

# Phase Structure in the Blend of Atactic Poly(vinyl alcohol) with Atactic Poly(vinyl alcohol-*block*-vinyl acetate)

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**ABSTRACT:** An almost fully saponified atactic poly(vinyl alcohol) and an atactic poly(vinyl alcohol-*block*-vinyl acetate) of which degree of saponification is 89 mol % were blended by a solution casting method. The phase structure of the blend film was analyzed by optical microscopy,  $^{13}\text{C}$ -NMR, and differential scanning calorimetry. The most remarkable structure of the blend was composed of cylindrical domains penetrating the film. The swelling behavior of the blend films was also investigated in the dimethylsulfoxide and water mixed solvents to find differences in solubility and

diffusion behavior between the matrix and the domain. The cylindrical domains could be selectively dissolved away in water and the film became porous. We tried to change the size of the cylindrical domain with various film preparation conditions. This aimed to turn the film into the useful filter membrane. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1807–1815, 2002

**Key words:** blends; block copolymers; films; swelling; phase separation

## INTRODUCTION

We have been studying binary blends among various poly(vinyl alcohol)s with different molecular structural factors including the syndiotacticity, the degree of saponification (DS), and the block character (blocky or random copolymers). The first pair of PVAs we studied were an atactic (a-) PVA and a syndiotacticity-rich (s-) PVA.<sup>1,2</sup> They are cocrystallizable with each other. This is a very reasonable result because they are chemically identical with each other. The syndiotacticity diad contents are 55 mol % for the a-PVA and 57 mol % for the s-PVA samples we used.<sup>1</sup> The only 2% difference over 55 mol % in the syndiotacticity is a significant one that can induce differences in the properties of PVA, such as solubility in water and gelation. The pair of a fully saponified a-PVA and a partially saponified PVA with a DS of 88.9 mol %, called b-PVA, is the blend that we report here. Because these two PVAs are mainly composed of a common structural unit of vinyl alcohol, the cocrystallization seemed

to be available. However, they showed a phase-separated morphology containing monodispersed mm-size cylindrical domains.

In this report, we will discuss how the domain structure can be controlled by the sample preparation method. Our aim of this work is to produce porous films from the a-PVA and b-PVA blends and use them as filtration membranes. The porosity could be obtained by selectively removing the domains through soaking the phase-separated blend films in water at room temperature, because the two phases are different in solubility. The desired size of the pore may be smaller than 10  $\mu\text{m}$  as a filter.

The swelling nature of poly(vinyl alcohol) films is quite extraordinary one in dimethylsulfoxide (DMSO) and water-mixed solvents.<sup>3,4</sup> The diffusion process of the solvent changed from the Fickian type to the Case II type depending on the solvent composition and swelling temperature. The swelling of the a-PVA and b-PVA blends was investigated in the DMSO and water solvents to analyze their phase structure.

## EXPERIMENTAL

### Samples

A commercial source, Gosenol NH-26, from the Nippon Synthetic Chemical Industry Co. Ltd., Japan,

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TABLE I  
Characteristic Data for PVA Samples Used

Sample	Residual sodium acetate (wt %) <sup>a</sup>	$\overline{DP}^b$	s-diad <sup>c</sup> (mol %)	DS <sup>d</sup>	Block character <sup>e</sup> $\eta$
A	1.66	2000	53.0	0.998	0.46
B	0.525	890	—	0.887	0.50
B'	0.218	810	51.5	>0.999	—

<sup>a</sup> Measured by a titration method (JIS K 6726).

<sup>b</sup> Average degree of polymerization determined by a solution viscometry method.<sup>5</sup>

<sup>c</sup> s-diad in mol % was measured by a <sup>13</sup>C-NMR method.<sup>7</sup>

<sup>d</sup> Degree of saponification determined by a titration method (JIS K 6726).

