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음이온성 Poly(bis[4-(3-aminophenoxy)phenyl]sulfone pyromellite)Imide Derivatives 한외여과막의 투과특성

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Influence of Ion Exchange Capacity on the Performance of Ultrafiltration Membrane Prepared from Anion Charged Poly(bis[4-(3-aminophenoxy)phenyl]sulfone pyromellite)imide Derivatives

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요 약: 상전환 방법으로 제조된 음이온 성 Poly(bis[4-(3-aminophenoxy)phenyl]sulfone pyromellite)imide(ACPI) 한외여과막의 순수 투과유속과 용질 배재도 측정치로 투과성능을 연구하였다. ACPI 한외여과막의 투과성능은 캐스팅 용액의 조성과 막 제조 및 측정조건에 영향을 받았다. Bovine serum albumin (BSA) 용액을 pH 2.5-9.0 상태에서 ACPI 한외여과 막의 상대투과유속과 membrane filtration index (MFI) 측정한 결과 BSA의 등전점에서 멀어 질수록 상대투과유속은 증가하고 막 오염정도를 나타내는 MFI는 감소하였다. 또한, 친수성인 ACPI 한외여과막의 이온교환용량(IEC)이 증가 할수록 상대투과유속은 증가하고, MFI는 감소하였다.

Abstract: Ultrafiltration membranes based on anion charged poly(bis[4-(3-aminophenoxy)phenyl]sulfone pyromellite) imide derivatives (ACPI) were prepared by the phase inversion method. The polymers have good solubility in aprotic polar solvents. The composition of casting solution and the casting conditions played an important role in determining the permeation characteristics of membrane because the membrane structure could be controlled by the preparation conditions. The extent of fouling-repression was observed by the relative ratio of permeate flux (J_t)/pure water flux (J_0) and the membrane filtration index (MFI). The characteristics were measured by aqueous solution of bovine serum albumin (BSA) over a pH range of 2.5~9.0. The ACPI membrane having a hydrophilic property was less fouled than the membrane prepared from the original polyimide. With increasing the ion exchange capacity of ACPI membrane, the relative ratio of flux was higher while the membrane filtration index was lower as compared with the original polyimide membrane. From the further away from isoelectric point of bovin serum albumin, the permeation was higher as well as the formation of fouling was more diminish. ACPI membranes having various their properties could be obtained. Further, it was proved that their permeation properties could be determined from the preparation conditions, various operating conditions, and different ion exchange capacity of anion charged polyimide derivatives.

Keywords: *anion, membrane, fouling, charged polyimide, membrane filtration index*

Introduction

Membrane processes have been used in a wide range of applications and still growing[1-3]. Their performances for any specified area depend on the membrane structure as well as the characteristic properties of the membrane materials. The membrane structure could be controlled by the preparation conditions, such as composition of casting solution, casting condition, and so on. The relationships between the structure and

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Table 1. Properties of the Anion Charged Poly(bis[4-(3-aminophenoxy)phenyl]Sulfone pyromellitic)Imides and its Original Polyimide[a]

Polymer No.	IEC (meq/g)	Tg (°C)	Viscosity (dL/g)
PI	0.00	245	0.79
ACPI-1	0.21	243	0.76
ACPI-2	0.41	248	0.75
ACPI-3	0.79	254	0.80
ACPI-4	1.02	258	0.85
ACPI-5	1.29	255	0.86
ACPI-6	1.41	254	0.84

[a] Data were obtained from the reference 18.

the preparation conditions have been studied[1-7]. The characteristic properties of membrane materials relate to the chemical nature of used polymers. For the use of specified area, the properties of polymer determine the successful application of membrane technology. Despite the technological relevance of ultrafiltration (UF) membrane in a wide range of application, its main limitation is reduce of the membrane performance due to fouling[7-12]. Fouling is formed on the surface of the membrane continue operation. It is an irreversible process owing to solute adsorption and pore blocking on the surface of membrane. Different techniques have been used to reduce or minimize the formation of fouling[3,7,13,14], for example, back flushing and back pulsing, introducing shear-enhanced modules, operating below critical flux, and using more hydrophilic materials. The polymers used for UF membranes such as polysulfone, polyethersulfide, polyamide, and so on, are quite hydrophobic and it is not always possible to prepare new polymers with requisite properties for specific applications. Those problems have been overcome through the modification of original polymers. The formation of fouling of hydrophilic membrane prepared from modified polymer could reduce that of original membrane[15-17].

The main objectives were to relate the performance of UF membrane and behavior of fouling formation to the ion exchange capacity of used materials. The anion charged poly(bis[4-(3-aminophenoxy)phenyl]sulfone pyromellitic)imides with various ion exchange capacity (IEC) and its original polyimide were obtained according to reference 18.

