

Effect of PEG Additives on Properties and Morphologies of Membranes Prepared from Poly(2,6-dimethyl-1,4-phenylene oxide) by Benzyl Bromination and In Situ Amination

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Received 12 October 2004; accepted 4 February 2005

DOI 10.1002/app.22425

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This study investigated the effect of PEG additive on the structure formation and permeation properties of membranes. The membranes were prepared from a bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide)/chlorobenzene/ethanol system using the phase inversion method with PEG as an additive. As expected, PEG with a fixed molecular weight (e.g., PEG 600) acted as a pore-forming agent, and membrane porosity increased as the PEG content of the casting solution increased. However, when the PEG content was fixed, the effect of PEG on the membrane properties and morphology was largely dependent on its molecular weight. It was found that when the molecular weight of PEG was less than 800, it acted as a pore former,

but when the molecular weight of PEG was more than 1000, the pore size and porosity of the resulting membrane decreased. These results can be explained by the membrane-forming system's thermodynamic and kinetic properties, which can be assessed by coagulation value and viscosity. Furthermore, the membranes were characterized for pure water flux and rejection of solute and by SEM observation. The filtration results agreed well with the SEM observations. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2414–2421, 2005

Key words: additives; phase separation; morphology; thermodynamics; kinetics

INTRODUCTION

Membrane science and technology has been developing rapidly since the Loeb–Sourirajan phase inversion method was put forward.¹ In the process of applying the phase inversion method, an initially single-phase homogeneous polymer solution consisting of polymer and solvent or a third component is cast onto a suitable substrate to form a thin film and is then immersed in a coagulation bath, which results in diffusive exchanges of solvent and nonsolvent and the solidification of the polymer.² Phase inversion has been found to be a versatile technique for asymmetric membrane preparation because the casting solution and the formation conditions can be varied widely to get the desired membrane structures by changing the main

factors, such as the composition of the polymer solution (additives, etc.), the solvent evaporation temperature, and the evaporation time, as well as the nature and temperature of the coagulation media.³ Adding a third component (often called an additive) into a casting solution has been one of the important techniques used in membrane preparation to change the membrane microstructures. Principally, such additives can be either organic or inorganic, as long as they are of lower volatility than the solvent and of proper solubility for the gelatin medium. Thus, the commonly used additives are methyl cellulose, glycerine, poly(vinyl pyrrolidone) (PVP), poly(ethylene glycol) (PEG), water, LiCl, and ZnCl₂.^{4–9} Examples of this are the study by Luccio et al. of the effect of different additives (such as PVP and LiNO₃) on the preparation of microporous membranes using phase inversion and the immersion precipitation technique;⁴ the investigation by Kim and Lee on the effect of PEG additive as a pore former on the structure formation of membranes and their permeation properties connected with changes in the thermodynamic and kinetic properties using a phase inversion process;⁵ and the study by Bottino et al. of the role of LiCl on the overall properties and mechanism of membrane formation.⁶

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Contract grant sponsor: Natural Science Foundation of China; contract grant numbers: 20106015 and 20376079.

Contract grant sponsor: National Basic Research Program of China; contract grant number: 2003CB615700.

Contract grant sponsor: Program for New Century Excellent Talents in University; contract grant number: NCET-04-0583.

Those studies explained the effect of additives on membrane morphology with a focus on the thermodynamics and kinetics of the phase-separation process, which was assessed by such parameters as coagulation value, viscosity, precipitation type, precipitation rate, and diffusion coefficient. Furthermore, driven by commercial interests, all the polymeric systems investigated were neutral or negatively charged. However, positively charged polymeric systems seem to be equally important because occasionally they are of significance in separating positively charged species, such as separating biomacromolecules below the isoelectric point and recovering cathode electrophoresis lacquer.

To that end and also as an extension of the research of our group on positively charged membranes designed for electrodialysis, diffusional dialysis, nanofiltration, and bipolar membrane preparation,^{10–13} a new route for preparing a positively charged and asymmetrical membrane for pressure-driven processes by in situ amination was reported in a previous article in this series.¹⁴ As reported in that article, the membranes were prepared directly from a casting solution comprised of trimethylamine (TMA) and bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) using the phase inversion method. The effects of charge density (i.e., the ratio of BPPO to TMA) and evaporation time on membrane performance and morphology were investigated.

