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Hideto Matsuyama[a]; Taisuke Maki[a]; Masaaki Teramoto[a]; Kiyotaka Kobayashi[a]
[a] Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto, Japan

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**Hideto Matsuyama,* Taisuke Maki,
Masaaki Teramoto, and Kiyotaka Kobayashi**

Department of Chemistry and Materials Technology, Kyoto Institute
of Technology, Matsugasaki, Sakyo-ku, Kyoto, Japan

ABSTRACT

Polysulfone (PSf) membranes were prepared by the immersion precipitation method from casting solution of PSf and a water-soluble polymer, poly(vinyl pyrrolidone) (PVP), in dimethylacetamide. The effect of the molecular weight of PVP on the phase separation rate during the porous membrane formation was investigated by the light scattering method. The plots of scattered intensity against scattered angle showed maxima, which indicated that the phase separation occurred by spinodal decomposition. The structure growth rate remarkably enhanced by the addition of PVP with the lower molecular weight due to both the deeper quench depth and the lower polymer concentration brought about by

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*Correspondence: Hideto Matsuyama, Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan; Fax: + 81 75 724 7580; E-mail: matuyama@chem.kit.ac.jp.

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the PVP leaching into nonsolvent bath. The increase of PVP molecular weight resulted in a decrease of the structure growth rate. Moreover, with the increase of the molecular weight of PVP, the membrane structures were changed from a macrovoid structure to a sponge structure.

Key Words: Polysulfone; Poly(vinyl pyrrolidone); Immersion precipitation; Light scattering, Phase separation.

INTRODUCTION

Phase separation of polymer solution has been widely utilized to prepare polymeric porous membranes.[1] Immersion precipitation is one of the most popular phase separation methods. In this method, a polymer solution is cast on a support or extruded through a die, and then immersed in a nonsolvent bath. The phase separation occurs due to the exchange of solvent and nonsolvent. In many cases, casting solutions contained water-soluble polymeric additives for improving the membrane properties. The most important effects of the additives are increase of hydrophilicity of the membrane surface, suppression of macrovoid formation, and enhancement of pore interconnectivity.[2]

Poly(vinyl pyrrolidone) (PVP) was usually used as the additive in the preparation of porous polysulfone (PSf) or polyethersulfone (PES) membranes. A lot of studies have been reported in these systems.[3–8] Matsuura et al studied the effect of PVP on the performance of polyethersulfone ultrafiltration membranes.[3] The interaction between PES and PVP was strongest when the PVP/PES weight ratio was unity. They concluded that such a strong interaction caused an increase in the pore size and consequently, increased the permeation rate. In addition, it was shown that PVP was leached out into water almost completely while the membrane was stored or pressure-treated. Boom et al calculated the thermodynamics for the system PES/PVP/n-methylpyrrolidone(NMP)/water.[4,5] Using a model for mass transfer in this quaternary system, initial composition paths (concentration profiles) were also calculated. Based on these studies of thermodynamics and kinetics, the effect of the additive on the membrane structure was discussed. Han and Nam investigated thermodynamic and rheological variation in polysulfone solution by the addition of PVP and its effect in the preparation of PSf membrane.[7] At a low concentration (5 wt%) of PVP, the variation in thermodynamic property controlled the demixing process, resulting in an enhanced phase separation of the solution. On the other hand, with further increment of PVP, the solution demixing was delayed because the kinetic hindrance due to viscosity buildup overwhelmed the thermodynamic factor. Recently, Kang and Lee investigated the effects of the molecular weight of PVP on the precipitation kinetics during the formation of an asymmetric polyacrylonitrile membrane. The precipitation kinetics was explored using the light-transmission method and optical microscope observation.[8]

Knowledge of the kinetic property, such as the phase separation rate, is essential to control and design the structure of membranes prepared by the immersion precipitation method. However, few studies have been reported on the phase separation rate in the membrane formation by the immersion precipitation method. In our previous work, the phase separation rate during the porous membrane formation by the immersion precipitation method was investigated by the light scattering in polyimide-NMP-water system.[9] In this work, the phase separation rate in the presence of PVP additive was studied by the light scattering method. The effect of PVP additive on the phase separation rate and the membrane structure was investigated.