<sup>e</sup> Block character was measured by a <sup>13</sup>C-NMR method.<sup>8</sup>

was used as received as the poly(vinyl alcohol) sample and called A. A commercial product of B-12F from Denki Kagaku Kogyo Co., Japan, was used as received. This is the poly(vinyl alcohol-co-vinyl acetate) sample and called B. Another PVA sample was prepared by fully hydrolyzing the B sample to estimate the syndiotacticity of B and called B'. The characteristic data for the PVA samples are listed in Table I. The content of residual sodium acetate in each sample and the DS values were estimated by titration according to the Japanese Industrial Standard for testing methods for poly(vinyl alcohol) (JIS K6726). The average degree of polymerization (DP) was determined after the sample was modified into a soluble polymer of poly(vinyl acetate) (PVAc) in benzene through acetylation. From the solution viscosity data of the PVAc sample in benzene at 30°C, the DP value was evaluated according to Nakajima et al.'s equation.<sup>5</sup> The s-diad (mol %) value in the table was the diad syndiotacticity  $r$  calculated from the triad tacticities of  $mm$ ,  $mr$ , and  $rr$  according to an equation of  $r = rr + 1/2 mr$  ( $m = mm + 1/2 mr$ ).<sup>6</sup> The triad tacticities of the sample were determined from the relative intensity of the triplet of CH carbon resonances of a <sup>13</sup>C-NMR spectrum measured for its deuterated dimethylsulfoxide solution (10 wt %), according to Wu et al.<sup>7</sup> The s-diad values obtained for the two samples [A and B (B')] indicate the atactic nature. The block character  $\eta$  was determined from a <sup>13</sup>C-NMR spectrum obtained for a solution of the sample polymer in D<sub>2</sub>O (10 wt %) at 60°C, according to Bugada et al.'s method.<sup>8</sup> The resultant  $\eta$  values around 0.5 mean that the vinyl acetate units are incorporated as blocky sequences in the samples A and B.

### Preparation of blend films

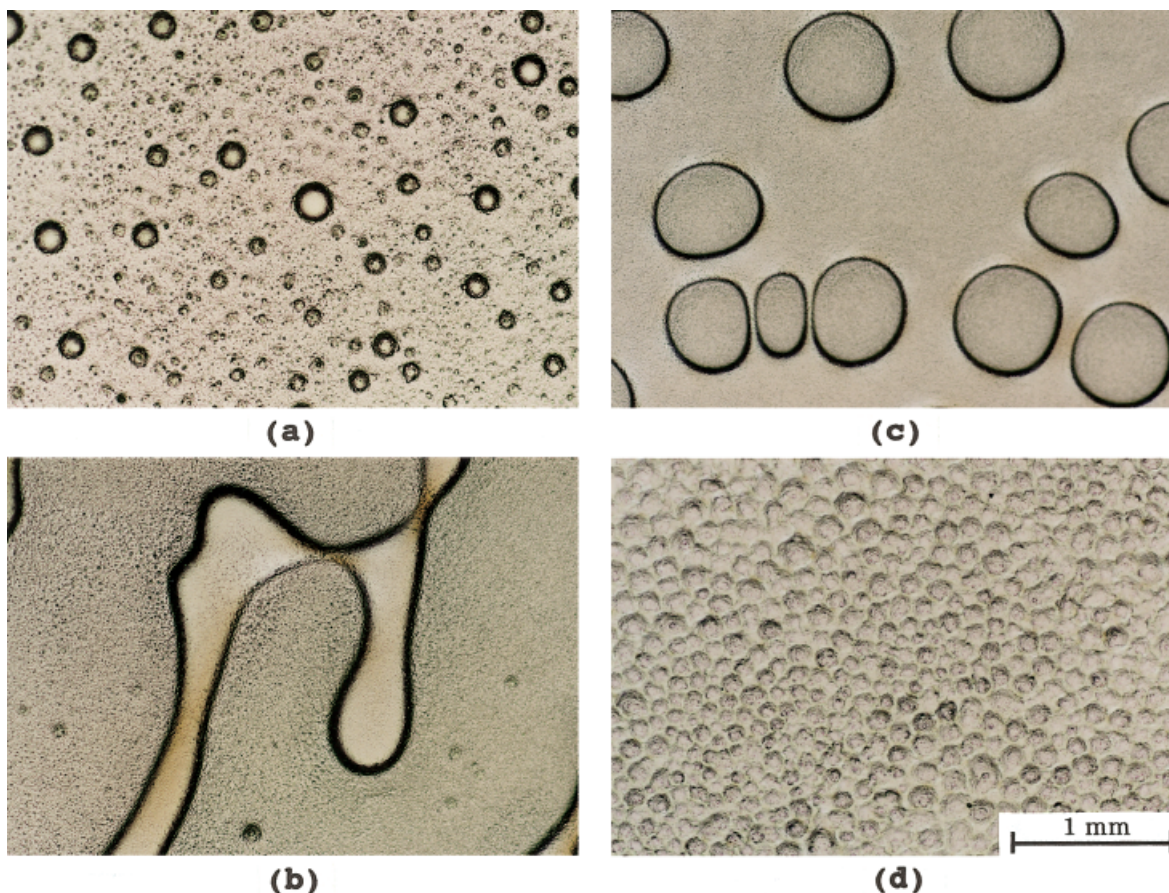
Blend films with each given blend ratio, A/B (wt/wt), were prepared by a solution casting method. The two polymers (5 wt %) of a given blend ratio was dissolved into water (10 mL) in a sealed test

