

Preparation and Recovery Properties of Homogeneous Modified Polysulfone Plate Affinity Membrane Chromatography with Thiohydroxy as Chelating Groups. I. Synthesis and Preparation of Plate Matrix Membrane

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ABSTRACT: A chloromethylation polysulfone (CMPSF), having good properties of membrane formation, spinnability, and reactive groups, was synthesized with Friedel–Crafts reaction, which could be used as reactivity matrix membrane materials. The effects of ZnCl₂ quantity, monochloro methyl ether quantity, reaction time, and reaction temperature on the chlorinity of CMPSF were investigated. The CMPSF plate matrix membranes were prepared with phase inversion by use of the CMPSF/additive/*N,N'*-dimethylacetamide (DMAc) casting solution and CMPSF as membrane materials. The focus of this study was primarily concerned with the relationship among such factors as species and contents of additives, CMPSF content in casting solutions, and temperature of solutions, and the morphological structure of the membrane, pore

size, porosity, and water flux of the membrane. It was concluded that these factors had obvious effects on the structure and the performance of the CMPSF matrix plate membrane, which could be improved within a wide range by changing the thermodynamic conditions of the casting solution. The effects of coagulation conditions on the microstructure and performance of CMPSF plate matrix membrane were also studied. It was found that the water flux of the CMPSF plate matrix membrane was at a maximum value by use of 10% DMAc solution as coagulation bath. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2117–2131, 2005

Key words: chromatography; matrix; membranes; separation techniques; Friedel–Crafts reaction

INTRODUCTION

Chelating affinity membrane chromatography is conveniently used to treat industrial wastewater and recover metal ions because it integrates the advantages of both modern membrane techniques and affinity chromatography techniques.^{1–6}

The chelating resin with *N* and *S* coordination atoms has good adsorptive capacity for Hg²⁺ because Hg²⁺ is a kind of soft acid or middle acid, whereas the organic *S* and *N* chemical compounds have the properties of a soft alkaline or mid-alkaline. According to the soft and hard acid–base theory, they easily form a chelating complex that is more stable. There are numerous reports concerning

the synthesis of thiohydroxy chelating resin. Most of the underlying studies used polystyrene (PS) or poly(methyl methacrylate) (PMMA) as the macromolecule carrier bringing into chelating groups with *S* and *N* through macromolecular reactions. The main chains of these macromolecule carriers are all carbon–carbon bonds. The adsorption of the resin for valuable and heavy metal ions is determined by the functions of chelating groups with lateral chains.

In our previous works,⁷ the high quality heterogeneous polysulfone (PSF) affinity plate filter membranes with chelating groups were prepared with phase separation by using blends of the chelating resin and polysulfone as materials.

In this study, we used PSF as the original material to synthesize chloromethyl polysulfone (CMPSF) with Friedel–Crafts reaction and produced a CMPSF membrane using the phase-inversion method. The CMPSF matrix membrane was reacted with sulfo-carbamide and hydrolysis under alkaline conditions, the homogeneous thiohydroxy modified polysulfone chelating affinity plate membrane chromatography was obtained, and its adsorption properties for Fe²⁺, Cu²⁺, Hg²⁺, and Zn²⁺ were also investigated.

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EXPERIMENTAL

Materials and reagents

Dichloromethane and 1,2-dichloroethane, analytically pure, were supplied by Tianjin Chemical Reagent Plant (China); monochloro-methyl ether was supplied by Nankai University Chemical Plant (China); zinc chloride, analytically pure, was supplied by Chemical Reagent Plant (China); sodium rhodanate, analytically pure, was supplied by Tianjin Yao-hua Chemical Plant (China); ferriammonium sulfate, analytical pure, was supplied by Tianjin Nankai Chemical Plant (China); and nitrobenzene and polyethylene glycol were supplied by Tianjin Chemical Reagent Plant.

Main apparatuses

A Vector 22 Fourier infrared spectrometer (with ART appendix) was made by Bruker (Darmstadt, Germany); S450 scanning electron microscope was made by Hitachi (Osaka, Japan).

Synthesis of CMPSF

A given amount of dried PSF was weighed and dissolved in dichloromethane (or 1,2-dichloroethane), to which mixture the complex of anhydrous zinc chloride/monochloro methyl ether was added dropwise; the reaction temperature was slowly increased to 40°C and the reaction lasted for 6 h. After the circumfluous reaction was finished, the solution was cooled to room temperature and the solution was slowly added to methanol with vigorous stirring, yielding CMPSF as a lump precipitate. It was repeatedly washed by hot distilled water until bubbling ceased. The precipitate was dried at a temperature between 60 and 70°C, after which the rough CMPSF was prepared. The rough CMPSF was sheared into small pieces, dissolved in DMAc, poured into distilled water maintained at 70–80°C, and stirred, after which the white stripe or floc was separated out. The refined CMPSF was prepared by filtering the precipitate, washing it three times with distilled water, and drying the precipitate at 60–70°C.

Determination of CMPSF chlorinity

Determination of CMPSF chlorinity was carried out by using the Woolhad method.⁸

Preparation of CMPSF matrix plate membrane

The matrix plate membranes were prepared by the phase-inversion method.⁹ Using CMPSF as the membrane material, PEG as the additive, and DMAc as the solvent, the three ingredients were mixed together in a certain ratio and heated to dissolve the

constituents, after which the casting solution was obtained after vacuum defoaming. The casting solution was poured onto a clear and smooth glass plate at a predetermined temperature. After evaporating in the air for seconds, the solution was cast into a thin film using a blade, and the glass plate was saturated in a DMAc water solution at a certain temperature to let it solidify into a membrane. By changing the casting solution temperature, evaporating time, and temperature and concentration of the coagulation bath, different test samples of plate membrane were produced at different ratios and conditions. The test samples of membrane were preserved in a 50% glycerin solution.

IR spectra of PSF and CMPSF

The PSF and CMPSF plate membranes were dried at 50–70°C. The dried membrane plates were placed directly on the ART crystal and firmly fastened by clips. The metal peg must be firmly screwed when fastening, and the ART annex must be securely fastened with the membrane plate onto Vector 22 Fourier infrared spectrometer.

SEM analysis of CMPSF matrix membrane

The CMPSF matrix membrane was soaked in glycerol (50 vol % ratio) for 24 h, after which the membrane was removed and the glycerol wiped from its surfaces. After stepwise dehydration, through the mass fraction of 50, 70, 90, and 100% EtOH in sequence, membrane samples were snapped by freezing them in liquid nitrogen; they were then fastened onto the sample table and the film were coated by ion sputtering. Thickness of the samples was about 20 nm. The morphological structure of the surfaces and cross section of the matrix membrane were observed by an S450 scanning electron microscope to determine the pore size with respect to membrane distributions.

