

Asymmetric Membranes Fabricated from Poly(acrylonitrile-co-N-vinyl-2-pyrrolidone)s with Excellent Biocompatibility

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ABSTRACT: Poly(acrylonitrile-co-N-vinyl-2-pyrrolidone)s (PANCNVPs) show excellent biocompatibility. In this work, PANCNVPs with different contents of *N*-vinyl-2-pyrrolidone (NVP) were fabricated into asymmetric membranes by the phase inversion method. The surface chemical composition of the resultant membranes was determined by Fourier transform infrared spectroscopy–attenuated total reflection. Field emission scanning electron microscopy was used to examine the surface and cross section morphologies of the membranes. It was found that the morphologies hardly change with the increase of NVP content in PANCNVP, while the deionized water flux increases remarkably and the bovine serum albumin (BSA) retention decreases slightly. Experiment of dynamic BSA solution filtration was carried out to evaluate the antifouling properties of the studied

membranes. The relative flux reduction of PANCNVP membrane containing 30.9 wt % of NVP is 25.9%, which is far smaller than that of the polyacrylonitrile membrane (68.8%). Results deduce that this improvement comes from the excellent biocompatibility of NVP moieties instead of the hydrophilicity change, because the water contact angles of these membranes fluctuate between 60 and 70°. Results from the membranes using poly(*N*-vinyl-2-pyrrolidone) (PVP) as an additive confirm that, to a certain extent, the PANCNVP membranes show the advantages of antifouling compared with the polyacrylonitrile/PVP blending membrane. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4577–4583, 2006

Key words: membranes; biocompatibility; surfaces

INTRODUCTION

Polyacrylonitrile (PAN) exhibits good mechanical properties and has been widely used as a membrane material.^{1–18} However, due to some inherent disadvantages, such as brittleness, relatively low hydrophilicity, and poor biocompatibility, modifications on PAN or PAN-based membranes must be made to meet the requirements of the increasingly extended applications. Therefore, many efforts have been paid to create a friendly surface for improving the hydrophilicity and biocompatibility of PAN-based membranes.^{1–12} Photoinduced graft polymerization surface modifications on the PAN ultrafiltration membrane were reported by Ulbricht et al.¹⁹ and recently by Frahn et al.⁶ Biomacromolecules such as human serum albumin, chitosan, and heparin were immobilized onto PAN-based membrane to improve their hemocompatibility and antibacterial activity.^{20,21} Poly(ethylene glycol) was also used to modify PAN-based

membrane for enhancing the antifouling property and biocompatibility.¹² In spite of some defects such as the leaching out of water-soluble additives during hydraulic permeation,²² blending was a versatile method to prepare PAN-based membranes. Yang et al.²³ prepared PAN/polyvinylidene fluoride blend membranes and pointed out that the molecular weight cut-off of the membrane can be varied in a wide range for various applications. Meanwhile, blending membranes using poly(*N*-vinyl-2-pyrrolidone) (PVP) as an additive were described by some researchers.^{13,24} Jung et al.¹³ fabricated asymmetric PAN membranes using PVP as additive and treated the membranes with hypochlorite also. They carefully studied the effect of the molecular weight of PVP on the membrane performances. On the other hand, incorporating various comonomers into PAN to improve the membrane hydrophilicity and/or biocompatibility has also been widely explored, in which includes *N*-vinylimidazole,⁹ acrylamide,^{25,26} acrylic acid,²⁷ vinyl acetate,²⁸ methylmethacrylate,²⁹ methyl 2-acetoxyacrylate,³⁰ maleic acid,³¹ 2-hydroxyethyl methacrylate,³² glycidyl methacrylate,¹⁰ α -allyl glucoside,¹¹ and phospholipid moieties.³² Properties for the membranes modified by these comonomers, such as antifouling, biocompatibility, solvent-resistance, and enzyme activity on the membrane surface, can be improved to some extent.

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TABLE I
Typical Characteristics of the Polymers and Dope Solutions

Sample	Polymer			Dope solution	
	$[\eta]$ (mL/g)	M_v (10^4 g/mol)	NVP ^a (wt %)	Polymer ^b (wt %)	Viscosity ^c (mPa s)
PAN	330.6	19.5	0	8	3,620
PANCNVP7	309.9	17.9	7.1	8	3,400
PANCNVP15	320.2	18.7	15.1	8	3,580
PANCNVP23	341.6	23.1	22.7	8	4,100
PANCNVP31	339.2	22.9	30.9	8	3,800

^a The content of NVP in the polymer calculated from ¹H-NMR.