tube at 120°C. It is very important to state that the total weight of polymer (0.526 g) and the volume of the solvent (10 mL), which are put in a test tube were our fixed standard values. (Characteristics of the macroscopically separated phase structure in the finally obtained dried film change with its evaporation rate of solvent during film casting. The rate can be mainly controlled by the amount of solution poured and the size of a Petri dish into which the solution was poured.) All amount of the solution thus prepared in the test was directly poured into a Petri dish of a 87-mm inner diameter, and they were kept at a constant temperature for 2 or 3 days to evaporate the solvent of water. For this evaporation, we used an air-circulating type of temperature-controllable box. The dried film thus obtained was further dried *in vacuo* at 50°C for 1 week and then at 150°C for 20 min. The preparation method described above is called the standard method with respect to the evaporation rate of solvent.

The evaporation rate was controlled in the other three methods, which were different from the standard one at the following points. To evaporate quickly, the same amount of solution poured into the same size dish as that in the standard method was kept under a reduced pressure (5 mmHg) which was realized by setting it in a vessel evacuated by an aspirator. To evaporate slowly, following two methods were adopted. In one of the methods, three times larger amount of the solution (31.579 g) than the standard method was poured into the Petri dish. In the other method, the standard amount of solution (10.526 g) was poured into the Petri dish and then the lid was set on the dish.

### Measurements

The phase structure of the blend films were observed by a Nikon microscope and the photographs obtained were analyzed using an image processing and analysis system, MacScope, by Mitani Co., Japan.



**Figure 1** Optical microscopic photographs taken for the A/B blend films with various blend ratios of A/B (wt/wt): (a) 34/66, (b) 35/65, (c) 40/60, and (d) 45/55.

$^{13}\text{C}$ -NMR measurements for the estimation of triad tacticities, *mm*, *mr*, and *rr*, and the block character of the PVA samples were performed on a Bruker AVANCE 400 NMR spectrometer.

Film specimens of a  $20 \times 30$ -mm size were cut out of a blend film for the swelling experiment. They were soaked in mixed solvents of DMSO and water of various mixed ratios at  $40^\circ\text{C}$ . The specimen was periodically taken out of the solvent to weigh the film. The swelling ratio is expressed as  $M_t/M_o$ , where  $M_o$  and  $M_t$  are the weight of specimen before swelling and after the swelling period of time  $t$ .

Differential scanning calorimetry (DSC) was performed as described in our previous article.<sup>3</sup> The crystallinity,  $X_c$ , was estimated by the following equation.

$$X_c(\text{wt } \%) = \Delta H / \Delta H_c \times 100 \quad (1)$$

where,  $\Delta H$  is the observed heat of fusion in  $\text{kJ}/(\text{mol VA unit})$  from the area of the melting endotherm and  $\Delta H_c$  is the reported heat of fusion for the PVA crystal phase [ $6.87 \text{ kJ}/(\text{mol VA unit})$ ] by Tubbs (VA means the vinyl alcohol unit).<sup>9</sup> For calculation of the  $\Delta H$  value, the molar fraction of the VA unit in the sample

was used, which was measured by the titration method.