The preliminary tests also indicated that some polymeric additives could be used in the casting solution system to adjust the structure of the resulting membrane. For example, when PEG was added to the casting solution, the membrane microstructures varied not only by content, but also by molecular weight. However, the trend was abnormal when applying PEG as an additive to membrane casting solutions. Therefore, the present work focused on the function of polymeric additives in preparing a positively charged membrane from BPPO. Special attention was given to the control of the morphology and performance of the formed membrane by changing the molecular weight of the PEG additive and the ratio of PEG to chlorobenzene in the casting solution, with the guidance of the thermodynamics (coagulation value) and kinetics (viscosity) of the phase separation process.

EXPERIMENTAL

Materials and bromination of PPO

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with an intrinsic viscosity of 0.57 dL/g in chloroform at 25°C was supplied by the Institute of Chemical Engineering of Beijing (China); chlorobenzene was used as the solvent. The bromine was of analytical grade. The bromination of PPO was achieved according to a

method reported in a previous article.¹⁵ The brominated polymer was conducted to ¹H-NMR (Unity plus 400) measurements for the precise determination of the bromine contents in the aryl and benzyl positions. Triethylamine (TEA) was chosen as a representative of the positively charged reagent and dissolved in dimethylformamide (DMF) to attain a concentration of 2 mol/L. Poly(ethylene glycol) (PEG), with average molecular weights determined as 400, 600, 800, 1000, and 2000, was used as received. Ethanol was used as the nonsolvent gelating medium. The gelatin, with an average molecular weight of about 69000 g/mol, was used as the probe molecule for the solute rejection test.

Membrane preparation

The casting solution was prepared with chlorobenzene as the solvent, the brominated polymer as the solute, and PEG as the additive. The solute concentration was about 16 wt %. PEG was added at a given amount, its content expressed as the weight ratio (wt %) of the added PEG to the total casting solution. Then a given amount of TEA-DMF solution was added and agitated until homogeneous. The solution was kept for some time and then cast onto a clean glass plate. After evaporation in the ambient air for 90 s, the membrane was immersed in an ethanol solution long enough to form a membrane. The membrane was repeatedly washed with deionized water and wet-stored.

Determination of cloud point and viscosity

Cloud point was defined as the added amount of ethanol in a casting solution of 40 g when the first appearance of turbidity had been visually observed and the turbidity did not redissolve at 25°C within 24 h. The viscosity of the casting solution was determined using a viscosity meter (Ubbelohde viscometer) in a 30°C water bath.

Membrane characterizations

Flux and separation experiments

The pure water flux and solute rejection tests were conducted with a dead-end membrane module, which can offer a membrane area of 12.6 cm² and is made of stainless steel that can endure a pressure difference of 1.0 MPa. Water flux was calculated as $F = W/At$, where W is the total volume of the permeate penetrating through the membrane during the experiment, A is the membrane area, and t is the operation time. Deionized (DI) water was used to measure the pure water flux of the membrane. The solute rejection rate was measured with the gelatin (average molecular weight 69,000 g/mol) as the retentate. The feed con-

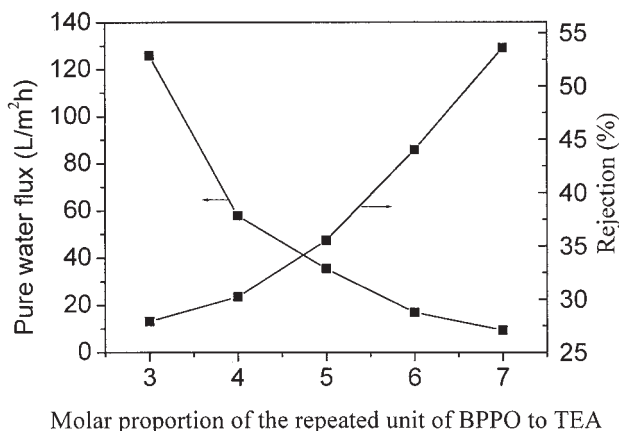


Figure 1 Effect of the ratio of BPPO to TEA on membrane permeability and the rejection of the gelatin solution at pH 4 at an operating pressure of 0.30 MPa.