^b The weight fraction of polymer in the dope solution.

^c The apparent viscosity of the dope solution from rotary viscometer.

One major problem with ultrafiltration is the loss of permeation flux caused by adsorptive fouling of biological molecules, such as proteins, on the surface and even inside the pores of membranes. It is generally accepted that increasing the biocompatibility and/or the hydrophilicity of the membrane surface can reduce membrane fouling. As described in our previous papers, *N*-vinyl-2-pyrrolidone (NVP) can be effectively incorporated into PAN by the water phase precipitation copolymerization process.³³ Furthermore, poly(acrylonitrile-*co*-*N*-vinyl-2-pyrrolidone) (PANCNVP) shows excellent hemocompatibility, which was confirmed by the experiments of platelet adhesion and plasma recalcification time test.³⁴ Recently, Kim et al.³⁵ synthesized low molecular weight poly(*N*-vinyl-2-pyrrolidone-*co*-acrylonitrile) to blend with polysulfone and better performance was reported for the blending membrane. In this work, the copolymers with different contents of NVP were fabricated into asymmetric membranes by phase inversion method and the anti-fouling properties of the membranes were studied.

EXPERIMENTAL

Materials

Polyacrylonitrile and poly(acrylonitrile-*co*-*N*-vinyl-2-pyrrolidone) (PANCNVP) with different NVP contents, designated as PAN, PANCNVP7, PANCNVP15, PANCNVP23, and PANCNVP31 in the following text, were synthesized in our laboratory using a water phase precipitation copolymerization process. Details for the characterization of the copolymers were described in our previous work³³ and the typical results are summarized in Table I. Dimethylsulfoxide (DMSO) was commercially obtained from Shanghai Chemical Agent (China) and purified by vacuum distillation before use. Poly(*N*-vinyl-2-pyrrolidone) (PVP) (K30, 40,000 g/mol) was purchased from Fluka and used as received. Bovine serum albumin (BSA, pI = 4.8, M_w = 66 kDa) was purchased from Sino-American Biotechnology and used as received. Other chemicals

were analytical grade and used as received without further purification.

Membrane preparation

Asymmetric PAN-based membranes were prepared by the following procedure. Homogeneous dope solutions as listed in Table I were formed at about 80°C with vigorous stirring for 6 h. After air bubbles were removed completely, the solutions were cast onto clean glass plates using a casting knife with a 150 μ m gate opening. The glass plates with the nascent membranes were placed in air for 10 min and then immersed into (30 \pm 0.5)°C ultrafiltered water for 24 h. After precipitation, the membranes were peeled off and preserved in 5 vol % formaldehyde aqueous solution for further use. Blending membranes of 8 wt % PANCNVP15 or PAN with 5 wt % PVP were also fabricated according to the above-mentioned procedure.

Viscosity measurements

Apparent viscosity for the homogeneous dope solution was determined by a rotational viscometer (NDJ-79, Electrical Machinery Plant, Tongji University) equipped with spindle 100 nos. and a temperature-control water bath at 80°C. The spindle was rotated in the medium for at least 5 min to a reading for temperature equilibration. Results are listed in Table I and Table II.

TABLE II
Composition and Apparent Viscosity of the Dope Solution Using PVP as an Additive

Sample	Polymer (wt %)	Additive (wt %)	DMSO (wt %)	Viscosity (mPa s)
PAN	8	0	92	3,620
PAN/PVP	8	5	87	4,650
PANCNVP15	8	0	92	3,580
PANCNVP15/PVP	8	5	87	4,350

FTIR-ATR characterization

FTIR-ATR spectra were acquired with a Vector 22 FTIR (Brucker Optics, Switzerland) equipped with an ATR accessory (KRS-5 crystal, 45°). The membranes were thoroughly dried before FTIR-ATR measurements. All spectra were taken by 32 scans at a nominal resolution of 4 cm⁻¹.