## RESULTS AND DISCUSSION

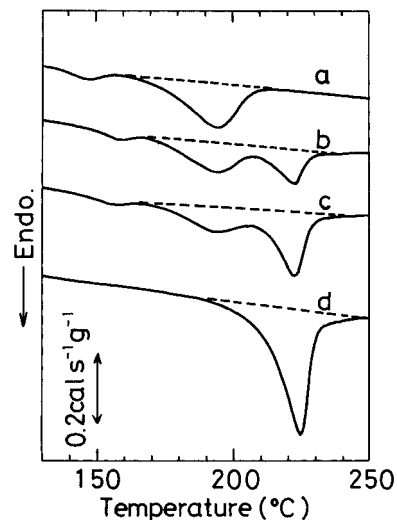
### Phase structure analysis

Figure 1 shows optical microscopic photos for the blend films with various blend compositions around a ratio of A/B (wt/wt) = 40/60. These blend films are between  $77$  and  $85 \mu\text{m}$  in thickness. The almost same thickness means that the evaporation of the solvent during film formation proceeded at the same rate between these four cases. The most remarkable structure found in the blends is circular domains as shown in Figure 1(c). All of the circular domains penetrate the film in its thickness direction. So we call this circular domain the cylindrical domain. The blend composition region where the cylindrical domains appear ranges the contents of the A component from 36 to 43 wt %. This region is called the d-region. Above a content of the A component of 45 wt %, the cylindrical domain never appears, and the surface of its film is covered by a

number of particle-like structures, so this region is called the p-region. The two regions overlap with each other. The particle-like surface structure can be also seen in Figure 1(b) and (c), but their particles are smaller than that in Figure 1(d). The p-region could be detected up to 55 wt % of the A content. The films over the 55 wt % content were transparent.

There are two types of domain-containing structure above and below an A content of 35 wt %. The shape of the domain seen in Figure 1(a) is not cylindrical but spherical. The region of the A content below 34 wt % is called the d'-region. The d'-region where the spherical domain could be detected narrowly ranged the A contents between 30 and 34 wt %. The films under the 30 wt % content were transparent. The 35 wt % content is called the boundary region. The change from the spherical domain containing structure in Figure 1(a) to the boundary structure in Figure 1(b) occurs by only 1% of change in the A content. The boundary structure seems to have a similar structure to that in Figures 1(c), but its periphery of the domain is not simply circular, while that in Figure 1(c) is circular in the film plane. The presence of the boundary structure means that a type of domain-containing structure changes to another type of one with the change in blend composition through the 35 wt % content. The minor component in a blend system must be the major component in its domain region. So the major component dominating domains is the A component in Figure 1(a) and the B component in Figure 1(c). This was partly ascertained by measuring regional blend compositions in the domain and the matrix of the 40/60 blend film. The two regions in the film was easily separated by cutting it by a usual blade cutter, because the domain size is as large as 0.5–1.0 mm in diameter. The regional blend composition was estimated from the DP value of the cut film that was measured by  $^{13}\text{C}$ -NMR and the DP values for the two neat polymers previously obtained by the titration method (0.995 for the A sample and 0.887 for the B sample). The calculation details are described in the Appendix section. The regional blend ratio A/B (wt/wt) thus estimated is 41/59 for the matrix and 25/75 for the domain. These results indicate that the component B is the dominating one in weight for both the regions, but it is the very dominating one in the domain region. The apparent total blend ratio of the whole area of the film was also calculated to be 38/62 from the two regional blend ratios indicated above and the total weight fractions of the two regions in the film, which is considered to be the same as the actual blend ratio of 40/60. This indicates that the film is constructed by these two phases.