centration of gelatin was 1 g/L with DI water as the solvent, and the pH of the solution was adjusted to 4 by adding hydrochloric acid, so the gelatin carried a net positive charge. The operating pressure was 0.20 MPa. The concentrations of the feed and the permeate solution were determined with an ultraviolet-visible spectrophotometer (TU-1910, Beijing Purkinje General Instrument Co. Ltd., Beijing, China) with a determining wave at 194 nm. The rejection rate (R) was calculated as $R = 1 - (C_p/C_f)$, where C_p and C_f are the concentrations of the permeate and the feed, respectively.

SEM observations

The cross-sectional morphologies of the asymmetric membranes were observed with a scanning electron microscope (XT30 ESEM-TMP PHILIP). The membranes were cryogenically fractured in liquid nitrogen and then coated with gold before observation.

RESULTS AND DISCUSSION

Effect of ratio of additive to chlorobenzene on membrane performance and morphology

For simplification, TEA was chosen as the positively charged reagent because it can directly dissolve in DMF as a pure reagent and does not need to be evaporated from its aqueous solution just like TMA. Although other amines, such as tri-*n*-propylamine (TPA) or ternary amines with a longer chain of alkyl group, also can be used as the positively charged reagent, they were not applied because with increasing molecular weight of the amine, the reaction between the bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) and the ternary amine be-

came difficult because of the steric effect. Figure 1 shows the effect of the ratio of BPPO to TEA on membrane permeability and the rejection of the gelatin solution at pH 4 when the membrane was prepared with PEG 400 (4.3 wt %) as the additive and with a 90-s evaporation. The results showed a trend similar to that in the TMA system, which was discussed in detail in our previous article.¹⁴ Our preliminary tests showed that a membrane casting solution containing a 6 molar proportion of the repeated unit of BPPO to TEA exhibited relatively excellent stability, and the prepared membrane possessed relatively high rejection with the proper flux, as shown in Figure 1. Thus, as an example in this series of tests, the molar proportion of the repeated unit of BPPO to TEA was fixed at 6 and the molecular weight of PEG was equal to 600. To investigate the effect of PEG concentration on membrane performance, the membranes were prepared with different amounts of PEG as the additive and with a 90-s evaporation. The results of the pure water flux and the rejection are presented in Figure 2. It is evident that a larger amount of PEG in the casting solution led to higher water permeability and lower rejection. To understand the membrane-forming mechanism of the investigated systems by the phase inversion process, the thermodynamics and kinetics of the membrane-forming system should be investigated. It is well known that coagulation value can be used as a measure of thermodynamic stability and that viscosity is indicative of the state of a solution and closely related to the processability and precipitation behavior of a casting solution in membrane formation.^{16–17} Thus, Figures 3 and 4 show the change in coagulation value and viscosity of the casting solution when the PEG content increased from 3.5% to 8.7%, respectively. The results indicate there was reduced ethanol tolerance of the systems or a less stable system

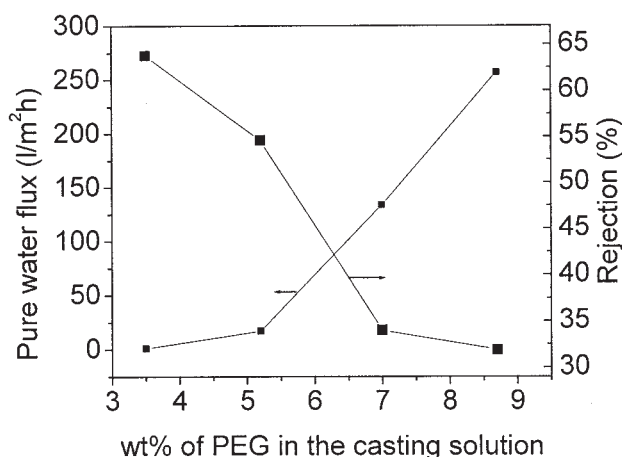


Figure 2 Effect of the amount of PEG additive in the casting solution on the pure water flux and the solute rejection of the membranes at a pressure of 0.20 MPa.