Morphology evaluation

Field emission scanning electron microscopy (FESEM, Sirion-100, FEI) was applied to study the morphologies of the asymmetric membranes. For this purpose, membrane samples were wetted and replaced with a water-ethanol-hexane sequence, dried at room temperature, and then fractured in liquid nitrogen. Before analysis, the samples were sputtered with gold using Ion sputter JFC-1100.

Water contact angle measurement

Static water contact angles on the membrane surface were measured by sessile drop method at room temperature with a contact angle goniometer (Dataphysics, OCA20, Germany) equipped with video camera. Typically, a water drop (~2 μL) was added on a dry membrane sample in the air, then the image was recorded after 5 s, and a static water contact angle was calculated from the image with software. At least 10 measurements of different water drops were averaged to get a reliable value.

Permeation tests

The solution reservoir was initially filled with deionized water, and a piece of membrane about 9.08 cm² was installed into the permeation cell. Each membrane was precompact for 30 min at 0.12 MPa. Then, the pressure was lowered to 0.10 MPa and the flux of deionized water (J_W) was measured. Next, deionized water in the reservoir was replaced by a 1.0 g/L BSA phosphate-buffered saline solution (PBS, pH = 7.4) and the flux was recorded as J_P at 0.10 MPa. To confirm the water flux recovery property of this BSA permeated membrane, the membrane was cleaned by vibrating in a 0.10M NaOH solution for 2 h and washing with deionized water three times, and then the water flux (J_R) was measured at 0.10 MPa again. The reported data were the mean values of triplicate samples for each membrane. The relative flux reduction (RFR) and the flux recovery ratio (FRR) were calculated as follow:

$$\text{RFR}(\%) = (1 - J_P/J_W) \times 100$$

$$\text{FRR}(\%) = (J_R/J_W) \times 100$$

After the permeation of deionized water at 0.12 MPa for 30 min, deionized water was changed to 1.0 g/L BSA phosphate-buffered saline solution (PBS, pH = 7.4). The BSA solution was filtrated for 2 min at 0.10 MPa, and then 10 mL of filtrate was collected at the same pressure. The BSA concentrations in the feed and filtrate were analyzed using a spectrophotometer (Shimadzu, UV2450, Japan) at 280 nm. The solute retention (R) was calculated by:

$$R = (1 - C_p/C_f) \times 100$$

where C_p and C_f are the BSA concentration in permeate and feed, respectively.

RESULTS AND DISCUSSION

To fabricate asymmetric membranes from PAN and PANCNVPs, dope solutions were carefully prepared. The viscosity molecular weight (M_v) and the NVP content of the polymers synthesized in this study are listed in Table I together with the compositions and the apparent viscosities of the dope solutions. It can be seen that, although the polymer concentration in the dope solution is kept at 8 wt %, the apparent viscosity of the dope solution varies from 3400 to 4100 mPa s due to the difference of the molecular weight of the polymer.

As shown in Figure 1, the chemical composition of the membrane surface was examined by FTIR-ATR. It is obvious that the copolymer membranes displayed complex spectra compared with those of the PAN membrane. Characteristic peak at 2243 cm⁻¹ is due to the stretching vibration of cyano group (-C≡N). The bands of the asymmetric and symmetric C-H stretching of the polymer main chain at 2850-2980 cm⁻¹ and the C-H deformation vibration at 1452 cm⁻¹ can also

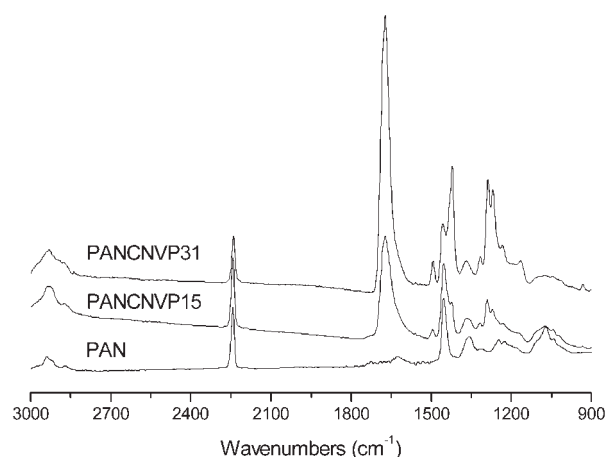


Figure 1 Typical FTIR-ATR spectra of PAN, PANCNVP15, and PANCNVP31 membranes.

