

Acrylonitrile–Maleic Anhydride Copolymer Membranes with Different Molecular Weights

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ABSTRACT: The structure and performance of acrylonitrile–maleic anhydride copolymer membranes with different molecular weights were investigated. The results showed that the water flux of the membrane decreased gradually with increasing molecular weight of the copolymer; the rejection increased only when there was an obvious increase of molecular weight. The addition of an additive (polyvinylpyrrolidone) largely decreased the water flux and rejection of the membrane when the concentration of the copolymer remained unchanged. The higher the molecular weight, the thicker were the transition layer and the wall of the support pore and the better was the anticompactness of the membrane. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2521–2527, 2002

Key words: acrylonitrile–maleic anhydride copolymer; membrane; molecular weight; structure and performance

INTRODUCTION

In past decades, a membrane technique was developed and applied in many fields and it will play a strategic part in most industries in the 21st century. To meet greater and greater application needs, the development of a novel membrane material and the modification of a membrane material in use as well as the relationship of the structure and performance of the membrane with its influencing factors have always been essential problems.

Polyacrylonitrile (PAN) is one kind of popular membrane material owing to its good chemico-physical stability and excellent antimicroorganism ability. The PAN membrane has been com-

mercialized and widely used in the clearance of small molecules and in the concentration of macromolecules and has become practical in water treatment and blood purification (hemodialysis and hemofiltration). To improve its performance, a variety of measures have been taken, which include copolymerization, blending, surface modification, and screening for the optimum casting conditions of the membrane.^{1–6} Recently, a few works^{7,8} related the properties of a membrane to the molecular weight of the membrane material. For example, to improve the mechanical strength of a PAN membrane to resist the backwash process, Henmi and Yoshioka⁷ prepared a hollow-fiber membrane with an ultrahigh molecular weight ($M_w = 7.0 \times 10^5$) PAN. As the result, not only the mechanical strength but also the flux of the membrane was greatly increased.

From the membrane formation mechanism by the phase-inversion method, the structure and performance of a membrane under the same cast-

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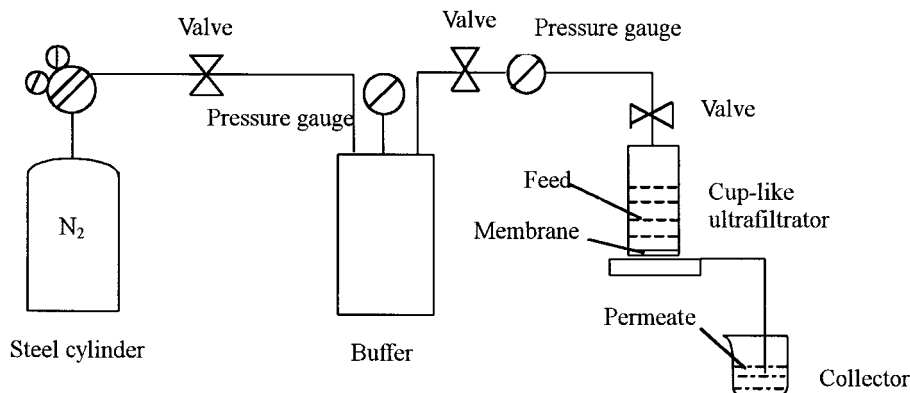


Figure 1 Schematic diagram of ultrafiltration apparatus.

ing conditions is directly related to the property of the polymer solution (casting solution), which is seriously affected by the molecular weight of the polymer. It is very important to know how the molecular weight influences the structure and performance of a polymeric membrane in order to prepare the required membrane. However, the effect of the molecular weight as a variable on the structure and performance of a membrane has not been investigated so far.

An acrylonitrile–maleic anhydride (AN–MA) copolymer membrane is one kind of modification PAN membrane. It can be used not only to immobilize an enzyme successfully,⁹ but also can be modified easily because of the existence of MA in the molecular chain of the copolymer. In the present work, the structure and performance of AN–MA copolymer membranes with different molecular weights (lower than 5.0×10^5) are discussed and compared.

EXPERIMENTAL

Materials

AN–MA copolymers were synthesized and characterized by elementary analysis (EA), Fourier transform infrared (FTIR), differential thermal analysis (DTA), and wide-angle X-ray diffraction (WAXD) (more details can be found in ref. 10). The molecular weights of the copolymers were measured by gel permeation chromatography (GPC; Shimadzu, LC-6A, polystyrene standard). Dimethyl sulfoxide (DMSO) and polyvinylpyrrolidone (PVP, $M_n = 10,000$) were purchased from the Aldrich Chemical Co. (Steinheim, Germany). Bovine serum albumin (BSA, $M_n = 67,000$) was

purchased from the Shanghai Institute of Biological Products (Shanghai, China). DMSO, PVP, and BSA were used without further purification.