Water flux measurement

The water flux was determined using equipment that was specially designed to evaluate the properties of ultrafiltration membranes (made in Tianjin Polytechnic University, China). The pressure was 0.1 MPa and the medium was ultrapure water. From the measured volume V of transmission liquid and ultrafiltration time t , the water flux Q was calculated from the following equation:

$$Q = \frac{V}{St} \quad (1)$$

TABLE I
Effect of ZnCl₂ Quantity on CMPSF Chlorinity

PSF (g)	CH ₂ Cl ₂ (mL)	CH ₃ OCH ₂ Cl (g)	ZnCl ₂ (g)	CMPSF chlorinity (%)
20	200	20	0.5	5.05
20	200	20	1.5	7.58
20	200	20	2.3	6.46

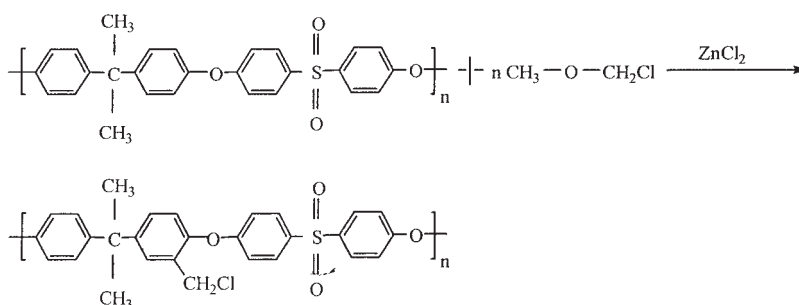
where S is the effective surface area of the membrane.

Porosity measurement

The membrane porosity was determined by means of the gravimetry method.¹⁰ We used glycerol as saturant, sheared a prescribed area of wet membrane, wiped the glycerol from the membrane surface, and weighed the wet membrane (W_w). Then the wet membrane was placed in a vacuum dry box to dry until its weigh was constant. Last, we weighed the dry membrane (W_d). Percentage porosity of the membrane P_r was calculated from the following equation:

$$P_r = \frac{W_w - W_d}{Sd\rho} \times 100\% \quad (2)$$

where d is the average thickness of membrane and ρ is the density of glycerol.



The effects of ZnCl₂ quantity on the chlorinity of CMPSF are shown in Table I. PSF (20 g) was dissolved in 200 mL of dichloromethane, and a prescribed quantity of ZnCl₂ was dissolved in 20 g of chloromethyl ether to form a compound. The reaction lasted for 5 h at 40°C. From Table I one can observe that the quantity of ZnCl₂ has substantial effects on the chloromethyl of PSF. The chlorinity of CMPSF increased quickly with increasing ZnCl₂ quantity, although the products would be easy to freeze if the ZnCl₂ quantity were in sufficiently large excess. The effects of the quantity of

TABLE II
Effect of CH₃OCH₂Cl Quantity on CMPSF Chlorinity

PSF (g)	CH ₂ Cl ₂ (mL)	CH ₃ OCH ₂ Cl (g)	ZnCl ₂ (g)	CMPSF chlorinity (%)
20	200	10	1.5	5.07
20	200	20	1.5	7.58
20	200	40	1.5	10.24

Membrane pore size measurement

The membrane pore size was determined by means of the filtering velocity method.¹⁰ The membrane pore diameter r_f was calculated from the following equation:

$$r_f = \sqrt{\frac{8 \times (2.90 - 1.75P_r)\mu LQ}{P_r\Delta P S}} \quad (3)$$

where P_r is the porosity, L is the thickness of the membrane, μ is the viscosity of the transmission liquid, Q is the flux, ΔP is the pressure, and S is the filtering area.

RESULTS AND DISCUSSION

Synthesis of CMPSF

In this study, CMPSF was obtained by the Friedel-Crafts electrophilic substitution reaction under anhydrous conditions using PSF as the original material, dichloromethane as the solvent, monochloro methyl ether as the chloromethyl reagent, and anhydrous ZnCl₂ as the catalyst. The specific reactions are expressed as

monochloro methyl ether on the chlorinity of CMPSF are shown in Table II. PSF (20 g) was dissolved in 200

TABLE III
Effect of Chemical Reaction Time on CMPSF Chlorinity

Reaction time (h)	PSF (g)	CH ₂ Cl ₂ (mL)	CH ₃ OCH ₂ Cl (g)	ZnCl ₂ (g)	CMPSF chlorinity (%)
4	20	200	20	1.5	3.28
5	20	200	20	1.5	5.62

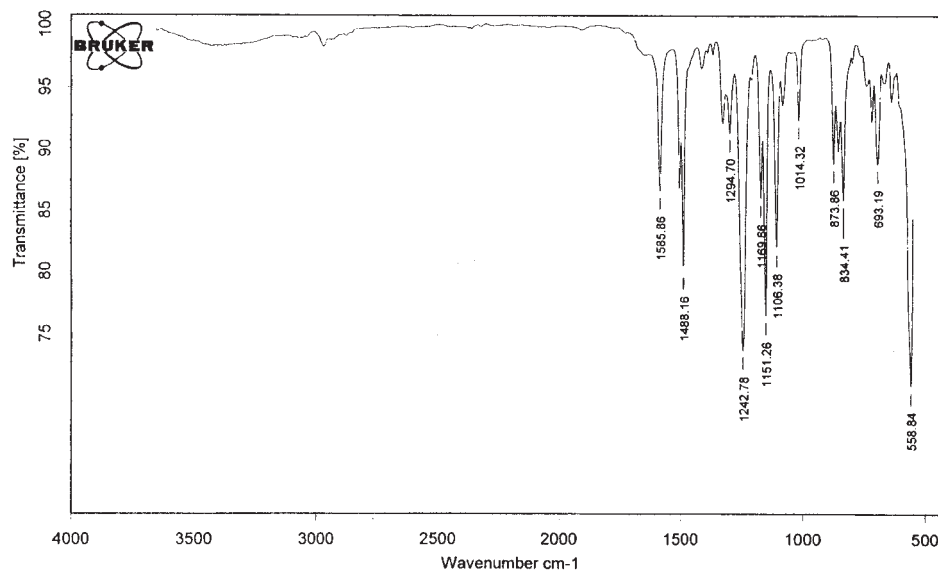


Figure 1 IR spectrum of PSF membrane.

mL of dichloromethane to form a solution. The complexes with different concentrations were added to the solution, and the reaction lasted for 5 h at the reaction temperature of about 40°C. The chlorinity of CMPSF increased with increasing content of monochloro methyl ether. The effects of reaction time on the chlorinity of CMPSF are shown in Table III. PSF (20 g) was dissolved in 200 mL of dichloromethane, and 20 mL of complex was added to the solution. Different samples reacted for different times when the reaction temperature was 40°C. The chlorinity of CMPSF increased with increasing time span of the reaction. At the initial stage of the reaction, the chlorinity of CMPSF increased sharply, and the rate of chlorinity increase decreased after 5 h. The reaction temperature should be controlled so that the circumfluence of monochloro methyl ether could occur when the chloromethyl reaction of polysulfone was in progress. If 1,2-dichloroethane were used as the solvent, the reacting system would not have to undergo circumfluence, and the temperature could be controlled at 40–45°C because the rate of chloromethyl would be only slight when the reaction temperature was too low and the monochloro methyl ether would easily dissipate when the reaction temperature was too high.

IR analysis of CMPSF matrix membrane

The IR spectra of polysulfone and CMPSF are shown in Figure 1 and Figure 2, respectively. Comparing Figure 1 with Figure 2, there was a strong single absorption peak in Figure 2, whereas Figure 1 had two absorption peaks at the vicinity of 1500 cm^{-1} . The existence of $-\text{CH}_2\text{Cl}$ was verified after PSF went

through the Friedel–Crafts reaction combined with the chlorinity test of CMPSF with the Woolhad method.