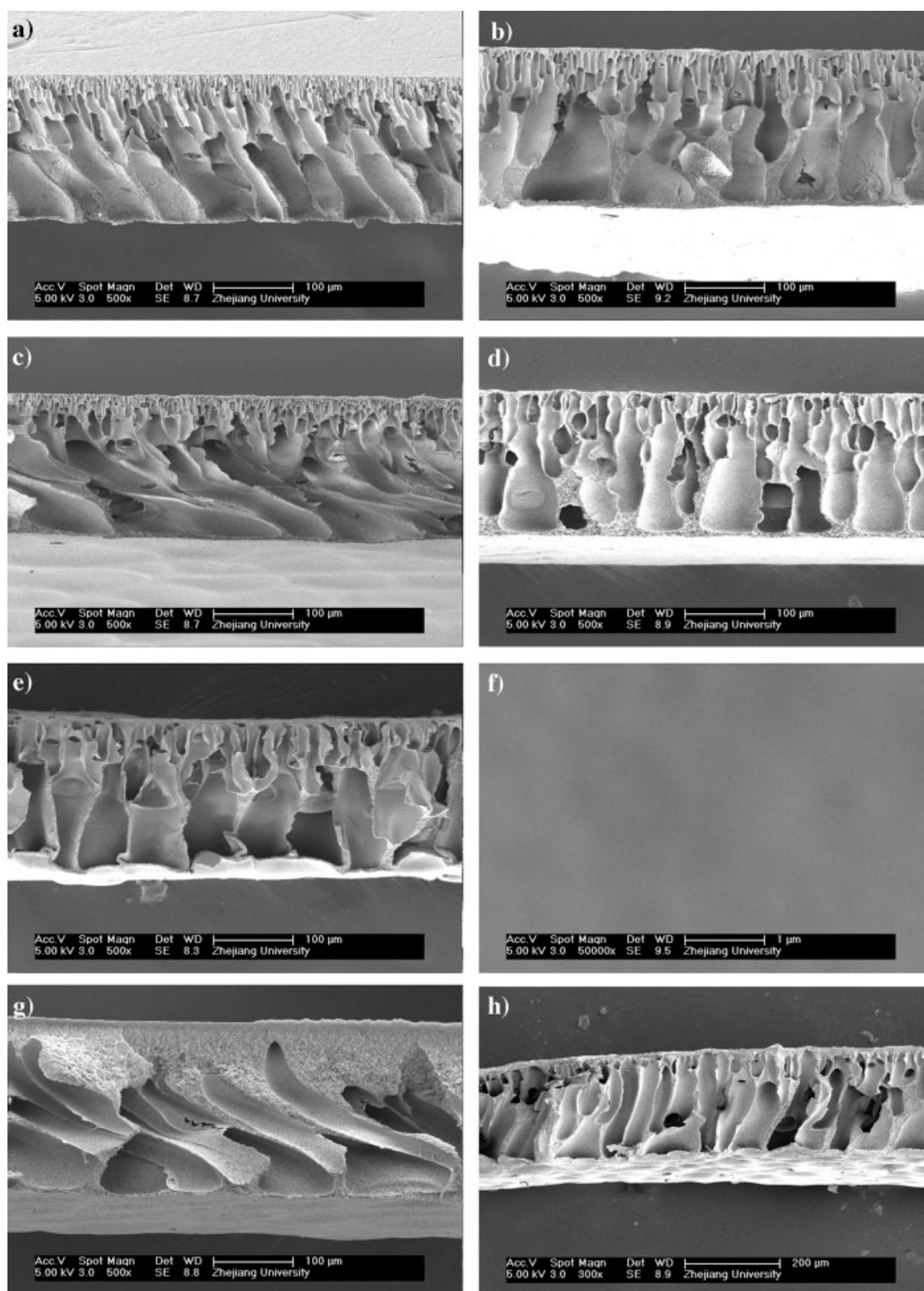


Figure 2 Micrographs of the PAN-based membranes: (a) PAN, (b) PANCNVP7, (c) PANCNVP15, (d) PANCNVP23, (e) PANCNVP31, (f) typical surface image, (g) PANCNVP15/PVP, (h) PAN/PVP.