Preparation of Casting Solution

Typically, a certain amount of a powdered AN–MA copolymer with or without PVP was dispersed in DMSO with stirring. The copolymer was swollen for 1.5 h at 40°C and then dissolved at 70°C for 2 h. The solution was filtered and degassed before use.

Preparation of Membranes

AN–MA copolymer membranes were prepared by the phase-inversion process, that is, the solution was cast on a dry and clean glass plate and spread with an applicator and then solidified in a coagulation bath (DMSO:H₂O = 20:80 v/v). The thickness of the membranes (measured with a Peacock dial gauge) was 22–29 μm. The resulting membranes were stored in distilled water to keep the pore from collapsing.

Determination of Membrane Performance

The water flux and rejection of the membranes were measured using the experimental apparatus described in Figure 1. To determine the water flux of the AN–MA copolymer membranes, first, the membranes were prepressed with pure water at room temperature (25°C) and 0.2 MPa; then, the permeate at 0.1 MPa was collected and weighted. The water flux was calculated according to the following formula:

$$J(\text{L m}^{-2} \text{ h}^{-1}) = \frac{V(\text{mL}) \times 600}{t(\text{min}) \times S(\text{cm}^2)} \quad (1)$$

Table I Molecular Weights and Compositions of AN-MA Copolymers

No.	$[\eta]$ (mL/g)	$M_{\eta} \times 10^{-4}$	$M_{w\text{GPC}} \times 10^{-4}$	$M_{n\text{GPC}} \times 10^{-4}$	$F_2^a \times 10^2$
10-8	126.20	9.26	9.38	3.83	4.3100
7-5	220.54	20.1	20.4	11.5	5.1290
10-5	254.12	24.5	25.1	12.2	3.3595
10-6	277.80	27.7	27.9	14.1	4.7630
10-1	321.29	33.9	33.7	15.7	3.7790

^a F_2 : mol fraction of MA in the copolymer.

where J is the water flux, and V , the volume of water through the S (cm^2) membrane during t min. The effective area of a membrane is 12.56 cm^2 .

Rejection was measured according to the following processes: a BSA solution of 500 ppm was ultrafiltrated at room temperature; then, the absorbances of the feed, retentate, and permeate solution at 280 nm were determined using a Model 751-G spectrophotometer made by the Optical Instrument Plant of Shanghai. Rejection was calculated according to the following formula:

$$R (\%) = \frac{A_f - A_p}{\frac{1}{2}(A_f + A_r)} \quad (2)$$

where R is the rejection, and A_f , A_r , and A_p , the absorbances of the feed, retentate, and permeate solution, respectively.

Morphological Structure of AN-MA Copolymer Membranes

The copolymer membranes were frozen and broken in liquid nitrogen; then, gold was sprayed on their

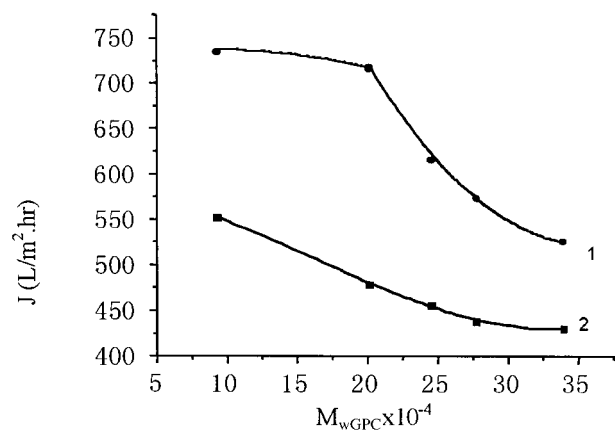


Figure 2 Effect of molecular weight on the water flux of an AN-MA copolymer membrane. Copolymer percent, 11%: (1) no PVP; (2) PVP:copolymer = 1:10.

surfaces and the thickness of gold sputtering was 14 nm. The morphological structure of the cross section of the membranes was observed with a Model Comscan-Series-4 scanning electron microscope (SEM) produced by the Cambridge Co. (Britain).

RESULTS AND DISCUSSION

Characterization of AN-MA Copolymer

The molecular weights and compositions of the AN-MA copolymers used in the present work are listed in Table I.

