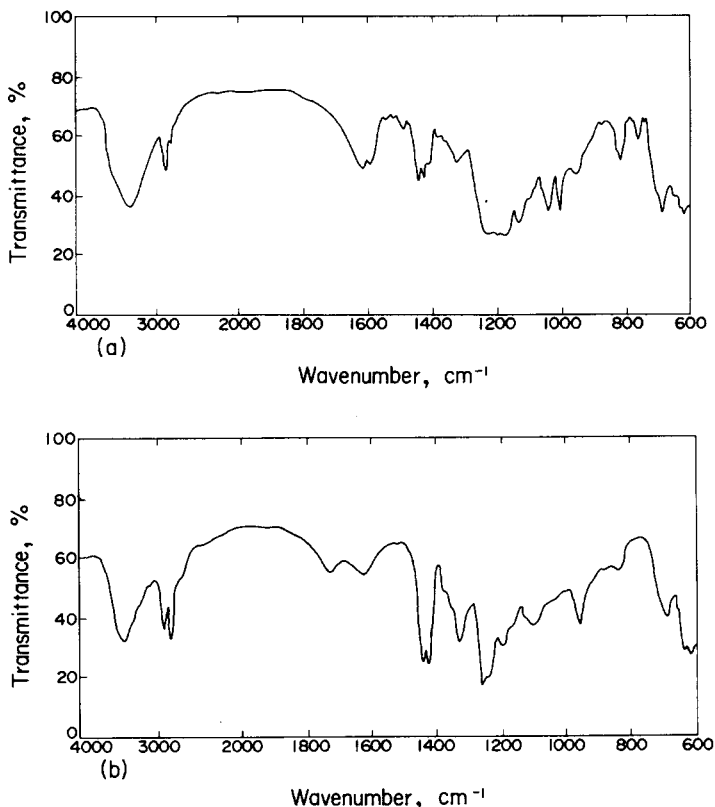
Fig. 1. Infrared spectra of (a) PM cation exchange membrane and (b) FPM porous membrane.

treatment. This must be one of the reasons for the hydrophilic nature of the porous membranes and also for their Cl contents being slightly lower than the calculated value for PVC. The spectrum does not show any evidence for the formation of the C=C double bond owing to the elimination of HCl from PVC because its absorption range overlaps with that of the band owing to the adsorbed water (1630 cm^{-1}).
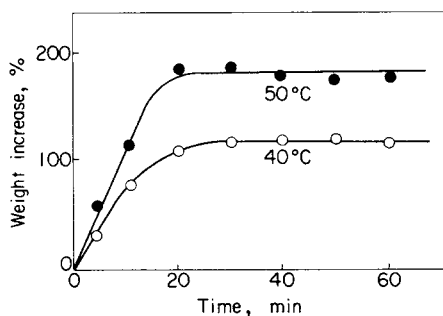

Fig. 2. Swelling behavior of PVC sheet in mixed solution of St, commercial DVB, and dioxane in a weight ratio of 90:10:25.

Pore Structure

Table III shows some structural characteristics of the porous membranes. The apparent pore radii are in the range of 0.015–0.040 μm. The porosity of the FSMB membrane is higher than that of the FSMA membrane, which must be primarily ascribed to the higher volume fraction of the R resin in the SMB membrane. This is consistent with the fact that the ion exchange capacity of the SMB membrane is higher than that of the SMA membrane (Table I). In this connection, the swelling behavior of the PVC sheet in the mixed monomeric solution at 40 and 50°C was studied. As can be seen from Figure 2, the equilibrium is reached within 25 min, regardless of the immersion temperature. It is noteworthy that the immersion temperature strongly affects the equilibrium monomer content of PVC.

The close observation of the FSMA membrane by scanning electron microscopy revealed its unique pore structure. As can be seen from Figure 3(b), the inner part of the membrane has a fine cellular structure with a high void volume; each cell opens into the neighboring cells via a number of pores through the cell walls. This pattern should result from the microphase separation of the St–DVB copolymer from the PVC gel phase during the polymerization. As PVC is miscible with the monomers but not with the copolymer, phase separation occurs necessarily. Apparently the average pore size at the surface [Fig. 3(a)] is smaller than that of the underlying cells. This surface layer having a higher polymer density looks quite thin [Fig. 3(c)]. The detailed mechanism of the formation of the surface layer is not yet elucidated.