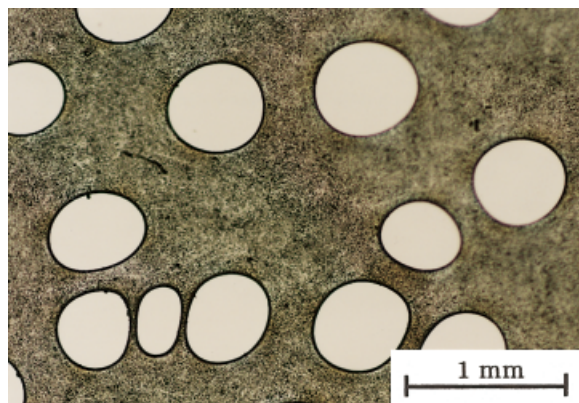
The phase structure of the 40/60 film was investigated through the crystal phase by DSC. The DSC traces for the two regions, the domain and the ma-



**Figure 2** DSC traces for the neat samples B (a) and A (d) and the A/B (wt/wt) = 40/60 blend samples ((b) and (c)). The DSC specimen for the blend samples were cut from the domain region for (b) and from the matrix region for (c).

trix, are shown in Figure 2 with those for the neat samples. There is a substantial distance between the peak melting temperatures of the two neat samples: 223 and 193°C for samples A and B, respectively. Further, as they are not miscible with each other in the crystal phase, the peak temperatures does not shift in the blend. It should be stated here that the precise composition cannot be estimated from the area corresponding to the melting endotherm peak because the crystallinity is not in proportion to the blend composition. However, the melting curves b and c in Figure 2 indicate that the content of B is larger in the domain (curve b) than the matrix (curve c).

There is a remarkable difference in solubility in water at room temperature between the two neat films. The B film easily dissolves, whereas the A film does not dissolve but only swells. Their crystallinity values were previously enhanced to their highest achievable levels by heat treatment. The observed values of the heat of fusion,  $\Delta H$ , from the area of the melting endotherm are 3.02 (43.9) and 1.90 kJ/(mol VA unit) (27.6 wt %) for the A and B samples, respectively. The attached values in the parentheses are the crystallinity ones. The difference in solubility of the neat films must be related to the difference in crystallinity. But the major factor that dominates the film solubility is crystal morphological factor such as the size of the crystallite and the molecular packing order in the crystallite. The size and the packing order in the B film must be less than those in the A film, because the sequence of the vinyl alcohol unit, the crystallizable unit, is shorter in the B molecule than in the A molecule. These difference



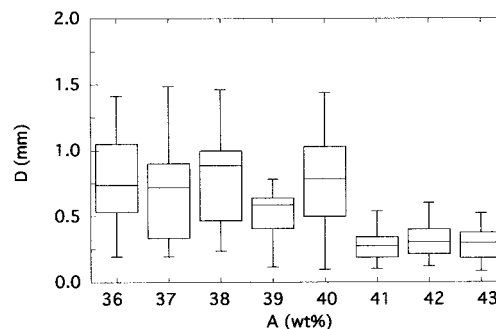
**Figure 3** An optical microscopic photograph for the A/B (wt/wt) = 40/60 blend film that was soaked in water and subsequently redried. The same position of the film was photographed as that before soaking treatment in Figure 1(c).

results in the lower melting temperature, the lower crystallinity, and the easy solubility in water of the B film.

The solubility behavior of the blend film changed above and below the boundary region. On soaking in water, the film in the d'-region dispersed into water, whereas the films in the d-region became porous films. The porous film thus obtained from the A/B (wt/wt) = 40/60 blend is shown in Figure 3. Because the film in the d'-region had the water-soluble matrix and the small spherical domains, the film could not maintain the film shape. On the other hand, the film in the d-region which is composed of the soluble domains and the insoluble matrix could keep the shape of the film. It is apparent that the blend film in the d'-region is unsuitable for a membrane filter. The easy solubility of the domain in the d-region is due to the small crystallite size and the low packing order in the crystal phase. This selective solubility of the domain can be also understood from the total crystallinity data by DSC: 27.2% in the domain and 32.5% in the matrix.