Molecular Weight and the Performance of AN-MA Copolymer Membranes

The performances of the membranes from the AN-MA copolymers with different molecular weights are listed in Figure 2 and Table II. Figure 2 displays the relationship between the water flux of the membrane and the molecular weight of the copolymer. The water flux of the membrane decreased gradually with an increasing molecular weight of the copolymer. The rejection increased only when there was an evident increase of the molecular weight (see Table II).

Compared with the case without an additive, both the water flux and rejection of the membrane were greatly decreased by the additive when the

Table II Effect of Molecular Weight on the Rejection of AN-MA Copolymer Membrane (Copolymer percent: 11%)

Rejection	$M_{w\text{GPC}} \times 10^{-4}$				
	9.38	20.4	25.1	27.9	33.7
Rejection 1 (%)	83	89	86	92	90
Rejection 2 (%)	77	87	84	84	86

1. No PVP; 2. PVP:copolymer = 1:10.

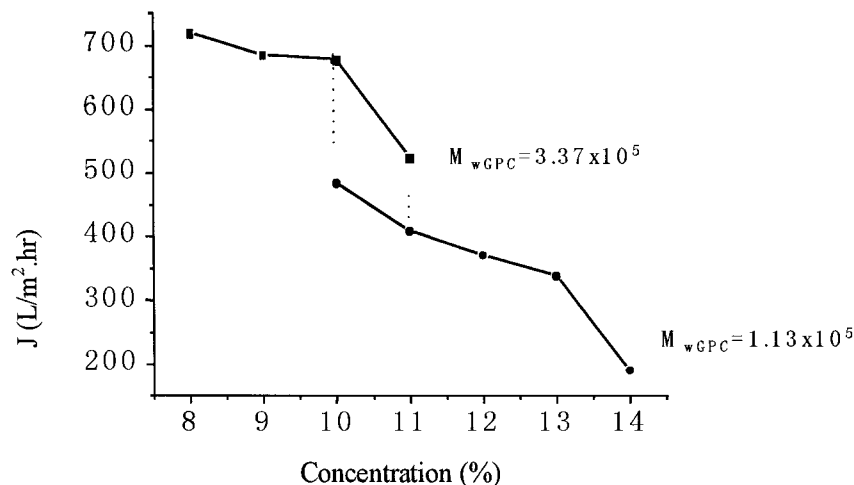


Figure 3 Effect of CCS on the water flux of AN-MA copolymer membrane.

concentration of the copolymer remained unchanged (Fig. 2 and Table II). Therefore, the addition of PVP is not helpful to increase the flux or the rejection of a membrane.

Effect of the Casting Solution Concentration on the Performance of AN-MA Copolymer Membranes with Different Molecular Weights

The concentration of the casting solution (CCS) is one of the main factors that affects the structure and performance of a membrane. We discussed elsewhere the effect of the CCS on the structure and performance of an AN-MA copolymer membrane with the usual molecular weight.¹¹ To the membrane with a usual molecular weight, the flux decreased and the rejection increased with

increasing CCS. Then, what is the case with a higher molecular weight? The results are shown in Figures 3 and 4.

From Figure 3, the water flux of a high molecular weight AN-MA copolymer membrane decreased gradually with increasing CCS, which coincides with that of a usual molecular weight membrane. The pattern of change resulted from the change of the viscosity and the thermodynamic state of the casting solution caused by increase of the concentration. In addition, to a high molecular weight AN-MA copolymer solution, besides the increase of viscosity, the natural entanglement of macromolecules, which influences the ratio of the number of network pores to that of aggregate pores, cannot be overlooked.

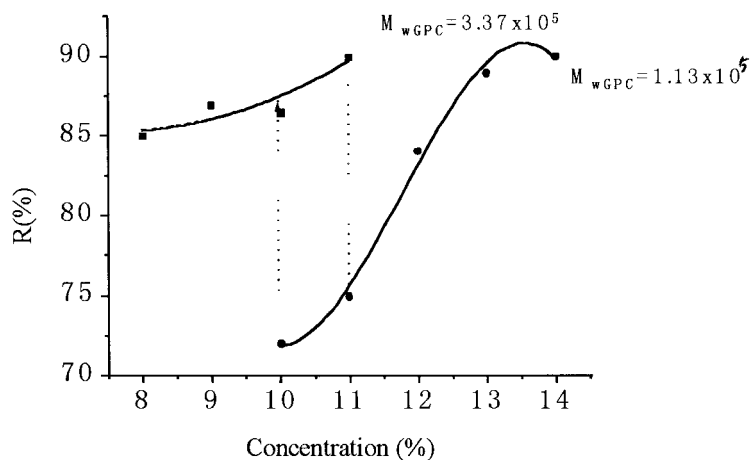


Figure 4 Effect of CCS on the rejection of AN-MA copolymer membranes with different molecular weights.