Effects of CMPSF concentrations in original casting solution on the matrix membrane structure

The structure and property of the membrane were determined not only by the nature of the membrane materials and membrane-forming process conditions but also by the thermodynamic conditions of casting solutions, such as concentration of polymer, type, and amount of additive and temperature of casting solutions. SEM micrographs of the cross section and surface morphological structure of matrix membrane with different CMPSF concentrations in original casting solutions are shown in Figures 3 and 4. Figure 3 shows that the membrane support layers gradually changed from a finger-shape structure to a sponge-shape structure with increasing CMPSF concentrations. From Figure 4 it can be seen that the pore size of the membrane dense layer changed from large to small and the dense layers gradually became denser with increasing CMPSF concentration; thus the water flux of the matrix membrane decreased continually.

Table IV shows the relationship between CMPSF concentration and properties of the matrix membrane. From Table IV it could be seen that water flux, pore size, and porosity of CMPSF matrix membrane all decreased with decreasing CMPSF concentration. Pore size and porosity of membrane decreased with increasing CMPSF content in the original casting solutions. As CMPSF content in the original casting solution increased, the net structure of the original solution became compact and thus the pore size and

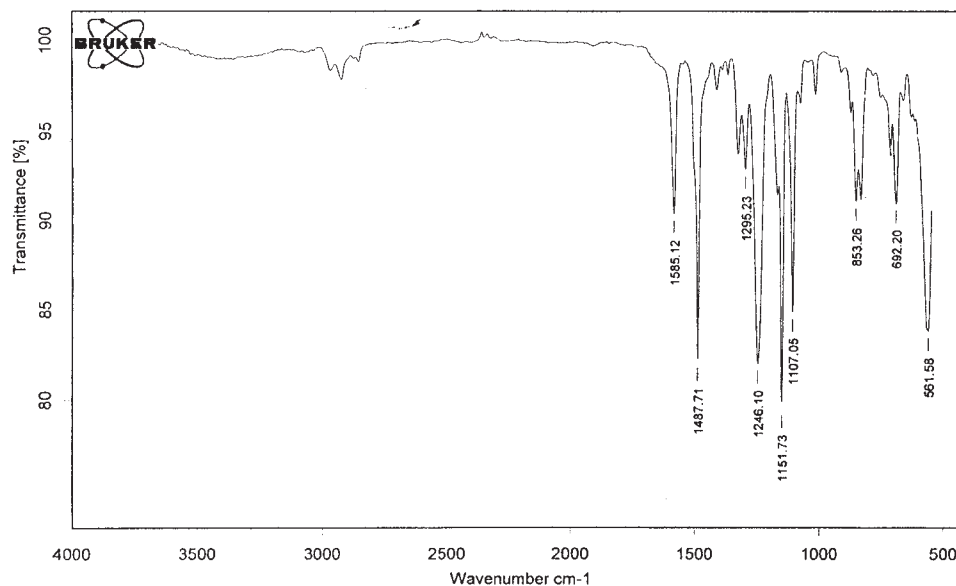


Figure 2 IR spectrum of CMPSF membrane.

porosity of the membrane were decreased. Meanwhile, as the CMPSF content increased, the viscosity of the casting solution increased, which caused the double diffusion rate between solvent and coagulating agent to decrease when the phase-inversion rate and coagulating rate gradually decreased. The finger-shape structure gradually transformed to a sponge structure, and water flux, pore size, and porosity of the matrix membrane decreased.

Effects of additive type on the structure of CMPSF matrix membrane

Table V shows the effects of additive types on CMPSF matrix membrane. The usual casting solution was a ternary system composed of polymers, solvent, and additive. After certain membrane materials and corresponding solvent were selected, according to the component to be separated, the additive was an active factor that could affect the morphological structure of the casting solution, and could determine both structure and function of the terminal membrane with other casting conditions: it is thus crucial for the casting process to choose the additives and to control the thermodynamical conditions of casting solution effectively. The additive played an important role in the process of forming the CMPSF matrix membrane by phase inversion. A Millipore filter membrane and ultrafiltration membrane could be obtained by either adding solvent to the coagulating bath or adding proper additives to the casting solution such as high polymer, solid inorganic salt or its dilute water solution, and organic agent. Different additives promote significant changes in both the structure and the properties of CMPSF matrix membrane. Figure 5 is the

cross-sectional SEM micrograph of CMPSF matrix plate membrane when the inorganic agent NH_4Cl and the organic agent ethanediol, respectively, were used as additive. From Figure 5 it can be seen that support layers of the CMPSF matrix membrane appeared as a loose finger-shape structure when the inorganic agent was used as additive, whereas support layers of the CMPSF matrix membrane appeared as a dense sponge structure when the organic agent was used as additive. The addition of dilute inorganic water solution changed the acting force between solute and solvent, and caused entanglement of CMPSF macromolecules into a large net structure, thus causing the micropore to enlarge. The solid inorganic salt NH_4Cl had additional effects that could produce pores when the solid inorganic salt was removed from the casting solution. The organic agent ethanediol as additive was a poor solvent to CMPSF, but was good for formation of net micropores on surfaces of the CMPSF matrix membrane such that pore size of the membrane was enlarged; however, it decreased the phase-transfer rate, and formed a sponge-shape support layer, which decreased both porosity and water circumfluence. High polymer additive PEG (MW 10000) was incompatible with CMPSF and left micropores in the membrane material when it was wiped away after casting.

Effect of inorganic additive on the structure of CMPSF matrix membrane

Changes in structure of the CMPSF plate membrane with inorganic additive content are shown in Table VI. From Table VI it can be seen that water flux, average pore size, and porosity of CMPSF membrane all increased with increase of additive NH_4Cl , and reached