Experimental

Materials

The poly(bis[4-(3-aminophenoxy)phenyl]sulfone pyromellite)imide(PI) and anion charged poly(bis[4-(3-aminophenoxy)phenyl]sulfone pyromellite)imides (ACPI, prepared according to previous paper[18]) were used as membrane materials. Their properties are described in Table 1. The polymer solution in N-methyl-2-pyrrolidone (NMP) was press-filtrated, followed by precipitation in a large quantity of methanol, and dried in *vacuo* at 110°C before using. Bovine serum albumin (BSA, MW 66 kDa, Sigma Chemical Co, St. Louis, USA) was dried before using. Its isoelectric point (IEP) was 4.9. Polyvinylpyrrolidone (PVP, MW 1×10^4, Aldrich Chemical Co., Milwaukee, USA) and polyethylene glycol (PEG, MW $0.6\sim5.0\times10^4$, Aldrich Chemical Co.) were dried under reduced pressure before using. Other laboratory grade reagents were used without further purification.

Evaluation

Solute retention (SR) and flux were calculated from the equations (1) and (2). The solute content was obtained by using a HPLC differential refractometer (Waters 410°C). The applied operating pressure was 1 kgf/cm^2.

$$SR\ (\%) = (1-C_p/C_f)\times100 \quad (1)$$

Where, C_p is solute concentration in permeated solution, and C_f is the solute concentration in feed solution.

Table 2. ACPI Membrane Performances with Different IEC[a]

Membrane No.	PWF[b] (L/m^{2}h)	Solute Retention (%)[c]	
		MW 20,000	MW 35,000
PI	215	75	87
ACPI-1	210	75	90
ACPI-2	200	77	90
ACPI-3	185	80	90
ACPI-4	180	84	>93
ACPI-5	175	85	>95
ACPI-6	170	85	>95

[a] Casting conditions were solvent, NMP; solvent evaporation period, 30s; solvent evaporation temperature, 25°C; RH, 65%; polymer content, 18%(w/w) in NMP; casting thickness, 200 μm. The accuracy of PWF and SR was less than 3 L/m^{2}h and 2%, respectively.
[b] Applied operating pressure was 1 kgf/cm^2.
[c] Feed solution was 1,000 ppm PEG solution.

$$\text{Flux (L/m}^2\text{h)} = \frac{\text{Volume of permeated water (L)}}{\text{Effective area (m}^2\text{)} \times \text{time (h)}} \quad (2)$$

The relative flux (RF) and membrane filtration index (MFI)[7] were obtained by using the equations (3) and (4)

$$RF = J_t/J_o \quad (3)$$

where, J_0 is the pure water flux, and J_t is the permeate flux at a time t.

$$MFI = (t/V_t) / V_t \quad (4)$$

where, V_t is accumulated volume of permeate flux at a time t.

Preparation of Membrane

The mixture, which consisted of polymer, solvents, and additive with the specific composition, was doped on the non-woven polypropylene fabric and followed by hand casting in a thermohydrostatic chamber. The casting speed was about 5 cm/s and the thickness was in the range of 150~300 μm. After the solvent evaporation, the casting membrane was immersed in a coagulation bath at about 4°C for 24 h, and then the membrane was washed free of used solvent with water.

Results and Discussion

Table 2 shows the typical pure water flux (PWF) and the SR of ACPI membrane as a function of IEC. The influence of IEC on the membrane performance was investigated over the IEC range from 0 to 1.41 meq/g. The membrane was cast with 200 μm thickness and 18%(w/w) solid content in NMP. The PWF tended to decrease while the SR slightly increased in proportion to increasing the IEC up to about 1.02 meq/g, and leveled off. The result probably related to the exchange rate of the solvent and the non-solvent. The behavior was similar to the previous papers[16,17]. The phase inversion from a solution state to a solid membrane was occurred by the exchange of a solvent and a non-solvent in the membrane. The structure of membrane might be dependant on the rates of diffusion between the solvent in the membrane to the surface of membrane and the coagulation non-solvent away from the surface into membrane[7,8,19]. Increasing the hydrophilic character of the membrane material, the diffusion rate of solvent across the membrane probably had a tendency to reduce because the interforce between a polymer and a polar solvent was enhanced with increasing hydrophilicity of polymer. Therefore, the denser membrane was induced. From the result, the rate of exchange of the solvent and the non-solvent might be influenced by the IEC of ACPI and also played an important role in determining the structure of the membrane.