Water Permeability

Figure 4 shows the effect of applied pressure on the water permeation rates of the porous membranes. Linear relationships can be observed between the pressure and the water permeation rate. The decreasing order of water permeability of the porous membranes was as follows: FSMB > FSMA > FPM, which was the same as the decreasing order of porosity.

At higher pressures (>7 kg/cm^2 for FSMA and FSMB, >11 kg/cm^2 for FPM), however, the observed water permeation rates deviated from the extrapolated lines; during continuous test for a long time, the water permeation rate gradually decreased from the initial high value. This drop in the water permeation rate must be due to the densification of the porous structure (compaction) of the membranes. The FPM membrane having a lower porosity is reasonably less

TABLE III
Structural Characteristics of the Porous Membranes

Membrane	Thickness, mm	Porosity[a]	Apparent pore radius,[b] μm
FPM	0.11	0.61	0.017
FSMA	0.15	0.76	0.034
FSMB	0.16	0.82	0.038

[a] Calculated from the wet and dry weights of the membrane, as described earlier.[10]
[b] Calculated from the water permeability by applying Hagen–Poiseuille law, as described earlier.[10]
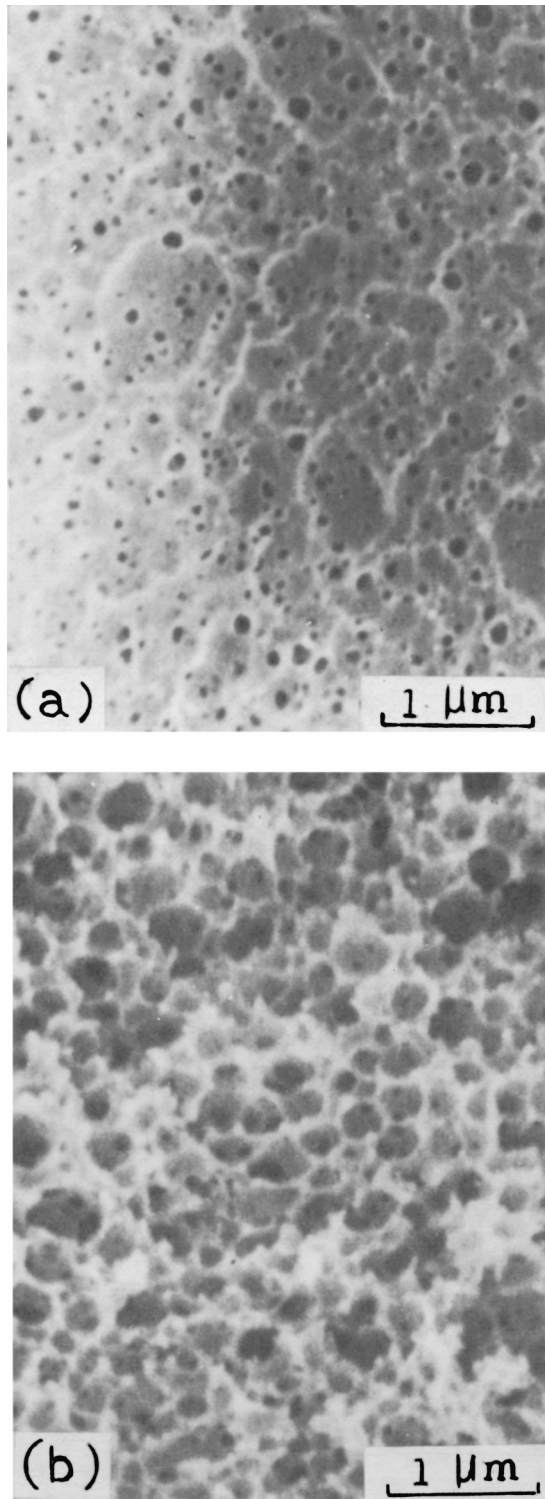
Fig. 3. Scanning electron micrographs of FSMA porous membrane: (a) surface structure; (b) inner structure; (c) surface layer covering a cellular wall.
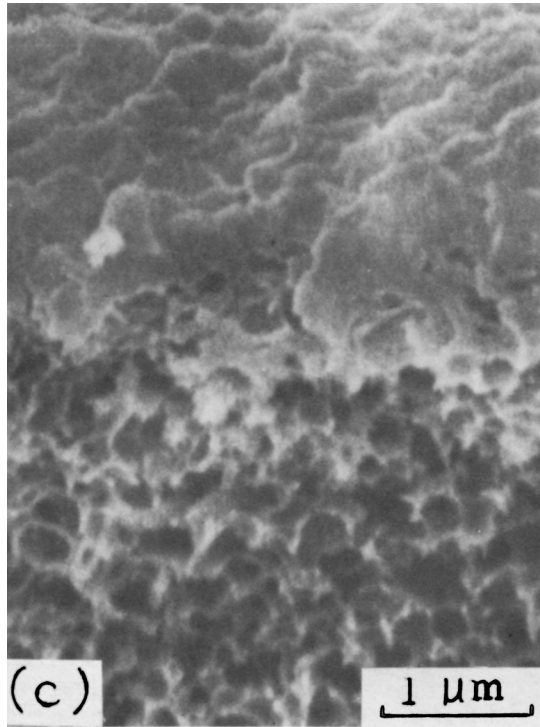
Fig. 3. (*Continued from previous page.*)