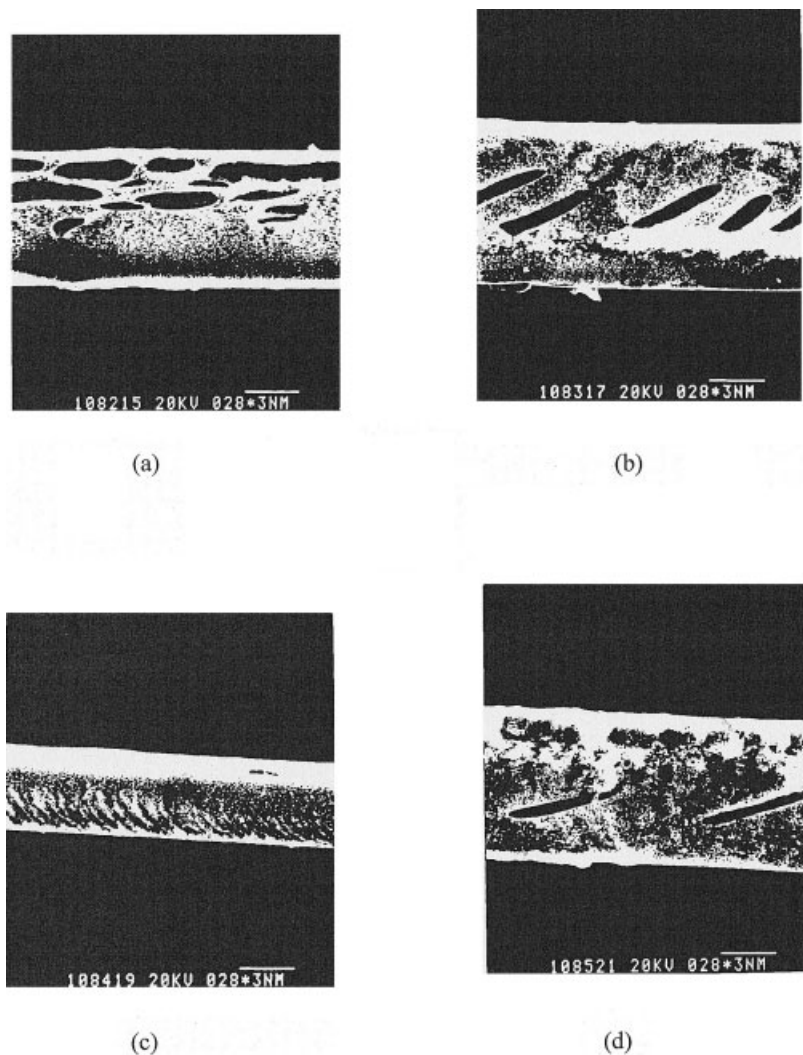


Figure 3 SEM micrographs of cross section of matrix membrane with different CMPSF contents: (a) 10%; (b) 12%; (c) 14%; (d) 16%.

their maximum value when the additive NH_4Cl content was 6%, concomitantly with the relationship between additive content and viscosity of the original casting solution. With increasing additive content, viscosity of the casting solution decreased continually; the double diffusion rate between solvent and coagulating agent increased; and pore size, porosity, and water flux of CMPSF matrix membrane all increased. When the additive content increased to over 6%, viscosity of the casting solution, which was related to gelation of the original solution, increased suddenly, the rate of double diffusion decreased, and a dense membrane structure formed.

Effects of polymer additive on the structure of CMPSF matrix membrane

Table VII shows the effect of polymer additive PEG (MW 10000) content on the CMPSF matrix membrane

structure. It can be seen from Table VII, that water flux, pore size, and porosity of the CMPSF matrix membrane all increased with increasing content of high polymer additive (percentage of entire solid amount) in the casting solution.

Figure 6 and Figure 7 show SEM micrographs, respectively, of the cross section and surface of the CMPSF matrix membrane with different contents of polymer additive PEG (MW 10000). From Figure 6, it can be seen that with increasing polymer additive, the cross-sectional structure of the membrane gradually changed from dense to loose, the pore size of the membrane changed from small to large, and the structure gradually changed from compact to loose. The SEM micrograph of the membrane surface revealed that the pore size of the membrane increased slightly with increasing polymer additive content. From Table VII it can be seen that the water flux obviously in-

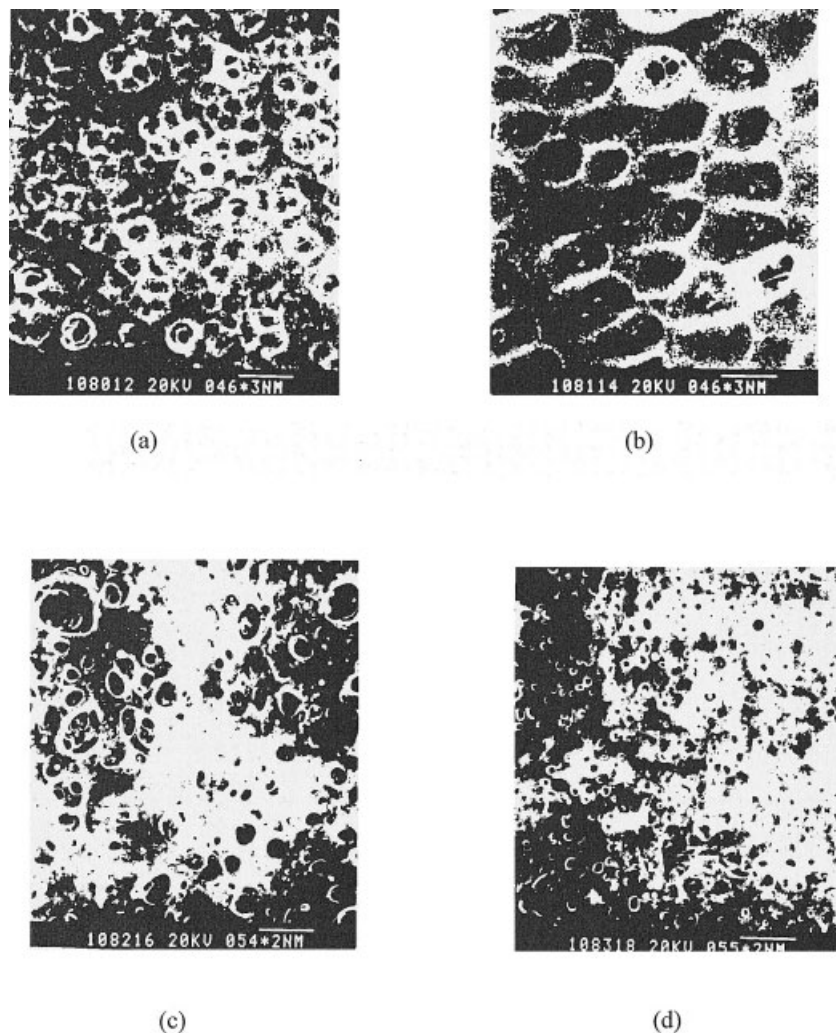


Figure 4 SEM micrographs of surface section of matrix membrane with different CMPSF contents: (a) 10%; (b) 12%; (c) 14%; (d) 16%.

creased with increasing additive content, which suggests that the increase of water flux was determined not only by the increase of pore size but also by the extent of contact between the membrane pores. The

formation process of the micropore membrane was a liquid–liquid phase-inversion process. Membrane structure was mainly determined by composition of

TABLE IV
Relationship Between CMPSF Concentration and Properties of Membrane^a

CMPSF content (%)	Water flux (L m ⁻² h ⁻¹)	Pore diameter (nm)	Porosity (%)
10	64.2	38.5	61.3
12	51.8	31.2	52.4
14	45.3	27.1	48.4
16	40.7	23.2	45.7
18	37.6	22.1	43.2
20	34.3	20.6	42.6

^a Additive content: 0%; casting solution temperature: 25°C; coagulating bath temperature: 25°C; ultrafiltration pressure: 0.1 MPa; effective area of membrane: 26.22 cm².

TABLE V
Effect of Various Additives on Structure of Matrix Membrane^a

Additive	Water flux (L m ⁻² h ⁻¹)	Pore diameter (nm)	Porosity (%)
Nonadditive	41.2	24.0	46.3
High polymer (PEG)	180.4	37.2	61.3
Dilute inorganic salt (NH ₄ Cl)	94.7	31.5	58.2
Solid inorganic salt (NH ₄ Cl)	101.5	34.8	60.1
Organic reagent (CH ₂ OH CH ₂ OH)	80.4	32.9	59.4

^a Casting solution temperature: 25°C; coagulating bath temperature: 25°C; ultrafiltration pressure: 0.1 MPa; effective area of membrane: 26.22 cm².