Fig. 1 represents the effect of polymer concentration in the dope solution on the PWF and the SR. The

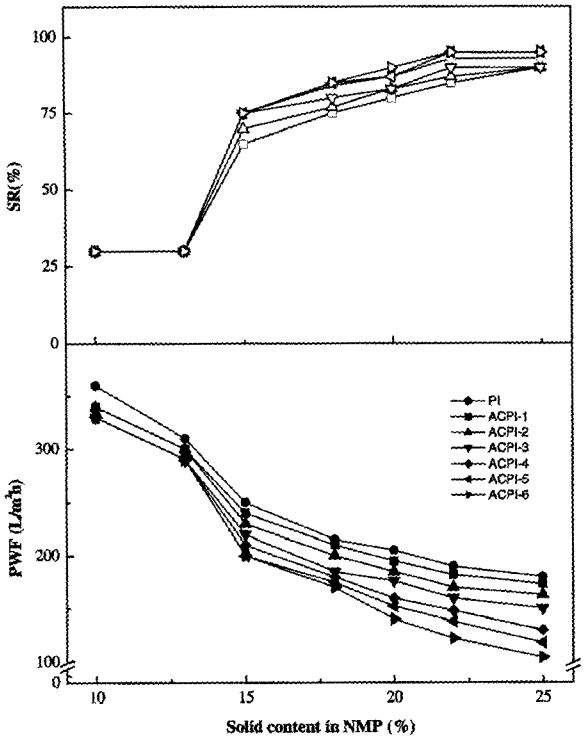

Fig. 1. The effect of polymer concentration in dope solution on the ACPI membrane performances. [a] Casting conditions were solvent, NMP; solvent evaporation period, 30 s; solvent evaporation temperature, 25°C; RH, 65%; casting thickness, 200 μm. [b] Feed solution was 1,000 ppm PEG (MW 2.0×10^4) solution.

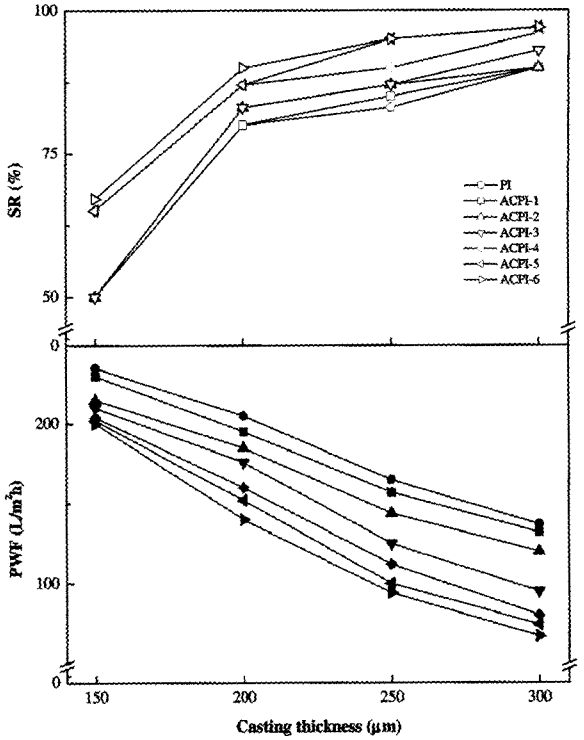

Fig. 2. The ACPI membranes performances with different casting thickness. [a] Casting conditions were solvent, NMP; solvent evaporation period, 30 s; solvent evaporation temperature, 25°C; RH, 65%; polymer content, 20%(w/w) in NMP. [b] Feed solution was 1,000 ppm PEG (MW 2.0×10^4) solution.

membrane was prepared with different solid content ranging from 10 to 25%(w/w) in NMP. The concentration of polymer was limited to the bases of the membrane performance. When the membrane was prepared below 10%(w/w) polymer content in NMP, both the permeation properties and the durability for operating were not satisfactory. From the result, the PWF with content of polymer gradually decreased up to 20%(w/w) in NMP, and above that concentration, it slightly diminished with increasing concentration, on the other hand, the SR increased in proportion to increasing the polymer concentration. The SR above 20%(w/w) was nearly unchanged. The value was to level off at a certain value. Increasing the polymer content in the dope solution leaded to increase of density in the active upper layer and also to a denser structure of the support layer[7,20]. It means that the SR tended to increase, while the PWF decreased with increasing the density of membrane. The variation of the SR diminished as the IEC of ACPI was increased. It was also related to the membrane structure.