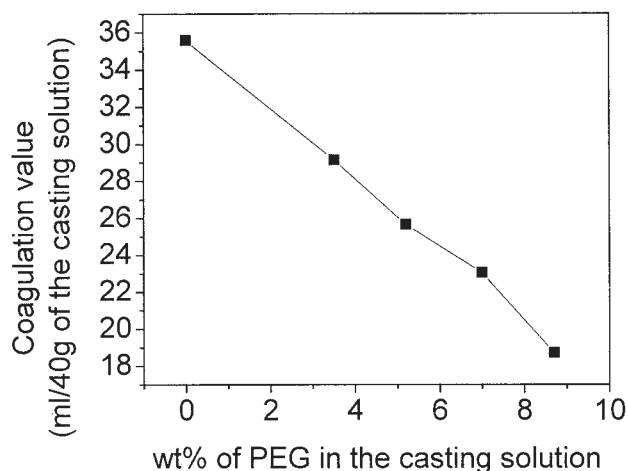


Figure 3 Effect of the amount of PEG additive in the casting solution on the coagulation value of 40 g of casting solution.

with the higher PEG content, which can enhance the precipitation rate and make a more porous membrane.¹⁸ However, the slightly increased viscosity of the casting solution with the addition of PEG suggests that it was a secondary factor in the membrane formation. Furthermore, because of the formation of hydrogen bonding between DMF and PEG,¹⁹ the effective solvating power of DMF for the polymer decreased gradually with an increase in PEG concentration as a result of the strong interaction between the PEG molecules and DMF, as shown in Scheme 1. To some extent, a decrease in solvent strength will induce an aggregation of the polymer chains in the casting solution.²⁰ A large amount of ethanol enters the space created between the polymer aggregates during the

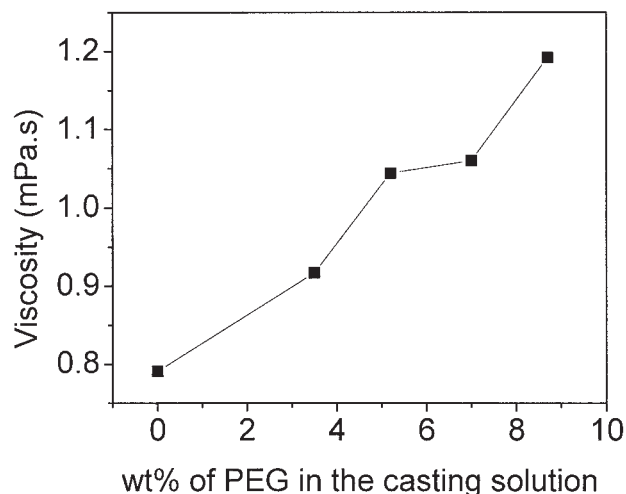
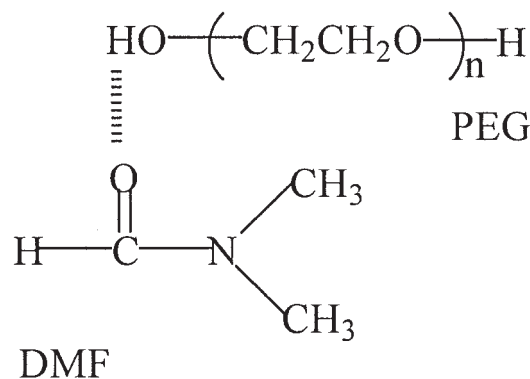


Figure 4 Effect of the amount of PEG additive in the casting solution on the viscosity of the casting solution.



Scheme 1 Schematic diagram of the interaction of hydrogen bonding between PEG and DMF.

coagulation process; this results in an increase in the pore size of the membrane.²¹ Therefore, the pore size and pore number increase with an increase in PEG content. These analyses are reasonable because they agree well with the cross-section observations of the membranes with SEM. Figure 5 shows the variation in membrane morphology relative to PEG concentration. It is clear from these images that the presence of fingerlike pores with a large number of macrovoids in the membrane increased with the amount of PEG added, and this effect became more apparent as PEG concentration increased. The membrane prepared from a small quantity of PEG [Fig. 5(a)] had only a few macrovoids. When 8.7% PEG was added to the casting solution, the membrane formed possessed abundant macrovoids [Fig. 5(d)]. Therefore, with the same polymer content, an increase in PEG content tended to substantially increase membrane permeability and decrease membrane rejection.