be found in all spectra. The peak at 1285 cm^{-1} is correspond to the C—N stretching vibration, and the peak at 1416 cm^{-1} is attributed to the deformation vibration of C—H of the NVP ring, which is shown as a

shoulder of the peak at 1452 cm^{-1} for overlapped with that of the polymer main chain.³⁶ Furthermore, the strongest peak located at 1666 cm^{-1} arises from the stretching vibration of carbonyl group (C=O) in

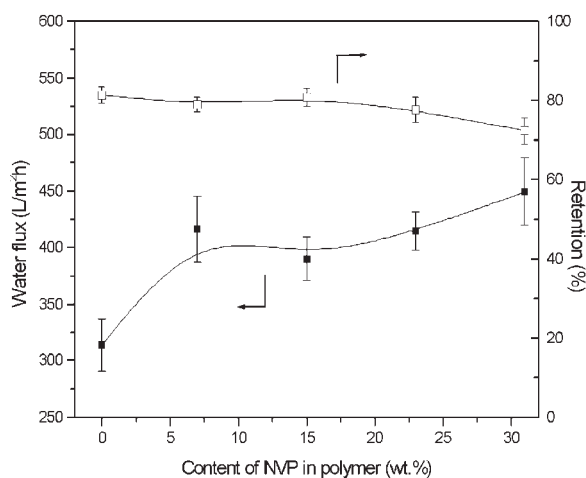


Figure 3 Pure water flux and BSA retention of the PAN-based membranes.

NVP. It is clear that the peak area at 1666 cm^{-1} increases with the content of NVP in the membrane.

FESEM micrographs for the cross section and surface of the studied PAN-based membranes are shown in Figure 2. It can be seen that the membranes with the whole range of NVP content, from 0 to 31 wt %, consist two distinct cross section morphologies—a selective dense surface layer supported by a much thicker highly porous layer. It seems that the incorporation of NVP hardly influences the cross section structures of the studied PAN-based membranes. Similar situation was observed for the surface morphologies of the membranes. There are no distinct pores can be observed on the membrane surface at a magnification of 50,000, as typically shown in Figure 2(f).

Figure 3 shows the water fluxes and BSA retentions of the membranes with different contents of NVP. It can be seen that the flux of deionized water has the tendency to increase with the content of NVP in the

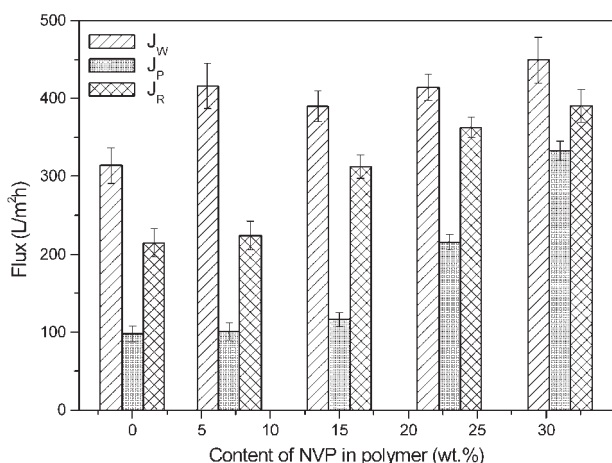


Figure 4 Permeation fluxes of pure water and BSA solution through the PAN-based membranes.

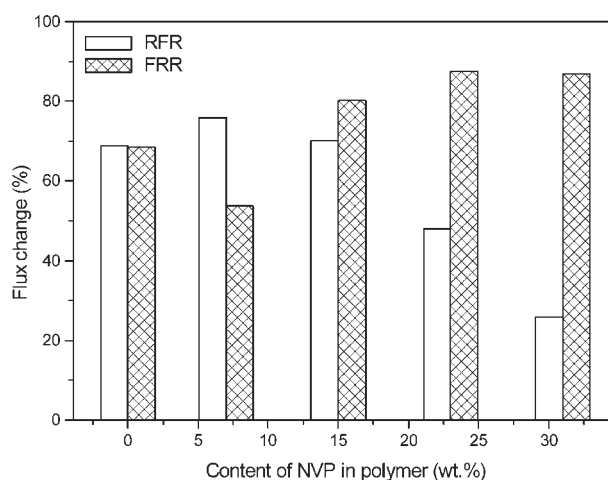


Figure 5 Flux changes of the PAN-based membranes during filtration and after chemical cleaning.

membrane and those of the copolymer membranes are remarkably larger than that of the PAN membrane, though the morphology of the cross section scarcely changes. Accordingly, the BSA retention of the membrane decreases slightly with the increase of NVP content. It should be noted that the PANCNVP7 membrane showed relatively high flux. This might be due to the low molecular weight of PANCNVP7 (viscosity of the dope solution), which caused remarkable macrovoids.