Fig. 2 represents the typical PWF and the SR as a function of casting thickness. The PWF gradually decreased with increasing thickness of casting membrane, on the other hand, the SR increased up to 200 μm, and above that thickness, it slightly increased. The variation of the SR with different thickness was relatively small compared to that of the PWF. This behavior might relate to the tortuous effect[7,21]. Tortuosity in the membrane was enlarged with increasing thickness; thus, the diffusion and the permeability constants through membrane might be inversely proportional to the membrane thickness. The SR was mainly dependant on the active upper layer of membrane and the PWF was

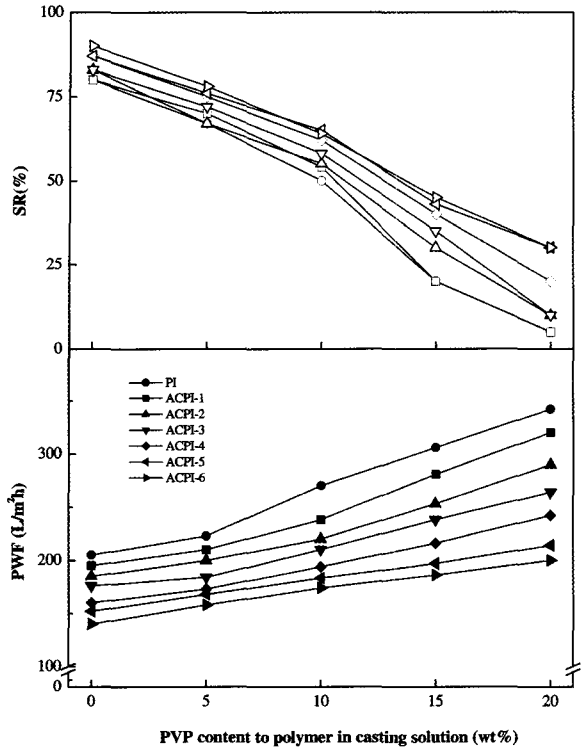

Fig. 3. The effect of additive content in dope solution on the ACPI membrane performances. [a] Casting conditions were solvent, NMP; solvent evaporation period, 30 s; solvent evaporation temperature, 25°C; RH, 65%; polymer content, 20%(w/w) in NMP; casting thickness, 200 μm. [b] Feed solution was 1,000 ppm PEG (MW 2.0×10^4) solution.

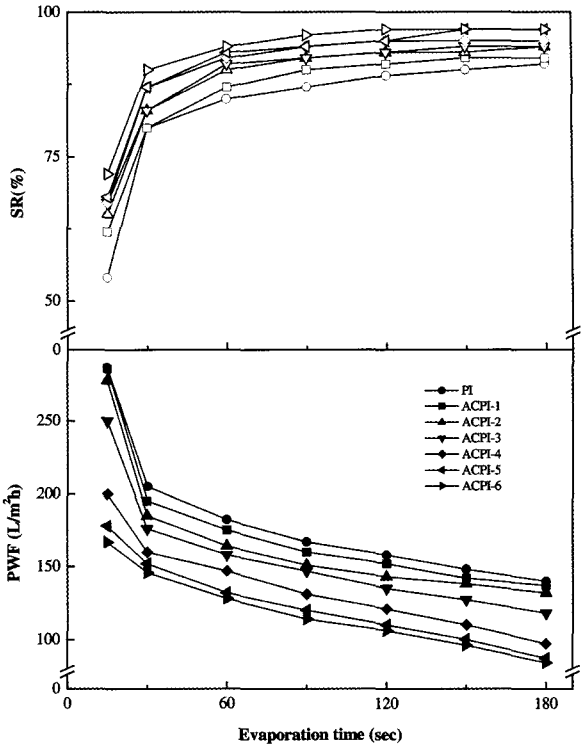

Fig. 4. The effect of solvent evaporating period on the ACPI membrane performances. [a] Casting conditions were solvent, NMP; solvent evaporation temperature, 25°C; RH, 65%; polymer content, 20%(w/w) in NMP; casting thickness, 200 μm. [b] Feed solution was 1,000 ppm PEG (MW 2.0×10^4) solution.

dependant to the upper layer as well as the support one.

In order to obtain the role of additive in the membrane performances, PVP (MW: 1×10^4) as an additive was added into the casting solution. The amount of the additive was varied from 0 to 20%(w/w) referring to polymer. PVP is hydrophilic polymer and dissolves well in water. Fig. 3 shows the variation of the PWF and the SR according to the amount of additive. The behavior represented a similar pattern as the previous papers[16,17,20]. As the amount of additive increased, the PWF through the membrane increased, while the SR gradually dropped in proportion to the content of additive. The result might relate to the porosity of the membrane[22-25]. While the nascent membrane was immersed in a coagulation bath and/or the solid membrane was rinsed with water, the hydrophilic additive might dissolve and flow out of the membrane. Therefore, the porosity within the active upper layer as well as the support layer was increased. The SR was dropped by the enlarged porosity of the denser upper layer. The additives probably could give membrane with different pore structure.