Effect of PEG molecular weight on membrane performance and morphology

PEG with average molecular weights of 400, 600, 800, 1000, and 2000 g/mol was chosen to investigate the effect of PEG molecular weight on membrane properties. The membranes were prepared with PEG of 7 wt % concentration in the casting solution and with a 90-s evaporation when the molar proportion of the repeated unit of BPPO to TEA was 6. The plots of the pure water flux and the solute rejection against the molecular weight of the PEG additive are presented in Figure 6. It was surprising to find that pure water flux increased with the molecular weight of the PEG additive and then decreased and attained a plateau at a molecular weight of 1000, but that the rejections of solute increased in all cases. These results might have occurred because of the thermodynamics and precipitation kinetics of the membrane-forming system and the change in the polymer-casting solution. The plots

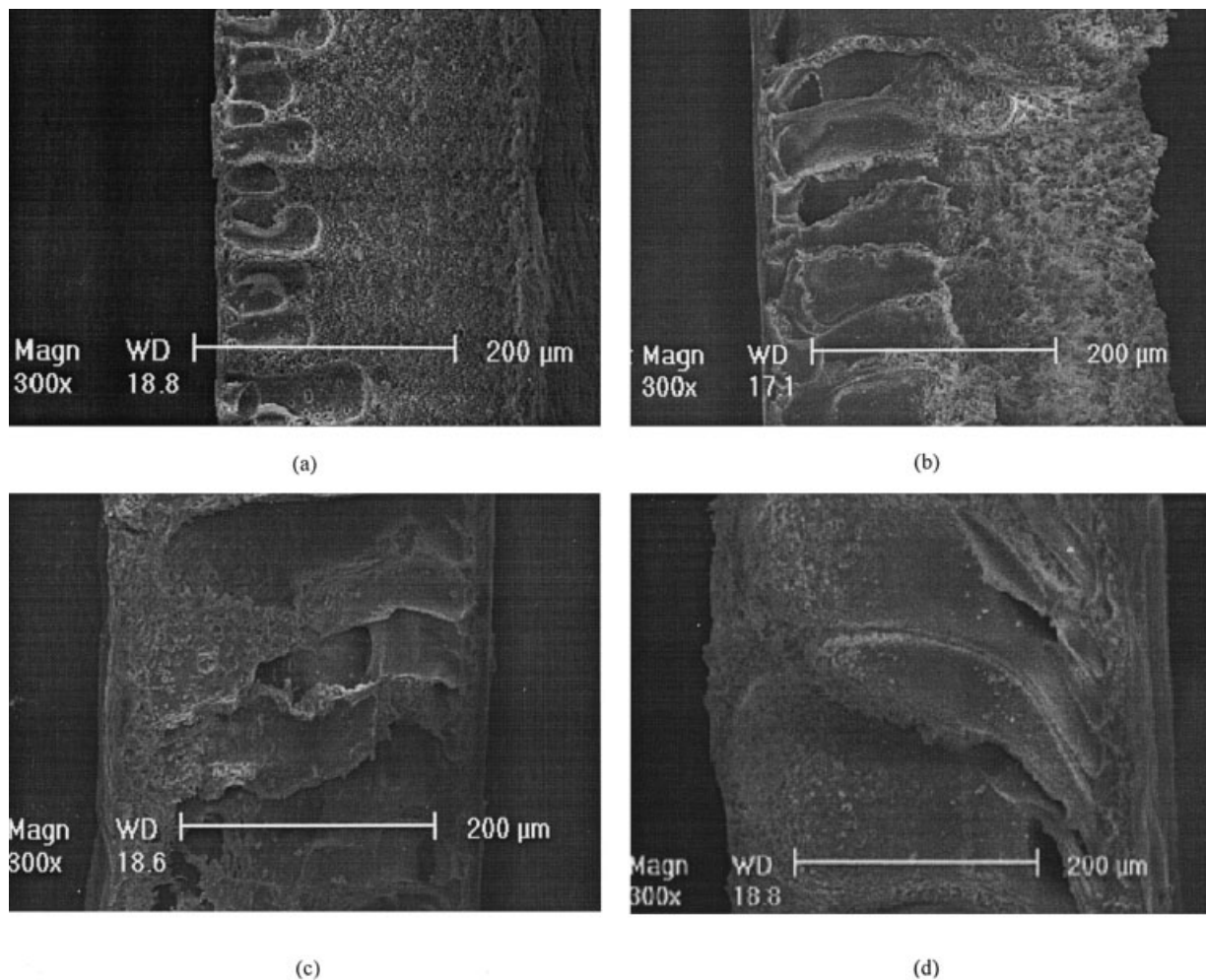


Figure 5 Morphological changes in the membranes prepared by varying the concentration of PEG in the casting solution: (a) 3.5 wt %, (b) 5.2 wt %, (c) 7.0 wt %, (d) 8.7 wt %.

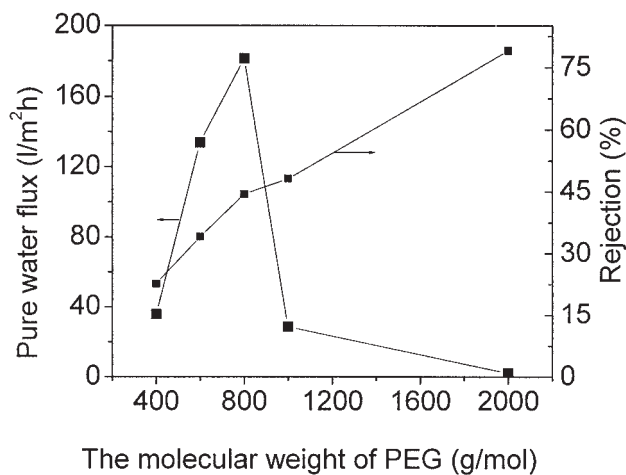


Figure 6 Effect of the molecular weight of the PEG additive in the casting solution on the pure water flux and the solute rejection of the membranes at a pressure of 0.20 MPa.

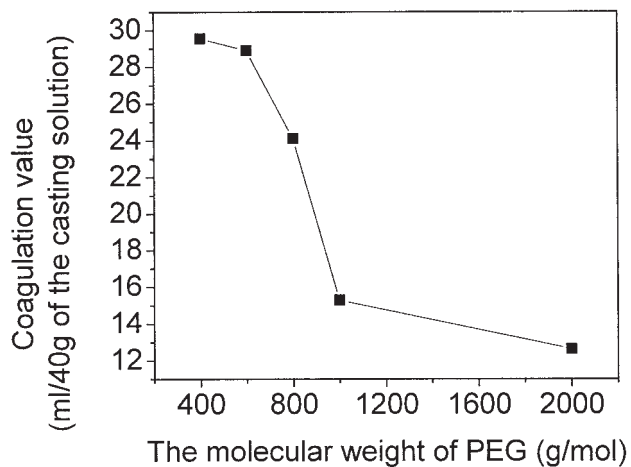


Figure 7 Effect of the molecular weight of the PEG additive in the casting solution on the coagulation value of 40 g of casting solution.

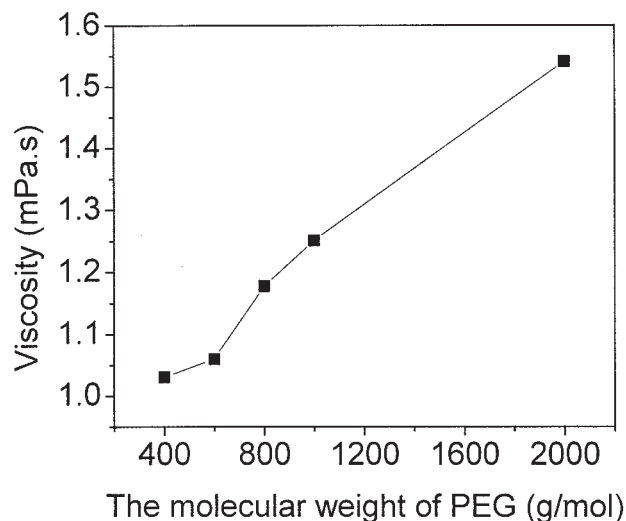


Figure 8 Effect of the molecular weight of the PEG additive in the casting solution on the viscosity of the casting solution.