EXPERIMENTAL

Materials

Polysulfone (Udel P3500, Mw = 59000) from Amoco was used as polymer. Dimethylacetamide (DMAc, Wako Pure Chemical Industries Ltd., Osaka, Japan) was used as solvent without further purification. Poly(vinyl pyrrolidone) was purchased from Aldrich Chemical Inc. Three kinds of PVPs with Mw of 10,000, 55,000, and 1,300,000 were used. These are abbreviated as PVP10000, PVP55000, and PVP1300000.

Membrane Preparation

Casting solution was prepared by dissolving PSf and PVP in DMAc in the glove box where humidity was controlled at less than 20 wt% to avoid the penetration of water vapor into the polymer solution. Concentrations of PSf and PVP were usually 15 wt% and 10 wt%, respectively. The solution was cast on the glass plate with a thickness of 254 μm and then, immersed in a water bath for 24 hours.

Membrane Characterization and Solution Viscosity

The dry membranes necessary for membrane characterization measurement were obtained by a freeze-drying method. PVP leached out from the polymer solution into the bath water during the membrane formation process. To measure the PVP retention factor in the membrane, an elementary analysis (Yanaco Co. Ltd., Japan, MF-5) was carried out. The surface elementary composition of the membrane was measured by XPS analysis (JEOL Co. Ltd., Japan, JPS-9010MC/SP). Both PVP and DMAc contain a nitrogen atom. For the membrane prepared from the dope containing no PVP, elementary analysis and XPS analysis were carried out. The nitrogen contents in the membrane were negligible in both analyses, which indicates that almost of all of the DMAc was removed from the membrane. Thus, it was confirmed that the nitrogen in the membrane is attributable to only PVP. For SEM observation, the dry membrane was immersed in liquid nitrogen, fractured, and coated with Pt/Pd. A cross section was viewed by a scanning electron microscope (Hitachi Co. Ltd., S-800) under an accelerating voltage of 15 kV. The viscosity of the casting solution was measured by viscometer (Shibaura System Co. Ltd., Japan, VG-DA) at room temperature.

Light Scattering Experiment

Light scattering measurement was carried out with a polymer dynamics analyzer (Otsuka Electronics Co., DYNA-3000). The polymer solution was cast on the glass plate with a thickness of 254 μm. Then, the solution was immersed in the nonsolvent bath located between the laser and the detector. The nonsolvent solution was mixture of water and DMAc. When pure water was used as the nonsolvent, the phase separation rate was too fast to be measured. The temperature of the nonsolvent was 298°K. The light scattering due to the phase separation after the immersion in the bath was followed at the time interval of 0.1 sec.

RESULTS AND DISCUSSION

Figure 1 shows the effects of PVP molecular weight and PVP content in the casting solution on the PVP retention factors. The PVP retention factor is the weight percentage of PVP, that remained in the membrane. The retention factor increased with an increase in the PVP molecular weight. This is reasonable because an increase in the molecular weight brings about a decrease

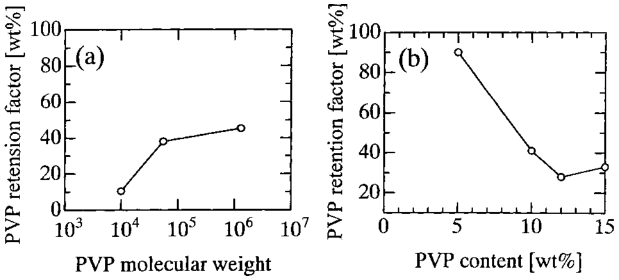

Figure 1. PVP retention factors. Immersion time in water bath was 5 min. (a) Effect of molecular weight. Concentrations of PSf and PVP in the casting solution were 15 wt% and 10 wt%. (b) Effect of PVP content in the casting solution. Total polymer concentration was 25 wt%. PVP molecular weight: 55,000.

in the PVP diffusivity and thus, PVP leaching into the water bath is prevented. The increase in the PVP content led to a decrease of the retention factor. As the PVP content increased, a large amount of PVP initially exists near the top surface contacted with water. The PVP molecule near the top surface leaches out into the water bath, which leads to the formation of porous toplayer. The decrease of the retention factor is owing to this porous structure.