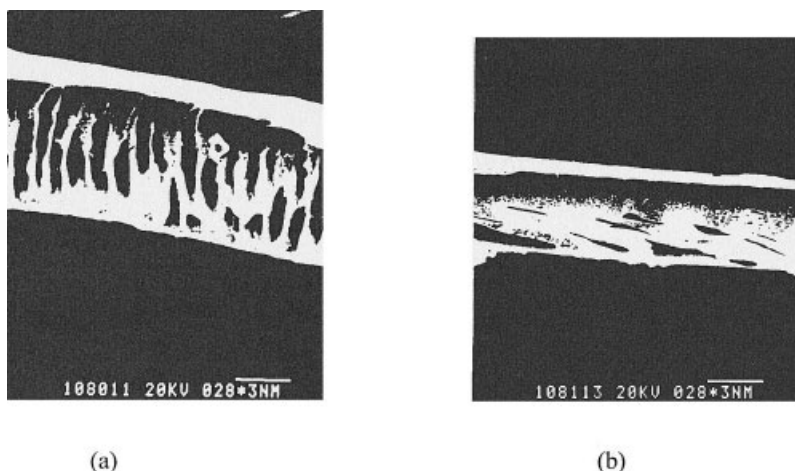


Figure 5 Effect of additives on structure of CMPSF membrane: (a) inorganic reagent; (b) organic reagent.

the local field in the casting solution during phase inversion. After phase inversion of the casting solution, the rich phase of CMPSF was continuous and gelled, after which it solidified into membrane continuous phase and formed the micropores of the CMPSF membrane; on the other hand, as the solvent (DMAc) and additive (PEG) dispersed in the polymer as the poor phase was being washed away, the poor phase grew increasingly larger and then intercrossed into the aggregations among micropores during casting. The precondition for the continuous growth of the poor phase was that the surrounding environment could continuously provide solvent for the poor phase before solidification of the rich phase.

In the casting system that used water as gel agent, the diffusion rate of solvent toward water was greater than that of water immersed into the casting solution. The further the casting solution composition diverged from cloud point composition, the later the phase inversion and the more the solvent (DMAc) overflowed. When the additive PEG content was low, the composition of the casting solution was diverged substantially from that of the cloud point. The overflow amount of solvent and the CMPSF concentration

before phase inversion were both significant, thus producing a dense top-layer structure and small pore size. The dense layers hindered the solvent DMAc from further interchanging with water, which successfully promoted formation of finger-shape micropores. With increasing PEG additive content in the casting solution, the composition of the solution approached that of the cloud point. The rate of phase inversion increased and the solvent overflowed less before phase inversion. The excessive amount of solvent provided good conditions for poor phase growth. The contact among membrane micropores increased, thus inducing formation of a loose top layer. The hindrance of the loose top layer from contacting the next layers decreased, thus favoring an intercrossed finger-shape structure. Although there was little change among pore sizes, their finger-shape contacts were good, osmosis resistance decreased, and flux of the membrane clearly increased.

Table VIII shows the effects of polymer additive PEG molecular weight on the structure of the CMPSF matrix membrane. From Table VIII it can be seen that water flux, pore size, and porosity of the CMPSF ma-

TABLE VI
Relationship Between Additive (Inorganic Salt) and Properties of CMPSF Membrane^a

Additive content (%)	Water flux (L m ⁻² h ⁻¹)	Pore diameter (nm)	Porosity (%)
0	41.2	24.1	46.3
2	101.5	34.8	60.1
4	140.7	41.2	65.7
6	187.5	44.3	69.1
8	39.0	23.1	45.4

^a Additive: NH₄Cl; casting solution temperature: 25°C; coagulating bath temperature: 25°C; ultrafiltration pressure: 0.1 MPa; effective area of membrane: 26.22 cm².

TABLE VII
Relationship Between Additive (High Polymer) and Properties of CMPSF Membrane^a

Additive content (%)	Water flux (L m ⁻² h ⁻¹)	Pore diameter (nm)	Porosity (%)
0	41.2	24.0	46.3
2	170.1	34.8	60.1
4	180.4	37.2	61.3
6	194.5	38.4	62.7
8	201.1	40.1	65.7
10	208.4	42.1	67.8

^a Additive: PEG(10000); casting solution temperature: 25°C; coagulating bath temperature: 25°C; ultrafiltration pressure: 0.1 MPa; effective area of membrane: 26.22 cm².