Fig. 4 represents the consequence of the evaporating period influence on the membrane performance. The longer the solvent evaporating period before immersing into a coagulation bath became, the denser the membrane structure formed. The SR increased with increasing the evaporating period at about 120 sec. The value of the SR above 120 sec nearly unchanged. On the other hand, the PWF gradually decreased with evaporating period. The result also related to the density of the upper layer as well as the support layer structure of membrane. The density of the membrane was influenced by the

Table 3. The Effect of the Composition of Solvent in Dope Solution on the ACPI Membrane Performances[a]

Membrane No.	PWF (L/m^2h)				Solute Retention (%)[b]			
	NMP/DCM (wt ratio)							
	80/0	75/5	70/10	65/15	80/0	75	70/10	65/15
PI	205	176	140	115	80	86	92	>92
ACPI-1	195	170	135	112	80	87	92	>90
ACPI-2	185	144	110	89	83	90	95	>97
ACPI-3	176	136	106	78	83	90	97	>97
ACPI-4	160	110	87	65	87	93	97	>97
ACPI-5	152	100	76	57	87	95	97	>97
ACPI-6	140	94	75	54	90	95	97	>97

[a] Polymer content was 20%(w/w) in NMP and other casting conditions were the same as in the preceding case. The accuracy of PWF and SR was less than 3 L/m^2h and 2%, respectively.
[b] Feed solution was 1,000 ppm PEG (MW 2.0×10^4) solution

solid content in the casting solution and/or the nascent membrane. Increasing the solvent evaporating period before immersing into a coagulation bath might induce to increase solid content in nascent membrane, thus, the denser membrane was formed. The relationship between the membrane morphology and the solvent evaporating period suggested that the membrane obtained with shorter solvent evaporating period exhibited more heterogeneously asymmetric structure, on the other hand, the structure of membrane with longer evaporate time was compact and homogeneously symmetric one[1,3, 6-8]. The period led to a compromise situation between the active layer thickness and the structure of support layer, which controlled the permeability and the retention. During the solvent evaporation in the casting membrane, the active upper layer, which was actually functional barrier for filtration, was formed in the first period, and then the structure of the support layer was determined by the diffusion of solvent to surface of membrane. The SR was mainly influenced on the active upper layer, but the PWF might be attributed to the configuration of the upper layer as well as the structure of support one.

The relationship between the membrane performance and the composition of solvents represents in Table 3. The composition of solvent systems played an important role in determining the structure of membrane[21,25-27]. The vigorous solvent evaporation on the surface of nascent membrane before coagulation might induce increase of polymer content. Thus the gradient of solvent concentration in the upper layer became smaller than that in the sublayer and the activity of the upper layer was more increased. In this investigation, the solvent systems composed of NMP and dichloromethane (DCM) as a cosolvent was used for preparing the asymmetric membrane with various structures. The PWF decreased, while the SR increased as the portion of DCM increase. The amount of evaporating solvent on the surface increased with increasing the portion of DCM in this solvent system, thus, the denser structure of membrane was formed. From the result, the membrane performance could be controlled by the introduction of various solvent systems.

Fig. 5 represents the effect of the composition of the coagulation bath on the membrane performance. The gelating medium composed the various ratios of water and NMP. The SR slightly increased with increasing the moiety of NMP in the coagulation bath up to the ratio of 15/85(w/w) NMP/water, and above that portion of NMP, the value maintained. On the other hand, the PWF shown as inversely proportional to the portion of NMP in the coagulation medium. Above the ratio of 40/60(w/w) NMP/water, the phase inversion of membrane very slowly proceeded or/and the formation of solid membrane did not occur apparently. The result was also explained by the exchange rate of the solvent