The nitrogen weight percents at both membrane surfaces measured by XPS analysis are summarized in Table 1. The top surface contacted with the water, while the bottom surface contacted the glass plate. In this table, the average nitrogen weight percentages are also included. The average nitrogen percentages are the average values inside the whole membrane and were calculated from the PVP retention factor. For all PVPs, the nitrogen weight percents at both surfaces were larger than the average value, which indicates that PVP was localized at both surfaces. Since PVP is a hydrophilic polymer,

Table 1. Nitrogen weight percents at both surfaces and solution viscosity.

PVP molecular weight	Nitrogen weight percent [wt%] Top surface	Bottom surface	Average value	Solution viscosity [Pa.s]
10,000	2.32	4.00	0.52	0.66
55,000	3.44	4.19	1.93	1.43
1,300,000	4.20	6.33	2.26	23.2

Concentrations of PSf and PVP were 15 wt% and 10 wt%, respectively.

it is likely to exist at the interface between the membrane and water and a part of it leaches out into the water bath. PVP was localized near the glass surface due to the hydrophilic silanol groups at the glass surface. The membrane peeled off the glass plate just after the glass plate was immersed in water. Therefore, another reason for the localization of PVP on the bottom surface may be the interaction between PVP and water similarly to the localization on the top surface.

Figure 2 shows an example of the light scattering experiment in a time interval of 0.2 sec. The maxima were observed in the scattered intensity I_s. This means that the phase separation occurred by spinodal decomposition rather than by nucleation and growth.[10] As time passed, the peak position of I_s shifted into the smaller angle region, which indicates the growth of the structure. The interphase periodic distance (interdomain distance) Λ is given by the following equation.[10]

$$\Lambda = \frac{\lambda_0}{2n_0 \sin(\theta/2)} \tag{1}$$

Here, n_0 is the refractive index, λ_0 is the wavelength of light in vacuo (633 nm), and θ is the scattered angle at which I_s showed the maximum. The values of θ were obtained from the experimental data of the light scattering, such as is shown in Fig. 2.

Figure 3(a) shows the time course of Λ when the water content in the nonsolvent bath was changed. In this experiment, only PSf was used and no PVP was added to the polymer solution. As the water content increased, the structure growth rate increased. It was reported that the structure growth rate

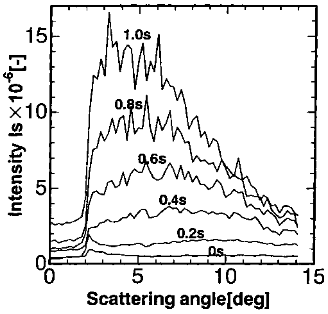

Figure 2. Light scattering profile. Concentrations of PSf and PVP in the casting solution were 15 wt% and 10 wt%. PVP molecular weight: 55,000. Weight ratio of water to DMAc in nonsolvent bath = 7:93.

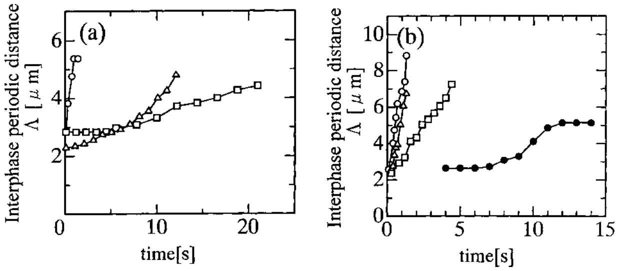

Figure 3. Time courses of the interphase periodic distance Λ. (a) Effect of nonsolvent bath composition. PSf alone. Polymer concentration = 20 wt%. ○: ratio of water to DMAc in nonsolvent bath = 10:90, △: 7:93, □: 5:95.(b) Effect of PVP molecular weight. Ratio of water to DMAc in nonsolvent bath = 7:93. Concentrations of PSf and PVP in the casting solution were 15 wt% and 10 wt%. ○: PVP molecular weight = 10000, △: 55000, □: 1300000, ●: PSf alone (25 wt%).

increased with the increase of the quench depth (distance from the spinodal line).[11,12] The higher water content leads to a high rate of water inflow into the polymer solution. Thus, the composition of the polymer solution moves deeper inside the spinodal line before phase separation occurs. This brings about a deeper quench depth.