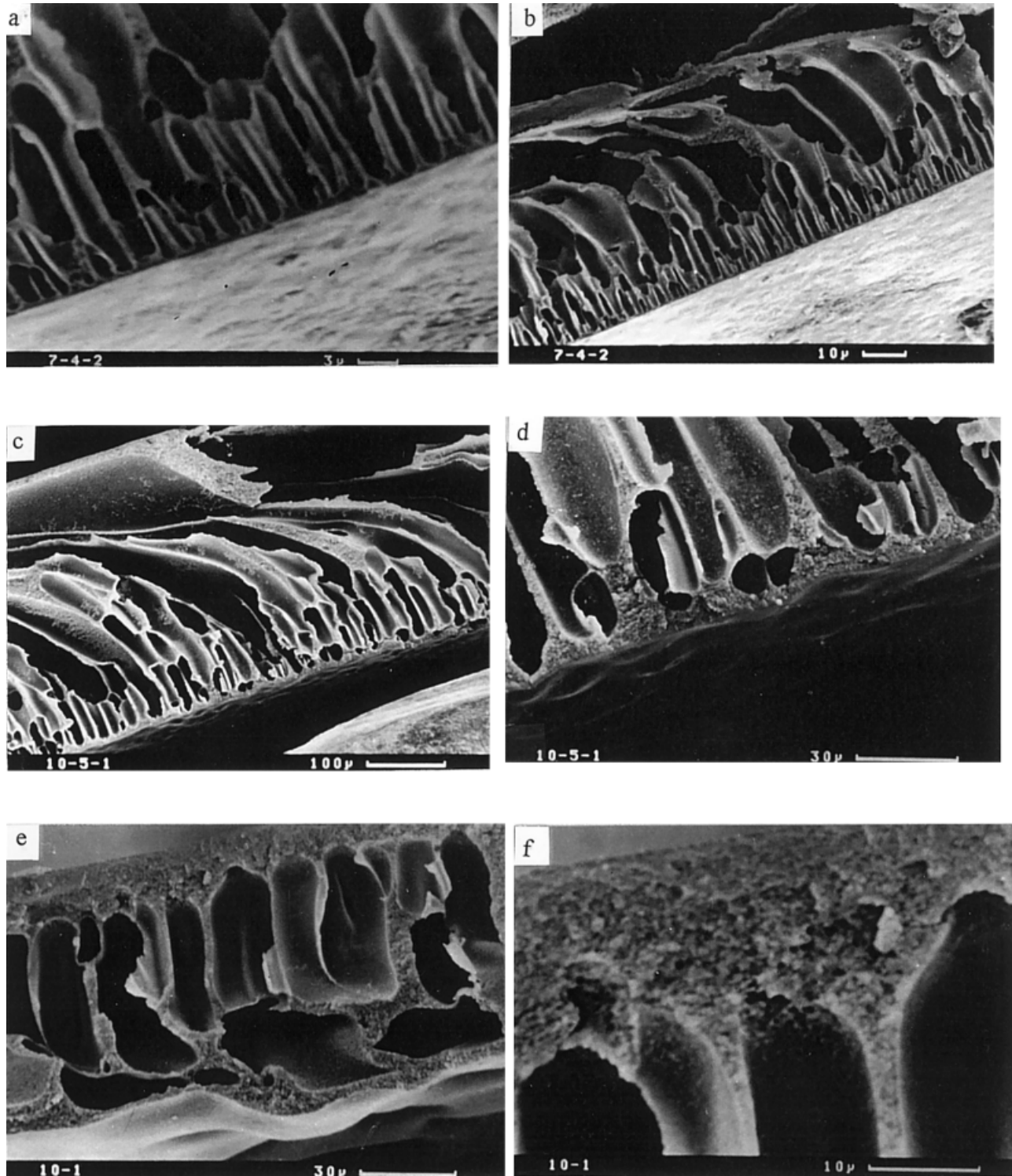


Figure 5 SEM photographs of the membrane cross sections with different molecular weights. Molecular weight: (a,b) 9.38×10^4 ; (c,d) 2.51×10^5 ; (e,f) 3.37×10^5 . (b), (d), and (f) are partial magnifications of (a), (c), and (e), respectively.