of the coagulation value and viscosity of the casting solution against the molecular weight of PEG are given in Figures 7 and 8, respectively. It can be observed that when the molecular weight of the PEG additive increased from 400 to 800 g/mol, coagulation value decreased rapidly, which predominately determined the membrane-forming process, and then decreased slowly from 1000 to 2000 g/mol. This indicates that the casting solution became thermodynamically less stable, and a membrane with porous structure was obtained when increasing the molecular weight of the PEG additive from 400 to 800 g/mol. However, the slight enhancement of viscosity of the casting solution with an increase in PEG molecular weight from 400 to 800 g/mol played an unimportant role in the membrane formation process. The result is in accordance with the cross-sectional observations of the membranes prepared by using PEG additives of different molecular weights. Figure 9 shows the SEM cross-section photographs of the membranes. Obviously, when the molecular weight of PEG was less than 800, fingerlike pores with a large number of macrovoids [Fig. 9(a–c)] were enhanced with an increase in the molecular weight of PEG.

It also can be seen from Figure 8 that the addition of PEG of different molecular weights made the viscosity of the solution apparently increase, especially with PEG1000 and PEG2000. Despite the decrease in coagulation value because of the increase in PEG molecular weight, the substantially increased viscosity of the casting solution played a dominant role in PEG additives of higher molecular weight. Because the viscosity of the casting solution can severely hinder the exchange rate of the solvent and the nonsolvent during the phase inversion process, it slows the precipitation

rate of the membrane. Thus, the viscosity of the casting solution can be used as an important parameter to influence the precipitation kinetics and then the formation of the resulting membrane morphology. In contrast, with an increase in the molecular weight of PEG, the intermovement between the polymer and PEG became slower because of the longer chain of the PEG molecule. The PEG molecule might still have been retained in the membrane after the phase inversion process was completed. This is similar to increasing the polymer content, which leads to a dense membrane.²² Furthermore, the interaction of hydrogen bonding between DMF and PEG, mentioned above, was reduced with an increase in the molecular weight because of the decrease in hydroxyls in PEG of a higher molecular weight. Thus, the effective solvency of DMF to the polymer was relatively powerful. The higher the molecular weight of PEG in the casting solution, the more powerful was the effective solvency of DMF to polymer. Therefore, the aggregations of the polymer chains in the casting solution weakened in PEG of higher molecular weights. A denser membrane was obtained because of the lower precipitation rate. These hypotheses found further support in the SEM observations, which are shown in Figure 9(d,e). Obviously, the macrovoid formation in the cross section was suppressed when the molecular weight exceeded 800.

Therefore, the role of PEG of different molecular weights in membrane forming was as a pore-forming agent when the molecular weight was less than 800. However, when the molecular weight was more than about 1000, PEG acted as a pore suppresser and promoted the formation of smaller pores and lower porosity in the resulting membrane, which had a higher rejection rate and lower pure water flux.

CONCLUSIONS

The effect of the molecular weight of PEG as an additive in a casting solution on membrane performance and morphology was investigated. It was found that when the molecular weight of PEG was fixed at 600, the pure flux increased and the solute rejection decreased with an increase in PEG content in the casting solution. This is consistent with most observations of additive function. When PEG of a different molecular weight with the same content was added into a casting solution, the pure water flux of the membrane increased with the molecular weight of the PEG additive and then decreased and attained a plateau at a molecular weight of 1000, but the rejection of solute increased in all cases. These results can be explained through the thermodynamics and kinetics of the membrane-forming system by measuring coagulation value and viscosity. For the lower-molecular-weight system, coagulation value, which decreased with PEG