To investigate the antifouling properties of these NVP-containing PAN-based membranes, BSA solution filtration experiments were carried out. Typical results are shown in Figures 4 and 5. The symbols, J_W , J_P , and J_R are defined as the flux of deionized water, BSA phosphate-buffered saline solution, and deionized water after chemical cleaning on the membrane with 0.10M NaOH, respectively. It can be seen from Figure 4 that, although J_W for the membrane with low

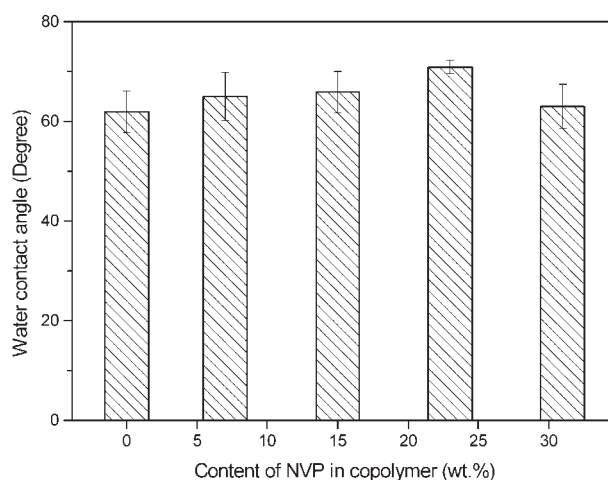


Figure 6 Water contact angles of the PAN-based membranes with different NVP contents.

TABLE III
Permeation and Antifouling Properties of PANCNVP15 Membranes
with and without PVP

Sample	J_W	J_P	J_R	RFR (%)	FRR (%)	Retention (%)	CA (°)
PANCNVP15	389.9	116.5	312.6	70.1	80.2	80.8	65.9 ± 4.3
PANCNVP15/PVP	350.2	111.5	287.4	68.2	82.1	86.7	50.1 ± 2.4

content of NVP (i.e., PANCNVP7) is larger than that of the PAN membrane, J_P is about 100 L/m² h for these two membranes. However, J_P increases evidently from 98 L/m² h for the PAN membrane to 215.9 L/m² h for the PANCNVP23 membrane and 333.1 L/m² h for the PANCNVP31 membrane. Furthermore, it is clear that J_R increases gradually with the content of NVP in the membrane. Figure 5 shows the relative flux reduction (RFR, $(1 - J_P/J_W) \times 100$) and the flux recovery ratio (FRR, $(J_R/J_W) \times 100$) by NaOH cleaning. Similarly, RFR decreases sharply with the content of NVP in the membrane except for the PANCNVP7 membrane. It can also be seen that FRR only increases slightly, which is due to the large value of J_P for the membrane with high content of NVP.

It can be concluded from the results mentioned earlier that the antifouling properties of the PAN-based membrane can be greatly improved by the incorporation of NVP except for membrane with very low content of NVP. This point is in accord with the results of hemocompatibility evaluation.³⁴ Although protein fouling is one of the key points for ultrafiltration membrane, questions remain about the mechanism of membrane protein fouling and there are quite different theories.^{37–40} Belford et al.⁴¹ concluded that the major contribution of protein fouling is from protein deposition during the dynamic and convective flow conditions. Since the BSA retention only decreases slightly with the content of NVP in the membrane, the difference of BSA fouling for membrane with various NVP content is likely induced by the fouling taken place on the membrane surface instead of that occurred in the pores. In other words, it is the membrane surface properties, rather than the membrane structures, to determine the antifouling properties of the studied PAN-based membranes. It is generally accepted that hydrophilic surface can improve the antifouling properties of membrane.^{40,42–44} However, the water contact angles of the asymmetric membranes, as shown in Figure 6, or those of the dense membranes reported previously,³⁴ does not decrease distinctly with the content of NVP in the membrane and seems disorderly and unsystematic. It is well-known that membrane with good biocompatibility can reduce protein adsorption and then improve its antifouling properties. Thus, one can envisage that the excellent biocompatibility of NVP endows the

studied PAN-based membrane with good antifouling properties.