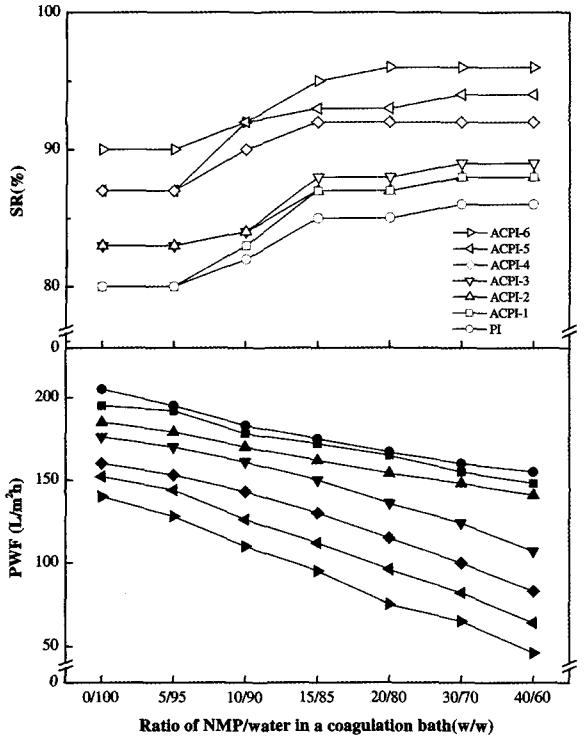

Fig. 5. The effect of composition of the coagulating systems on ACPI membrane performances. [a] Casting conditions were solvent, NMP; solvent evaporation period, 30 s; solvent evaporation temperature, 25°C; RH, 65%; polymer content, 20%(w/w) in NMP; casting thickness, 200 μm. [b] Feed solution was 1,000 ppm PEG (MW 2.0×10^4) solution.

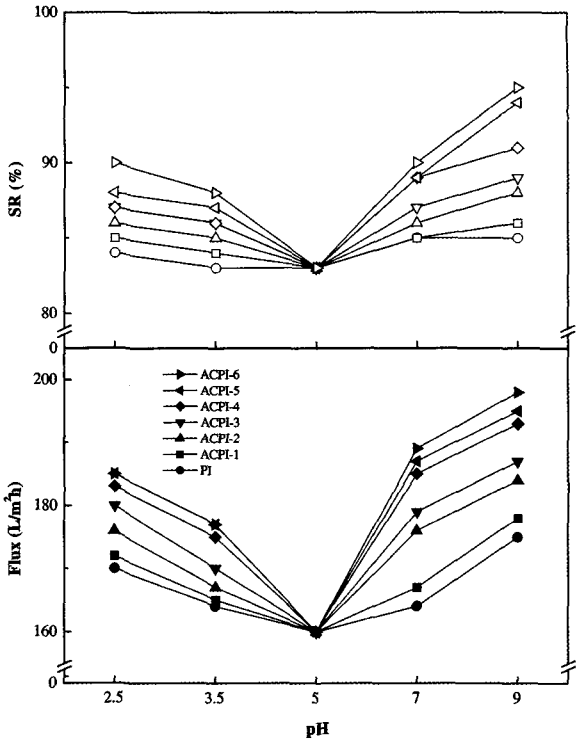

Fig. 6. The ACPI membrane performances at different pH conditions. [a] Feed solution was 1,000 ppm BSA (MW 66 kDa) solution.

and the non-solvent[2,7,12,13]. The exchange rate of the solvent and the non-solvent across the membrane might be changed by the different composition of coagulation bath. The changed rate could induce various structure of membrane because the rate of solvent exchange determined that of a phase separation. Increasing the portion of NMP in gelating bath, the rate of phase inversion reduced and the denser membrane probably formed. The composition of coagulation bath played the important role in the formation of membrane structure.

Fig. 6 shows the membrane performance at different pH conditions. Those membranes had similar permeation properties. It was observed that at pH values away from the IEP of the BSA (IEP=4.9), the permeation properties shown higher. This behavior might relate to the electrostatic force[7,8,16,17]. As the pH values far away from IEP, the protein acquired significant net charge and enlarged because electrostatic repulsion occurred. At the lower pH conditions, the degree of proton dissolution in SO_3H groups of ACPI membrane had a tendency to reduce and the BSA was positively charged. On the other hand, at the higher pH state, both the BSA and the membrane were negatively charged because of increasing the dissolution of proton in SO_3H groups of ACPI membrane[28-31], therefore, the electric repulsion occurred between the membrane and the BSA.

$$R-SO_3H \underset{H^-}{\overset{OH^-}{\rightleftharpoons}} R-SO_3^- + H^+$$

To evaluate the fouling behavior of ACPI membrane and to compare ACPI membrane with PI membrane having similar permeation characteristics, besides the PWF, the relative ratio of PWF and permeate flux and the MFI were used. The permeation properties of the