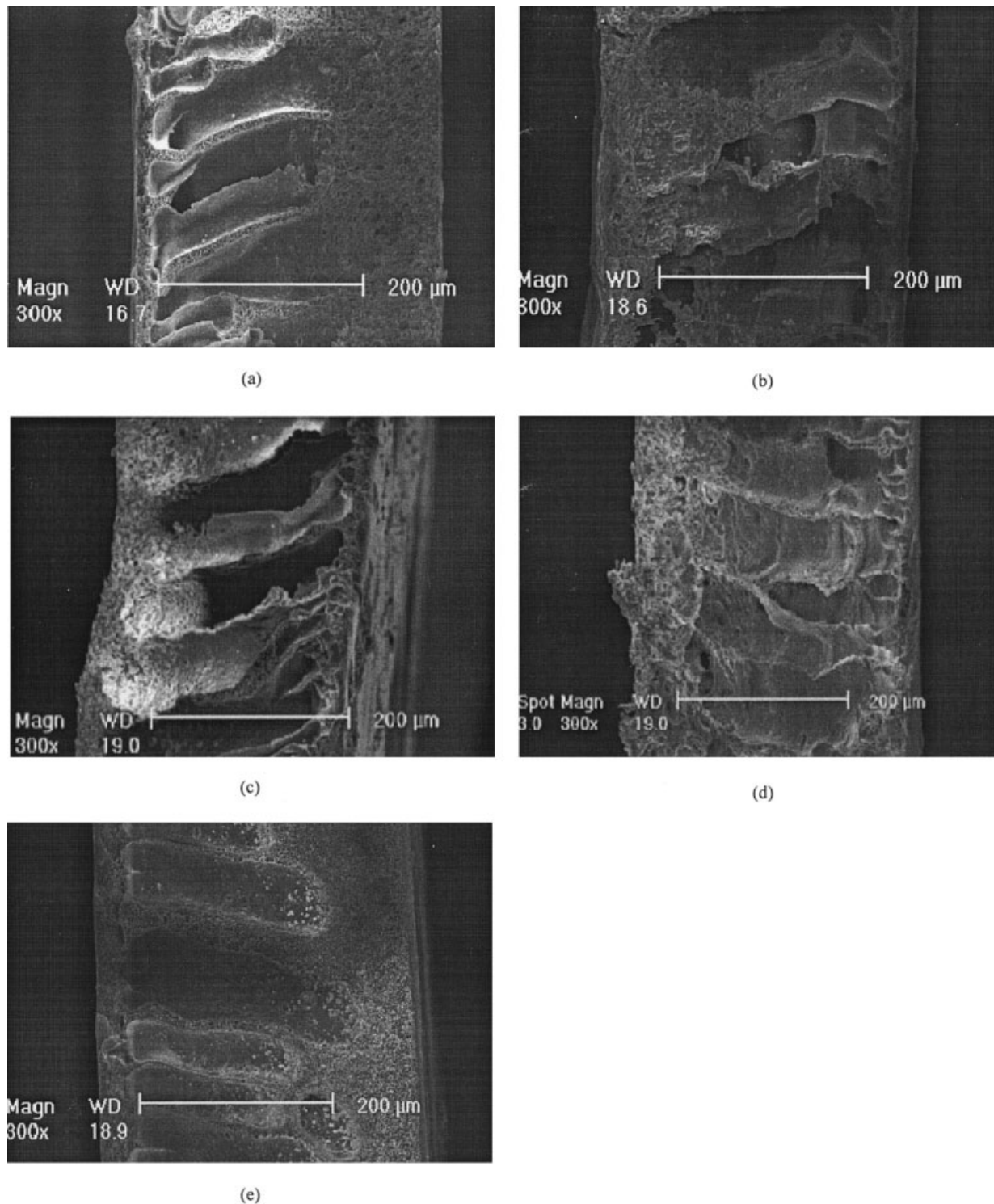


Figure 9 Morphology of the membranes prepared by varying the molecular weight of PEG additive: (a) 400 g/mol, (b) 600 g/mol, (c) 800 g/mol, (d) 1000 g/mol, (e) 2000 g/mol in the casting solution.

content, played a decisive role and tended to make the phase simultaneously demix and form a porous membrane; for the higher-molecular-weight system, the viscosity, which increased with PEG molecular weight, played a decisive role and tended to cause a delay in the phase demixing and the formation of a

dense membrane. These results are supported by the SEM observations of samples with different PEG contents and molecular weights.

Special thanks are given to Mrs. Mona L. Jacobs for reviewing the English.

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