susceptible to compaction than the other membranes. At any rate, it is evident that the three porous membranes have sufficient resistance to compaction for practical purposes.
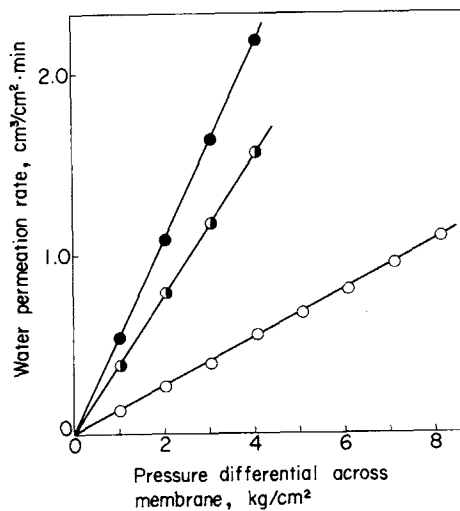

Fig. 4. Water permeation rate–applied pressure curves for FPM (–O–), FSMA (–◑–), and FSMB (–●–) membranes.

Rejection Characteristics

Table IV shows the rejection characteristics of the porous membranes. They were capable of complete separation of coliform bacteria in secondary sewage; no colonies appeared after the cultivation of the filtrates. They could also completely retain *Serratia marcescens*. These findings clearly indicate that the porous membranes are entirely free from continuous voids larger than 1 μm in diameter. In the case of the filtration of the acrylic emulsion, the three porous membranes gave clear filtrates without any resin globules about 0.1 μm in diameter. In view of the apparent pore sizes of the porous membranes, it is assumed that two kinds of bacteria and the 0.1-μm resin particle were mechanically retained by the membranes.

All the membranes unexpectedly showed considerably high rejections (>90%) of hemoglobin. In particular, the FSMA membrane retained hemoglobin very efficiently. On the other hand, Congo Red passed through them freely. These findings suggest a possible applicability of these membranes for the concentration of relatively high-molecular-weight solutes accompanied by the removal of lower-molecular-weight impurities.

Influence of Membrane Surface Structure on Properties of the Membranes as Filters

As shown above, the pore structure of the FSMA membrane near the surfaces is different from that at the inner part. In order to elucidate the influence of the surface layer on the properties of the porous membrane, the following experiments were carried out.

Both surfaces of the SMA membrane were scraped off carefully by using a blade, and thus five cation exchange membranes of different thicknesses were obtained and subjected to hydrogen peroxide treatment. The water permeabilities and rejection characteristics of the resultant porous membranes were determined.