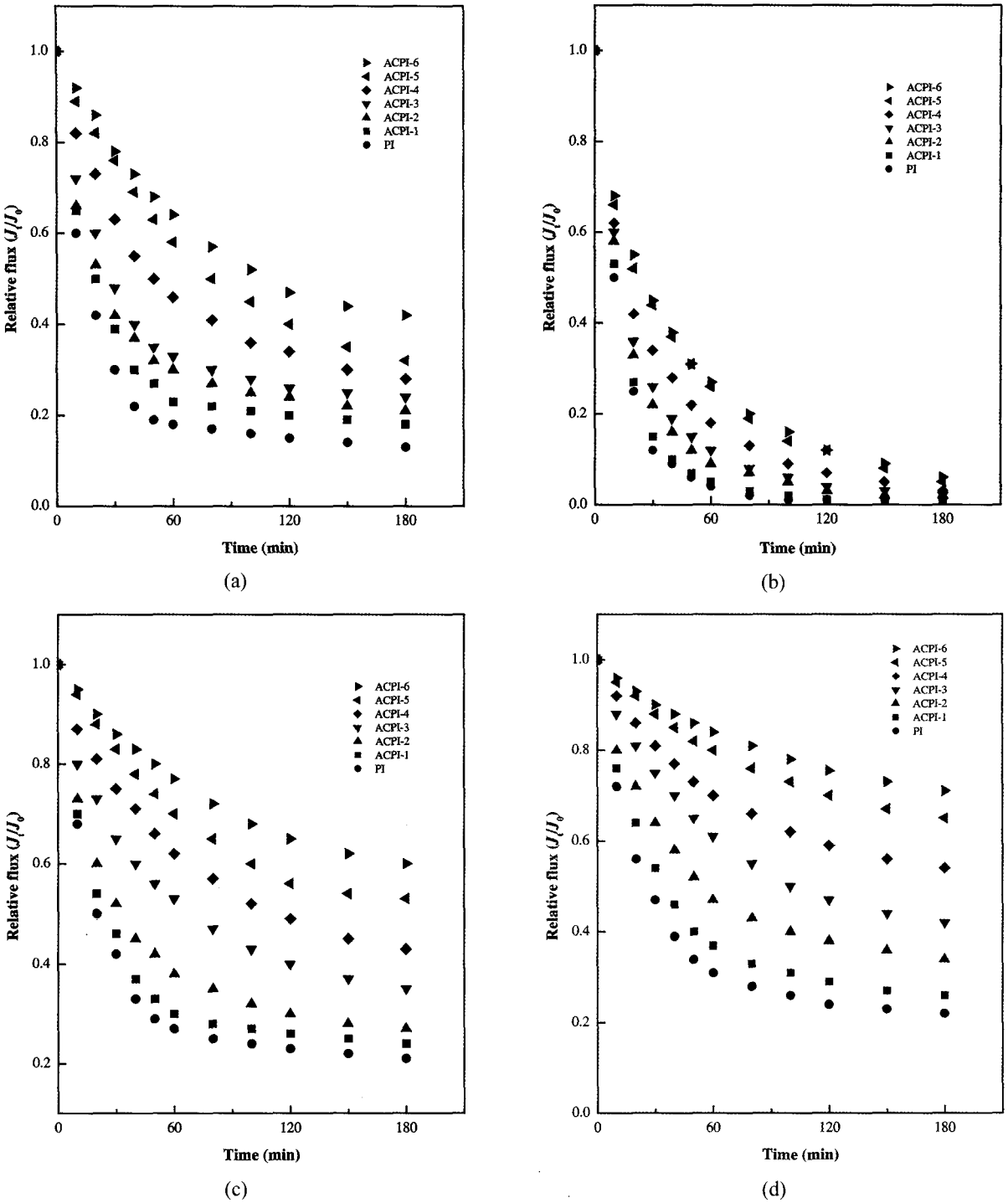

Fig. 7. The relative flux versus operating time of ACPI membranes in the a) pH 3, b) pH 5, c) pH 7, and d) pH 9. [a] Feed solution was 1,000 ppm BSA (MW 66 kDa) solution.

membranes were about PWF 205 L/m^{2}h and SR 80% to PEG (MW 2×10^4). MFI was the calculated from a plot of t/Vt as a function of the accumulated amount of permeate flux (Vt)[7]. The relative flux represents in Fig. 7 series and the MFI is summarized in Table 4. The flux at a constant pressure dropped to the initial

Table 4. The Effect of pH in the Continue Operation on the MFI of ACPI Membranes[a]

Membrane No	MFI			
	pH 3	pH 5	pH 7	pH 9
PI	0.097	0.108	0.062	0.040
ACPI-1	0.090	0.100	0.058	0.030
ACPI-2	0.070	0.080	0.047	0.024
ACPI-3	0.045	0.053	0.034	0.020
ACPI-4	0.033	0.038	0.026	0.017
ACPI-5	0.024	0.032	0.018	0.012
ACPI-6	0.020	0.028	0.015	0.009

[a]Feed solution was 1,000 ppm BSA(MW 66 kDa) solution.