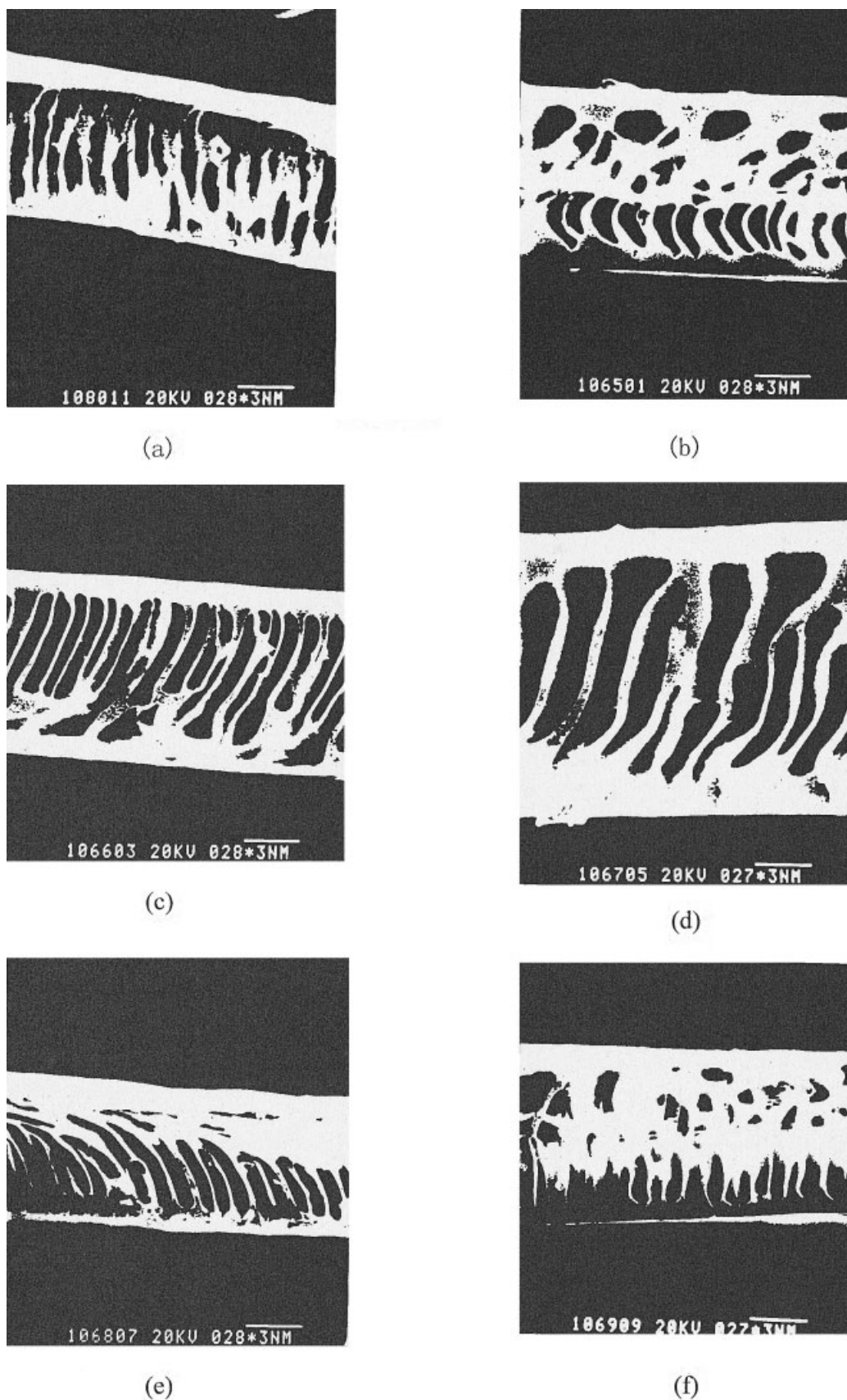


Figure 6 SEM micrographs of cross section of CMPSF matrix membrane in casting solution with different polymer additive contents: (a) 0%; (b) 2%; (c) 4%; (d) 6%; (e) 8%; (f) 10%.

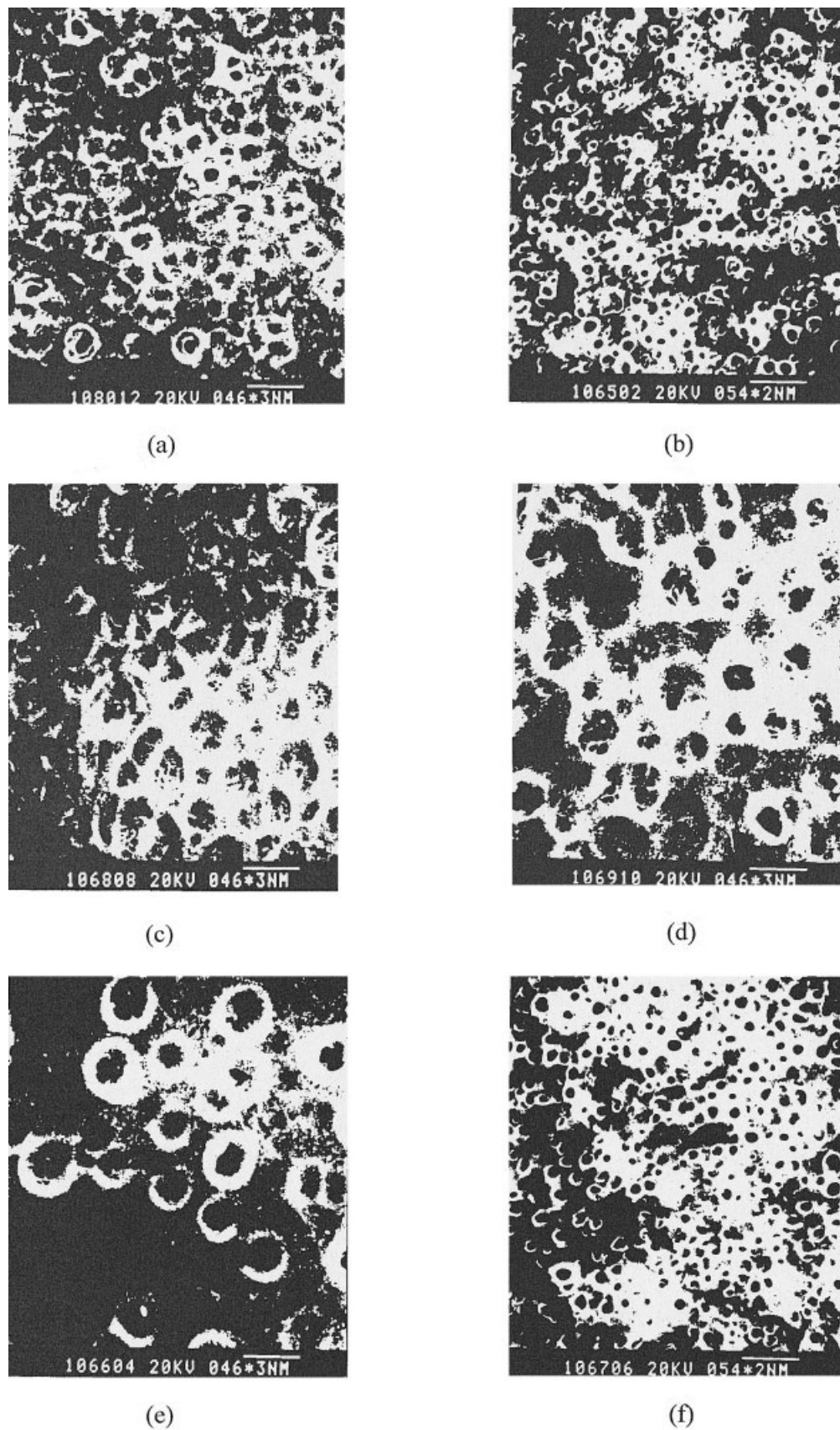


Figure 7 SEM micrographs of surface section of CMPSF matrix membrane in casting solution with different polymer additive contents: (a) 0%; (b) 2%; (c) 4%; (d) 6%; (e) 8%; (f) 10%.

TABLE VIII
Relationship Between Additive Molecular Weight and Properties of CMPSF Membrane^a

Molecular weight (PEG)	Water flux (L m ⁻² h ⁻¹)	Pore diameter (nm)	Porosity (%)
400	76.3	28.4	51.9
600	81.5	30.1	57.4
10000	180.4	37.2	61.3
20000	201.3	43.6	68.5

^a Additive: PEG 4%; casting solution temperature: 25°C; coagulating bath temperature: 25°C; ultrafiltration pressure: 0.1 MPa; effective area of membrane: 26.22 cm².

trix membrane all increased with increasing PEG molecular weight, attributed to the fact that PEG was not compatible with CMPSF and took up a certain volume in the casting solution. Through phase inversion, the micropores were produced after PEG was removed by dissolution in the coagulating agent. Obviously, the larger the PEG molecular weight, the larger the micropores on the membrane. With increasing PEG molecular weight, the number of micropores on the membrane dense layer increased. Thus the loose layer favored an increase of the double diffusion rate between solvent and coagulating agent when support layers of the membrane were forming, which would accelerate coagulation of the loose layer, causing the membrane structure to become looser. Besides, the additive molecules dispersed into the macromolecule chains and destroyed the binding force among them, and thus the relatively loose net structure was formed. With increasing additive PEG molecular weight, the binding force among the molecules of polymer CMPSF became weak. The amount of crosslinked points decreased, which caused the casting solution structure to become looser and the double diffusion rate between solvent and coagulation to increase. With increasing coagulating rate, the water flux, pore size, and porosity of the CMPSF membrane all decreased.