Figure 5 shows the relative water permeabilities of these porous FSMA membranes (A–E) as a function of the decrease in membrane thickness. It can be seen that the surface layer of the FSMA membrane is responsible for about 20% of the resistance of the entire membrane and that the thickness of the layer is below 3 μm. In spite of the presumption that the rejection characteristics would be governed by the surface layer, even the porous membrane (E), about 30 μm thinner than the FSMA membrane, also showed rejection of approximately 100% for 0.1-μm acrylic resin globules and for hemoglobin. The reason for the high hemoglobin rejections of the three porous membranes has remained obscure;

TABLE IV
Rejection of Porous Membranes for Various Solutes and Dispersers

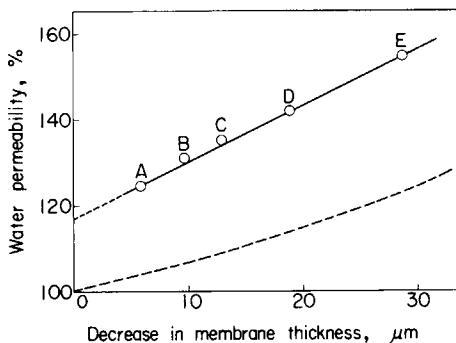| Solute or disperser	Rejection R_s, %		
	FPM	FSMA	FSMB
Coliform bacteria	100	100	100
Serratia marcescens	100	100	100
Acrylic resin particles (0.1 μm)	$\approx$100	$\approx$100	$\approx$100
Hemoglobin	95.0	>99.5	90.0
Congo Red	$\approx$0	$\approx$0	$\approx$0

Fig. 5. Change in water permeability with thickness of the FSMA membrane by scraping it off equally from both surfaces: (–O–) experimental value; (- - -) theoretical curve on the assumption of homogeneous structure of the FSMA membrane.

carboxyl groups present at the membrane pore surface might play a significant role.

Influence of Heat Treatment

Figure 6 shows the water permeabilities and rejection characteristics of the porous membranes which were obtained from the previously heat-treated cation exchange membranes. The heat treatment at >75°C resulted in changes in the properties; the water permeability progressively increased with increasing heating temperature; simultaneously the rejection of hemoglobin decreased (from >99.5% to 80%), though the rejection of 0.1-μm resin globules remained unchanged.

Heat treatment at temperatures higher than the softening point of PVC should decrease the restraining force of PVC against the swelling of the R resin and consequently against the expansion of the membrane. Hence, it can be reasonably assumed that the pore size of the resulting porous membrane becomes larger with increasing temperature of the heat treatment.
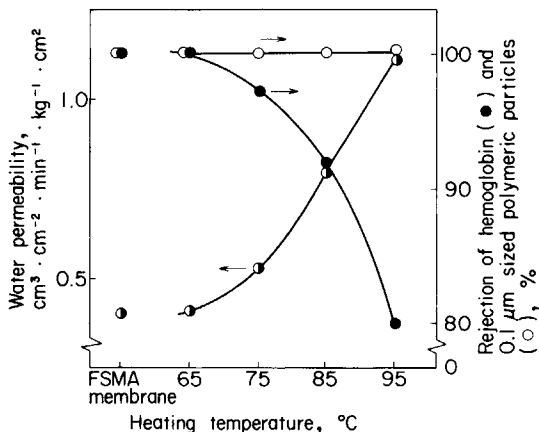

Fig. 6. Some characteristics of porous membranes obtained from cation exchange membranes (SMA) heat treated at several temperatures for 30 min.

CONCLUSIONS

Porous membranes of PVC were obtained by the hydrogen peroxide treatment of cation exchange membranes prepared by the soaking and the paste methods. Their structure and properties as filters, such as water permeability and rejection characteristics, were investigated. Heat treatment of a cation exchange membrane was also carried out to alter the properties of the resulting porous membrane. The results obtained suggest the applicability of the porous membranes prepared by the present method as MF or UF membranes.

A better understanding of the mechanism of the phase separation during the copolymerization of St and DVB in the PVC gel phase is the key to the preparation of more effective porous membranes. Polymerization temperature, DVB and BPO contents of the paste or the soaking solution, etc., may be utilized to control permeability and rejection characteristics of the porous membranes.

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