Since PAN-based membranes with good antifouling properties can be obtained by the incorporation of NVP, PVP was used as an additive to modulate the membrane structures. As summarized in Table II, dope solution containing 8 wt % PANCNVP15 and 5 wt % PVP was fabricated into asymmetric membrane; PAN membrane using 5 wt % PVP as an additive was also attained. FESEM micrographs for the cross section of the PAN-based membranes containing PVP are shown in Figure 2. Figure 2(g, h) are membranes fabricated from PANCNVP15 and PAN with PVP, respectively. It can be seen that the addition of PVP can depress macrovoids to some extent only for PANCNVP membrane. However, as shown in Table II, the viscosity increment induced by the PVP addition for the PAN dope solution is not less than that for the PANCNVP dope solution. Kang et al.⁴ proposed that the viscosity was an important factor influencing the precipitation rate. Smolders et al.⁴⁵ suggested that the formation of macrovoids in phase inversion membranes was controlled by delayed or instantaneous demixing. However, it is noticeable that, not only the viscosity of dope solution but also the polymer species can affect the final membrane morphologies.

Table III shows the results of the permeation and antifouling properties of PANCNVP15 and PANCNVP15/PVP membranes. It can be seen that, though the water contact angle of PANCNVP15/PVP was only 50.1° compared with that of PANCNVP15 membrane (65.9°), the improvement on the antifouling properties of the membrane caused by the addition of PVP is very small, which is far from that induced by increasing the content of NVP in the copolymer. For example, the RFR value of PANVNP31 membrane is 25.9%, which is far smaller than that of PANCNVP15/PVP membrane (68.2%). Therefore, to a certain extent, the copolymer membranes show the advantages of antifouling compared with the PAN/PVP blending membrane.

CONCLUSION

PANCNVPs with different contents of NVP were fabricated into asymmetric membranes by the phase inversion method. Although the morphologies of the

membranes hardly change with the increase of the NVP content in the membranes, the deionized water flux increases remarkably and the BSA retention decreases slightly. Results from the dynamic BSA solution filtration elucidate the remarkable improvement of the antifouling properties of the copolymer membrane except for that with very low content of NVP. It seems that this improvement comes from the excellent biocompatibility of NVP moieties instead of the change of surface hydrophilicity, because the water contact angles of these membranes fluctuate between 60 and 70°. Results from the membranes using PVP as an additive or not also confirm that the PANCNVP membranes show the advantage of antifouling compared with the polyacrylonitrile/PVP blending membrane.