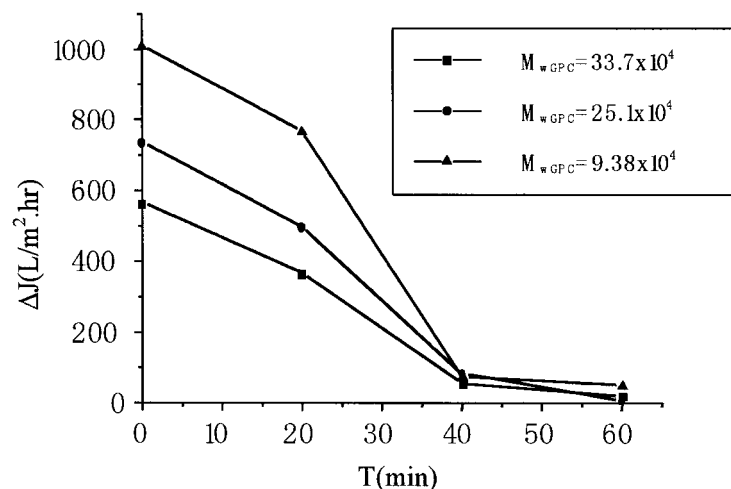


Figure 6 Molecular weight and the compactness of AN-MA copolymer membrane.

As shown in Figure 4, although the rejection of a high molecular weight AN-MA copolymer membrane increased with increasing CCS, the increase was not as quick as that of a usual molecular weight membrane. Moreover, it also can be seen from Figures 3 and 4 that, under the same CCS, both the water flux and the rejection of the membrane with a high molecular weight were higher than those of a membrane with the usual molecular weight. This suggests that a membrane with high water flux and rejection can be prepared by using a polymer with a high molecular weight under a lower casting concentration. The result is coincident with that of ref. 7.

Structure of AN-MA Copolymer Membranes with Different Molecular Weights

The performance of a membrane is closely related to its structure. Besides the casting conditions of membrane and type of polymer, the structure of a membrane also is influenced by the molecular weight.

Figure 5 shows scanning electron microscopic photographs of the cross sections of AN-MA copolymer membranes with different molecular weights. It can be seen from the figure that, with increasing molecular weight, the structure of membrane changed in the following aspects:

1. Both the thickness of the transition layer (the spongelike layer under the skin layer) and the pore wall of the support layer (the fingerlike or columnlike layer) increased,

and the higher the molecular weight, the thicker were the layer and the wall.

2. The pore shape of the support layer transformed from fingerlike to columnlike and from irregular to somewhat regular, and macrovoids in the support layer lessened gradually.

Compared with the effect of the CCS on the structure of the membrane, it was clear that the effect of the molecular weight was similar to the former in some aspects (such as the thickness of the transition layer and the pore shape of the support layer¹¹). But the latter seemed stronger.

Compactness of AN-MA Copolymer Membranes with Different Molecular Weights

It is well known that porous polymeric membranes will exhibit irreversible deformation during a pressure-driven process (which is defined as the compaction of the membrane). The compaction will decrease the permeability of the membrane. Therefore, increasing the anticompactness of a membrane is crucial to keep water flux constant with time.

Usually, a membrane should be prepressed before use so as to make the structure of membrane steady. Under the same conditions of prepressure, the change of the water flux of the membrane from different molecular weight polymers is different. The less the water flux changes, the better was the anticompactness of the membrane.

The compactness of AN-MA copolymer membranes with different molecular weights was in-

investigated using pure water as the feed solution to exclude the probability of the foulness of the membrane. The result is shown in Figure 6. It can be seen that, under the same conditions, the higher the molecular weight was, the less the flux decreased and, therefore, the better was the anticomcompactness of the membrane. This may result from that the membrane with a higher molecular weight has a thicker transition layer and pore wall of the support layer.

CONCLUSIONS

Molecular weight evidently affected the structure and performance of the membrane. The water flux of the membrane decreased gradually with increasing molecular weight of the copolymer; rejection increased only when there was an evident increase of the molecular weight. The addition of an additive (PVP) greatly decreased the water flux and the rejection of the membrane when the concentration of the copolymer remained unchanged. The higher the molecular weight, the thicker were the transition layer and the wall of the support pore and the better was the anticomcompactness of the membrane.

It can be concluded from the results that increasing molecular weight is helpful to prepare a membrane with a high water flux and rejection from a lower concentration solution. Thus, the

consumption of the copolymer will be decreased and the production cost of the membrane will be lowered, which is very beneficial to promote the application and dissemination of the membrane technique on industry.

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