The effect of the PVP molecular weight on the structure growth rate is shown in Fig. 3 (b). In all cases, the total polymer concentration in the casting solution was fixed to be 25 wt%. The fastest growth rate was obtained when PVP10000 with the lowest molecular weight was added. Since PVP is a hydrophilic polymer, the existence of PVP promoted water inflow, which leads to a deeper quench depth. This is the reason for the large growth rate. Another reason is the leaching of PVP into the water bath, as described previously. The PVP leaching brought about a decrease in the polymer concentration and thus, the promotion of the growth rate. As of the molecular weight of PVP increased, the growth rate decreased. Even in the case of PVP1300000, however, the growth rate was faster than in the case of PSf alone. The decrease in the growth rate is owing to both the increase of the solution viscosities, (the experimental data are included in Table 1) and the decrease in PVP leaching (shown in Fig. 1).

Figure 4 shows the cross-sectional morphologies of several membranes. The membranes prepared with PVP10000 and PVP550000 showed macrovoids as well as that prepared with PSf alone. However, the addition of PVP1300000 led to a sponge structure rather than a macrovoid structure. Similar disappearance of the macrovoid structure by the addition of PVP with

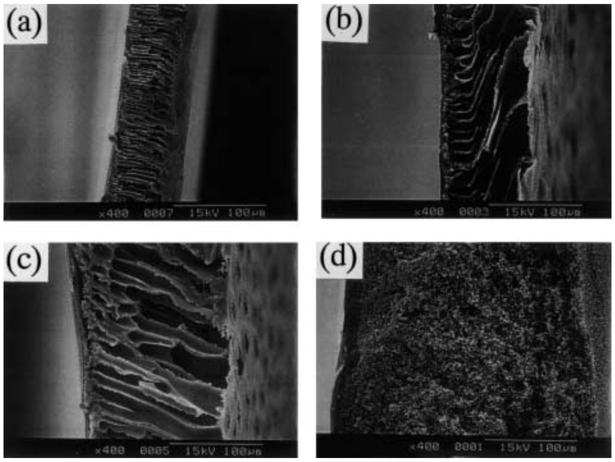

Figure 4. Cross-sectional morphologies. (a) PSf alone (25 wt%), (b) PVP molecular weight = 10000, (c) 55000, and (d) 1300000. Right and left sides correspond to top and glass surfaces, respectively. Concentrations of PSf and PVP in the casting solution were 15 wt% and 10 wt%.

high molecular weight was reported by Kang and Lee in the polyacrylonitrile membrane formation.[8] For macrovoid formation, the membrane must have a skin to limit the penetration of a large amount nonsolvent into the sublayer below the skin and must prevent nuclei formation after a few nuclei, which were the origins of the macrovoids, formed.[13] The formation of a lot nuclei cannot make the macrovoids. Therefore, a porous top layer can suppress macrovoid formation and leads to a sponge-type structure. In the membranes prepared with PVP10000 and PVP55000, the distance from the top surface to the starting point of a macrovoid was larger than that in the membrane prepared with PSf alone. PVP is likely to leach out from the membrane and the structure (pore) growth rate became faster with PVP, as described in the light scattering section. This leads to the formation of the porous top layer. Thus, a larger distance from the surface to the starting point of the macrovoid is necessary to limit the penetration of a large amount of nonsolvent into the sublayer. The higher molecular weight of PVP with lower diffusivity prevents the aggregation of the polymer molecules in the top layer, resulting in the formation of more porous top layer.[13] This is the reason that the whole sponge structure was obtained with the addition of PVP1300000.

CONCLUSION

The effects of a PVP additive on porous polysulfone membrane formation were investigated by an immersion precipitation method. The phase separation rate during membrane formation was measured by light scattering. A faster structure growth rate was obtained with the addition of PVP with a lower molecular weight. This was due to both the deeper quench depth and the lower polymer concentration brought about by the PVP leaching into the nonsolvent bath. The growth rate decreased with an increase in the molecular weight of PVP.

The membrane prepared with PVP with a low molecular weight showed macrovoids, while the addition of PVP with a high molecular weight suppressed the macrovoid formation and led to a sponge structure formation. The formation of a sponge type membrane was attributable to the porous toplayer.

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