References

- Ulbricht, M.; Belfort, G. *J Membr Sci* 1996, 111, 193.
- Etheve, J.; Dejardin, P.; Boissiere, M. *Colloid Surf B* 2003, 28, 285.
- Jung, B. *J Membr Sci* 2004, 229, 129.
- Kang, J. S.; Lee, Y. M. *J Appl Polym Sci* 2002, 85, 57.
- Kurkuri, M. D.; Aminabhavi, T. M. *J Appl Polym Sci* 2004, 91, 4091.
- Frahn, J.; Malsch, G.; Matuschewski, H.; Schedler, U.; Schwarz, H. H. *J Membr Sci* 2004, 234, 55.
- Chiang, W. Y.; Lin, Y. H. *J Appl Polym Sci* 2003, 90, 244.
- Belfer, S.; Bottino, A.; Capannelli, G. *J Appl Polym Sci* 2005, 98, 509.
- Godjevargova, T.; Konsulov, V.; Dimov, A.; Vasileva, N. *J Membr Sci* 2000, 172, 279.
- Hicke, H. G.; Lehmann, I.; Malsch, G.; Ulbricht, M.; Becker, M. *J Membr Sci* 2002, 198, 187.
- Xu, Z.-K.; Kou, R.-Q.; Liu, Z.-M.; Nie, F.-Q.; Xu, Y.-Y. *Macromolecules* 2003, 36, 2441.
- Nie, F.-Q.; Xu, Z.-K.; Huang, X.-J.; Ye, P.; Wu, J. *Langmuir* 2003, 19, 9889.
- Jung, B.; Yoon, J. K.; Kim, B.; Rhee, H. W. *J Membr Sci* 2004, 243, 45.
- Dayal, R.; Godjevargova, T. *Macromol Biosci* 2005, 5, 222.
- Oh, N. W.; Jegal, J.; Lee, K. H. *J Appl Polym Sci* 2001, 80, 2729.
- Wan, L.-S.; Xu, Z.-K.; Huang, X. J.; Che, A. F.; Wang, Z.-G. *J Membr Sci* 2006, 277, 157.
- Wan, L.-S.; Xu, Z.-K.; Wang, Z.-G. *J Polym Sci, Part B: Polym Phys* 2006, 44, 1490.
- Wan, L.-S.; Xu, Z.-K.; Jiang, H.-L. *Macromol Biosci* 2006, 6, 364.
- Ulbricht, M.; Matuschewski, H.; Oechel, A.; Hicke, H.-G. *J Membr Sci* 1996, 115, 31.
- Lin, W. C.; Liu, T. Y.; Yang, M. C. *Biomaterials* 2004, 25, 1947.
- Liu, T. Y.; Lin, W. C.; Huang, L. Y.; Chen, S. Y.; Yang, M. C. *Biomaterials* 2005, 26, 1437.
- Kang, J. S.; Kim, K. Y.; Lee, Y. M. *J Membr Sci* 2003, 214, 311.
- Yang, M. C.; Liu, T. Y. *J Membr Sci* 2003, 226, 119.
- Qin, J. J.; Cao, Y. M.; Li, Y. Q.; Li, Y.; Oo, M. H.; Lee, H. W. *Sep Purif Technol* 2004, 36, 149.
- Rangarajan, P.; Bhanu, V. A.; Godshall, D.; Wilkes, G. L.; McGrath, J. E.; Baird, D. G. *Polymer* 2002, 43, 2699.
- Han, W. L.; Gregor, H. P.; Pearce, E. M. *J Appl Polym Sci* 1999, 74, 1271.
- Mandal, S.; Pangarkar, V. G. *J Membr Sci* 2002, 209, 53.
- Zhang, C.; Du, Z. J.; Li, H. Q.; Ruckenstein, E. *Polymer* 2002, 43, 2945.
- Godjevargova, T.; Gabrovska, K. *Macromol Biosci* 2005, 5, 459.
- Tanaka, H.; Okazaki, T.; Tezuka, Y.; Hongo, T.; Takahashi, Y. *Polymer* 2002, 43, 1189.
- Nie, F.-Q.; Xu, Z.-K.; Wan, L.-S.; Ye, P.; Wu, H. *J Membr Sci* 2004, 230, 1.
- Huang, X.-J.; Xu, Z.-K.; Wan, L.-S.; Wang, Z.-G.; Wang, J. L. *Macromol Biosci* 2005, 5, 322.
- Wan, L.-S.; Xu, Z.-K.; Huang, X.-J.; Wang, Z.-G.; Wang, J.-L. *Polymer* 2005, 46, 7715.
- Wan, L.-S.; Xu, Z.-K.; Huang, X.-J.; Wang, Z.-G.; Ye, P. *Macromol Biosci* 2005, 5, 229.
- Kim, J. H.; Kang, M. S.; Kim, C. K. *J Membr Sci* 2005, 265, 167.
- Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman & Hall: New York, 1974.
- Jim, K. J.; Fane, A. G.; Fell, C. J. D.; Joy, D. C. *J Membr Sci* 1992, 68, 79.
- Kelly, S. T.; Opong, W. S.; Zydney, A. L. *J Membr Sci* 1993, 80, 175.
- Tracey, E. M.; Davis, R. H. *J Colloid Interf Sci* 1994, 167, 104.
- Mueller, J.; Davis, R. H. *J Membr Sci* 1996, 116, 47.
- Belfort, G.; Davis, R. H.; Zydney, A. L. *J Membr Sci* 1994, 96, 1.
- Kull, K. R.; Steen, M. L.; Fisher, E. R. *J Membr Sci* 2005, 246, 203.
- Taniguchi, M.; Belfort, G. *J Membr Sci* 2004, 231, 147.
- Wavhal, D. S.; Fisher, E. R. *Langmuir* 2003, 19, 79.
- Smolders, C. A.; Reuvers, A. J.; Boom, R. M.; Wienk, I. M. *J Membr Sci* 1992, 73, 259.