Effects of casting solution temperature on the structure of CMPSF matrix membrane

Table IX shows the relationship between the structure of the matrix membrane and temperature of the casting solution. It can be seen from Table IX that water flux, pore size, and porosity of CMPSF matrix membrane gradually decreased with increasing casting solution temperature, but when the temperature of the casting solution reached 45°C, water flux, pore size, and porosity of CMPSF matrix membrane notably increased afterward. The diffusion rate of solvent toward the coagulating bath increased with increasing casting solution temperature. Because of the rapid outflow of solvent, the local concentration of CMPSF on the membrane surface was too great; the dense skin

layer formed, and thus water flux, pore size, and porosity of the matrix membrane all showed a decreasing trend. Meanwhile, according to characteristics of the polymer dilute solution, the intrinsic viscosity [η] of the solution decreased with increasing temperature of the casting solution. Because of the decrease of casting solution viscosity and increase of fluidity of casting solution, the thickness of the membrane decreased, the flowing resistance was reduced, and the water flux increased under the same casting conditions. With increasing casting solution temperature, viscosity of the casting solution decreased continuously, and thus the double diffusion rate between the solvent and coagulating agent accelerated. The fast speed of coagulation caused the matrix membrane structure to become looser, thus causing the increasing trend of pore size, porosity, and water flux of the membrane: when the temperature of the casting solution reached 45°C, this trend was dominant. With further increases of temperature of the casting solution, the water flux, pore size, and porosity of matrix membrane all increased.

Effects of nonsolvent additive on dynamics factor De of membrane formation

Strathmann et al.¹¹ used optical microscopy to record changes of forward peak displacement D^2 with time t , when the ternary phase equilibria of the polymer/additive/solvent penetrated into the coagulating bath to precipitate. It was found that D^2-t showed a good linear relation. Kang et al.¹² simply described the formula as

$$D = 2(De,t)^{1/2}$$

where D is the forward peak displacement in the phase separation; De is the dynamics factor (mm s⁻¹) of membrane formation; and t (s) is the time immersed in the coagulating bath. In the practical gel process, the composition of the precipitant changed with the

TABLE IX
Relationship Between Casting Solution Temperature and Properties of CMPSF Membrane^a

Temperature (°C)	Water flux (L m ⁻² h ⁻¹)	Pore diameter (nm)	Porosity (%)
20	140.6	41.3	65.8
25	135.2	40.1	64.8
30	130.6	39.4	63.4
35	122.4	38.6	62.3
40	118.9	37.5	61.1
45	121.5	37.9	61.7
50	135.7	40.7	65.1

^a Additive: PEG(10000); content 4%; coagulating bath temperature: 25°C; ultrafiltration pressure: 0.1 MPa; effective area of membrane: 26.22 cm².

TABLE X
Effect of PEG Concentration on the Structure of CMPSF Membrane^a

CMPSF	Casting solution composition (%)			Water flux (L m ⁻² h ⁻¹)	Pore diameter (nm)	Porosity (%)
	PEG	DMAC	PEG/CMPSF			
15	0	85	0	41.2	24.0	46.3
15	5	80	1/3	189.2	40.2	61.2
15	10	75	2/3	208.4	42.0	67.8
15	15	70	1/1	178.3	37.1	57.4

^a Additive: PEG(10000); coagulating bath temperature: 25°C; ultrafiltration pressure: 0.1 MPa; effective area of membrane: 26.22 cm².

continuous overflow of solvent, and thus the linear relation between D^2 and t was changed. Sun¹³ pointed out that every segment of the gel rate curve was composed of several sections of segments with different rate constant k_i values and the rate constant of every segment corresponded to different structure layers on the membrane cross section. The property of the asymmetric membrane was mainly determined by the skin layer structure of the membrane. The skin layer structure of the matrix membrane also determined the gel behavior of the subsequent layer during membrane formation, and thus the study of membrane layer gel dynamics behavior is important for understanding the properties and phase-inversion process of the membrane. Table X shows the effects of PEG concentration in casting solution, which consisted of CMPSF = 15% on the membrane structure. It can be seen from Table X that pure water flux first increased and then decreased with increasing ratio of PEG/CMPSF. When PEG/CMPSF = 2/3, water flux, pore size, and porosity of the matrix membrane all reached their maximum value. On one hand, the existence of polymer additive PEG changed the phase-equilibrium relation of the casting solution and increased the homogeneous internal space of the solution, which in turn increased the required amount of nonsolvent during the phase inversion; moreover, the existence of PEG increased the viscosity of the casting solution and hampered the movement of the macromolecular chain in the casting solution. These two aspects both delayed the occurrence of phase inver-

sion. On the other hand, PEG was a kind of hydrophilic polymer that could be dissolved in water, and thus the immersing rate of the nonsolvent could be accelerated to promote phase inversion by increasing the affinity between the casting solution and the precipitant. Because of resistances and competition between the two aspects, when PEG/CMPSF was at a ratio of 2/3, the two aspects achieved equilibrium, the De value reached to a maximum value, the phase-inversion rate was the largest, and the asymmetry membrane with high porosity was readily formed. These phenomena proved that nonsolvent additive PEG changed the casting solution system with respect to the thermodynamic equilibrium relation and the dynamics rate of membrane formation. Such changing trends of De had important effects on the ultimate structure and separating properties of the matrix membrane.

Effects of water content in casting solution on dynamics factor De of CMPSF matrix membrane

Table XI shows the effects of water content in the CMPSF/PEG/DMAc/H₂O casting solution on the structure of the matrix membrane. It can be seen from Table XI that water flux, pore size, and porosity of matrix membrane all increased with increasing water content in the casting solution. When a given amount of water (less than the water content at cloud point) was added into the casting solution, the composition of the casting solution approached the phase-inver-

TABLE XI
Effect of Water Content on the Structure of CMPSF Membrane^a

CMPSF	Casting solution composition (%)			Water flux (L m ⁻² h ⁻¹)	Pore diameter (nm)	Porosity (%)
	PEG	DMAC	H ₂ O			
15	10	85	0	208.4	42.1	67.8
15	10	72	3.0	227.4	47.7	69.3
15	10	71	4.0	257.3	54.6	75.4
15	10	70	5.0	268.7	59.2	79.8
15	10	69	6.0	291.0	61.1	81.6

^a Additive: PEG(10000); coagulating bath temperature: 25°C; ultrafiltration pressure: 0.1 MPa; effective area of membrane: 26.22 cm².

TABLE XII
Relationship Between Evaporation Time and Properties of CMPSF Membrane^a

Evaporation time (s)	Water flux (L m ⁻² h ⁻¹)	Pore diameter (nm)	Porosity (%)
20	140.1	32.1	43.2
40	148.4	33.2	45.8
60	160.2	35.8	47.6
80	168.4	37.5	52.3
120	194.5	38.4	62.7
140	170.3	37.3	53.6
160	162.5	36.4	49.2

^a Additive: PEG (10000) 6%; casting solution temperature: 25°C; coagulating bath temperature: 25°C; ultrafiltration pressure: 0.1 MPa; effective area of membrane: 26.22 cm².

sion curve, the water amount needed in phase inversion was reduced, and the forward peak displacement rate of phase inversion was accelerated. When the *De* value increased, the casting solution had a swift separation; the polymer concentration at the phase-inversion point decreased; and pore size, porosity, and water flux of the matrix membrane all increased.