Table 5. Permeation Properties of Dried ACPI Membranes Treated with Various Drying Agents[a]

Drying agent	Membrane No	PWF (L/m^2h)	SR (%)
Wetb	PI	200	78
	ACPI-1	200	78
	ACPI-3	200	78
	ACPI-6	200	78
Glycerin	PI	170	85
	ACPI-1	170	83
	ACPI-3	180	80
	ACPI-6	185	80
Water	PI	120	93
	ACPI-1	135	90
	ACPI-3	145	90
	ACPI-6	165	90
Mixture[c]	PI	140	90
	ACPI-1	150	90
	ACPI-3	160	90
	ACPI-6	175	90

[a] Feed solution was 1,000 ppm PEG(MW 2.0×10^4) solution. The accuracy of PWF and SR was less than 3 L/m^2h and 2%, respectively.
[b] Untreated membrane.
[c] The mixture was consisted of water and glycerine (1:1 w/w).

value and the permeate flux gradually reduced during the continuous operation because of the formation of fouling on the surface of membrane. The values provided a direct compare of the fouling tendency of membrane. The higher the value of the relative flux, the better the antifouling in membrane. The relative flux for the BSA solution increased with increasing the IEC of ACPI membrane. The value also increased as pH value further away from the IEP of the BSA. The formation of fouling induced the increase of MFI value. Increasing the IEC of ACPI membrane leaded to lower value of MFI. At the higher pH condition, the value of MFI also reduced. From the result, the hydrophilic ACPI membrane reduced the formation of the fouling and the pH condition played the important role in the fouling formation[31].

The relationship between the change of membrane performance and the drying conditions was investigated and the variation of membrane properties is shown in Table 5. The membranes tested had also similar permeation properties. To prepare dried membrane, the original membrane in wet state was immersed in

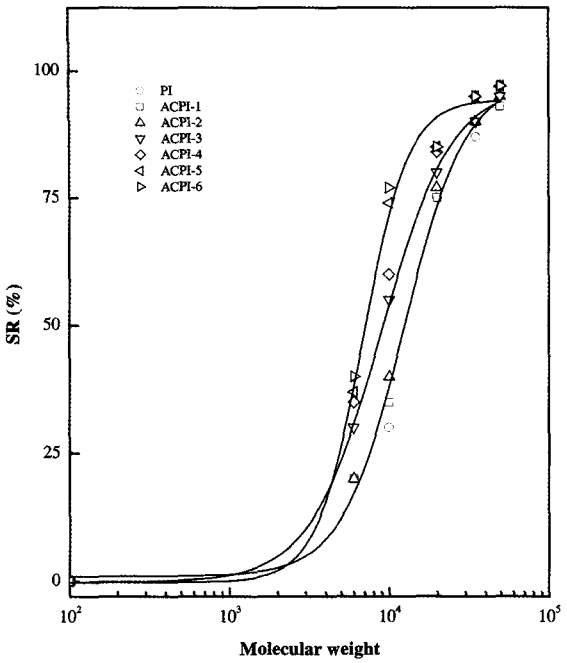

Fig. 8. The molecular cutoffs of ACPI membranes.

different agents for 24 h, dried at room temperature for 4 days, and followed dried in *vacuo* at 100°C for 4 h. The PWF of treated membrane was diminished some, while the SR revealed nearly the same value compared to original membrane. The result was similar pattern as previous investigation[20]. But the variation of the PWF and the SR obviously diminished with increasing IEC of ACPI membrane. The result might relate to the membrane structure and the change of the intermolecular force between polymer main chains in membrane[21, 30]. While the membrane was dried, the interaction between polymer chains might be changed because the force was dependant on the nature of the polymer chain and the distance separating them. Thus, the membrane was subject to shrinkage during dry.

The molecular weight cut off has been used frequently to indicate the permeate properties of a membrane[7, 21]. The cut off was defined as that molecular weight which was 90% retention by the membrane. The SR of the membrane was calculated in the range of molecular weight from 0.6×10^4 to 5.0×10^4 and the result is shown in Fig. 8. All the membranes were cast with 200m thickness, 18%(w/w) solid content in NMP, and 30 sec solvent evaporation period. The values of the ACPI were about 20,000 and they could be also controlled by the preparation and operation conditions.

Conclusion

The anion charged ACPI UF membranes were prepared from the phase inversion method. The permeation characteristics of ACPI membranes could be verified under various casting conditions as well as the nature of used polymer as membrane materials. They were played an important role in determining the structure of the membrane. The fouling resistance decreased with increasing IEC of hydrophilic ACPI membrane and was also influenced by the pH of the operating conditions. The permeate characteristics was higher at pH values away from the IEP of the BSA. The behavior might relate to the natures of the ACPI membrane and BSA molecule, the variation of electrostatic interaction between the membrane and the BSA and among BSA molecules, and the conformational change of the BSA under different pH conditions. The dried ACPI membrane shown nearly the same permeate behavior as compared to the corresponding wet one. All the membranes were easily fabricated because the ACPI well dissolved in aprotic polar solvents.

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