Effects of evaporating time on the structure of CMPSF matrix membrane

The quality of affinity membrane chromatography was determined by membrane materials and membrane-forming conditions. When the membrane material was fixed, the structure of casting solution and desolvating speed could finally affect both the structure and the properties of CMPSF matrix membrane. Table XII shows the effects of evaporating time on the structure of CMPSF matrix membrane. It can be seen from Table XII that water flux, pore size, and porosity of CMPSF matrix membrane all reached their maximum value when the evaporating time was 120 s. Both the volatilization effect and the hygroscopic effect of DMAc controlled the evaporating process. The hygroscopic effect of the solvent was substantial when the evaporating time was short. On one hand, with increasing evaporating time, the CMPSF macromolecules gathered from the homogeneous scattering net structure to form a macromolecular aggregate, and thus water flux, pore size, and porosity of the matrix membrane all increased. On the other hand, with increasing evaporating time, the solvent concentration decreased, the casting solution viscosity increased, and the DMAc hygroscopic speed decreased sharply. When evaporating time reached 120 s, the volatilization of the solvent was relatively significant. With increasing evaporating time, the binding forces among the CMPSF macromolecules increased, which caused CMPSF macromolecules to shrink upon desolvating, and thus a relatively dense structure was formed. The pore size on the membrane skin layer and porosity

inside matrix membrane decreased and thus the water flux of the matrix membrane decreased.

Effects of coagulating bath concentration on the structure of CMPSF matrix membrane

Changes in structure of the CMPSF matrix membrane, with different NaCl concentrations in the coagulating bath, are shown in Table XIII. The coagulating value was the necessary flocculant volume (coagulation medium) to cause a certain polymer to begin to produce precipitation in its dilute solution. The coagulating value can represent the relationship between the coagulating speed and the structure of the matrix membrane. The greater the coagulating value, the slower the desolvating speed; then the membrane having a compact structure was readily formed. It can be seen from Table XIII that the coagulating value of the membrane reached its maximum value, and water flux, pore size, and porosity of the membrane reached their minimum value when 10% NaCl solution was used as the coagulating bath. When the concentration of NaCl solution was less than 10%, the desolvating speed was fast, the coagulation was severe, and the membrane of loose structure was readily formed with increasing concentration of coagulating bath, whereas when the concentration of NaCl was above 10%, with further increases of the concentration of coagulating bath, the coagulating value decreased, the desolvating speed became fast, and the membrane structure became loose instead.

Effects of coagulating medium on the structure of CMPSF matrix membrane

Table XIV shows the effects of the different coagulating media (H₂O, NaCl solution, DMAc water solution) on the structure of CMPSF matrix membrane. It can be seen from Table XIV that the different coagulating

TABLE XIII
Relationship Between Coagulating Bath Concentration and Properties of CMPSF Membrane^a

Concentration (%)	Coagulating quantity (mL)	Water flux (L m ⁻² h ⁻¹)	Pore diameter (nm)	Porosity (%)
4	3.43	180.8	36.6	56.6
8	3.50	166.7	31.7	54.8
10	3.56	150.3	28.3	51.7
12	5.51	160.2	29.8	53.7
14	3.14	184.1	37.1	58.8
18	2.01	186.2	37.3	58.1
20	1.86	194.5	38.4	62.7

^a Evaporation time: 10 s; additive: PEG(10000) 6%; casting solution temperature: 25°C; coagulating bath temperature: 25°C; ultrafiltration pressure: 0.1 MPa; effective area of membrane: 26.22 cm².

TABLE XIV
Relationship Between Coagulating Medium and Properties of CMPSF Membrane^a

Coagulating medium	Coagulating quantity (mL)	Water flux (L m ⁻² h ⁻¹)	Pore diameter (nm)	Porosity (%)
H ₂ O	3.49	165.4	30.8	54.1
10% NaCl solution	3.56	150.3	28.3	51.7
10% DMAC solution	3.43	180.8	36.6	62.4

^a Evaporation time: 10 s; additive: PEG(10000) 6%; casting solution temperature: 25°C; coagulating bath temperature: 25°C; ultrafiltration pressure: 0.1 MPa; effective area of membrane: 26.22 cm².

media had significantly different effects on the coagulating value and the structure of the membrane. When 10% NaCl solution was used as the coagulating bath, the coagulation value increased and the desolvating speed was relatively slow, so the structure on the membrane surface and inside the membrane was homogeneous and compact, which caused water flux, pore size, and porosity of CMPSF matrix membrane to decrease.

Effects of coagulating bath temperature on the structure of CMPSF matrix membrane

Table XV shows the effects of coagulating bath temperature on the structure of CMPSF matrix membrane. Changes of coagulating bath temperature had complex effects on the structure of CMPSF membrane. Experimental results showed that, at a range of 25–45°C, with increasing coagulating bath temperature, the diffusion rate of the coagulating agent in the casting solution increased, which caused a loose membrane structure at the initial stage of increasing temperature; therefore, water flux, pore size, and porosity of CMPSF matrix membrane all increased. With the further increase of the coagulating bath temperature, the pores on the membrane surfaces shrunk, and the water flux, pore size, and porosity of CMPSF matrix membrane all decreased. When the temperature was

above 45°C, but did not reach the casting solution temperature (because the temperature difference became increasingly small), pore size on the membrane surface increased and the water flux increased as well. When the coagulating bath temperature was above 55°C, the temperature difference became greater, so the structure inside the membrane became loose, the porosity increased, and water flux and pore size continued to increase.

CONCLUSIONS

High-quality CMPSF matrix plate membranes, which were synthesized by Friedel–Crafts electrophilic substitution reaction under anhydrous condition using PSF as the original material, dichloromethane as solvent, monochloro methyl ether as chloromethyl reagent, and anhydrous ZnCl₂ as catalyst, were prepared by phase inversion. The structure and properties of CMPSF matrix plate membrane were determined not only by the nature of the membrane materials and the membrane-forming process conditions but also by the thermodynamic conditions of casting solutions, such as the concentration of polymer, the type and amount of additive, and the temperature of the casting solutions. It was crucial for the casting process to choose the additives with care and to control effectively the thermodynamic conditions of casting solution. Nonsolvent additive PEG changed the casting solution system with respect to both the thermodynamic equilibrium relationship and dynamics rate of membrane formation. The changing trend of *De* and desolvating speed, which was controlled by such factors as coagulating bath temperature, different coagulating bath media, and coagulating bath concentration, could influence the ultimate structure and separating properties of CMPSF matrix plate membrane.

TABLE XV
Relationship Between Coagulating Temperature and Properties of CMPSF Membrane^a

Coagulating temperature (°C)	Water flux (L m ⁻² h ⁻¹)	Pore diameter (nm)	Porosity (%)
25	183.2	34.8	56.7
35	190.4	38.1	61.8
45	181.4	33.6	55.2
55	184.7	35.7	57.4
65	187.6	36.4	59.3

^a Evaporation time: 10 s; additive: PEG(10000) 6%; casting solution temperature: 25°C; coagulating medium: H₂O; ultrafiltration pressure: 0.1 MPa; effective area of membrane: 26.22 cm².

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