The cylindrical domain-containing structure appeared in the region from 36 to 43 wt % of the A content was analyzed by the image processing and analysis system. The size distribution of the domain was shown in Figure 4. The following features can be induced from this figure. First, the average diameter is not a monotonously decreasing function of the content. Second, the average values below 40 wt % are twice larger than those above 41 wt %. The percentage of surface area of the whole domains in the film surface,  $x$ , was estimated as a function of the A content, as shown in Figure 5. It shows that the  $x$  is an decreasing function of the A content.

It is concluded from Figures 4 and 5 that the decrease of the  $x$  is mainly due to the decrease of the

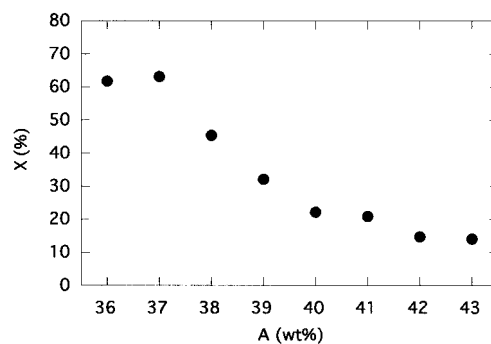


**Figure 4** The diameter of the domain in the blends in the d-region is plotted against the content of the A component. The upper and lower bars represent the maximum and minimum values, respectively. The box means the region in which the 50% of the observed values are contained and the line located in the almost central level of the box means the average value.

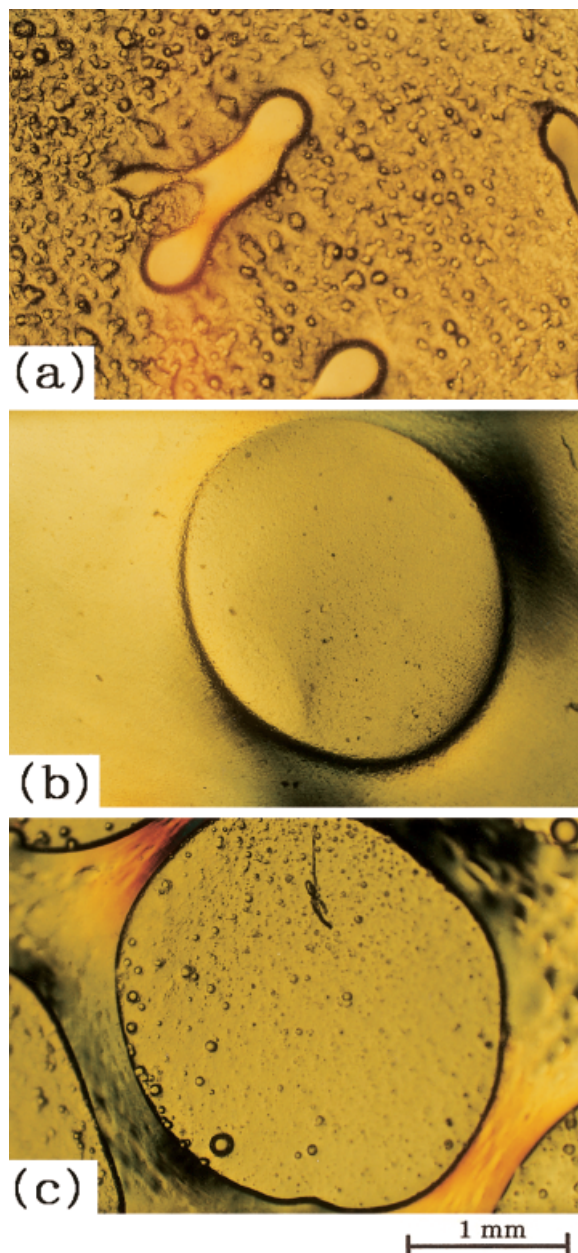
number of the domains. The twice difference in the domain size below 40 wt % and above 41 wt % indicates that the domains coalesce with each other in the film preparation process. The smaller domains above 41 wt % must be frozen in more previous stage of the coalescence compared with those below 40 wt %.

#### The domain size control by evaporation rate

Our aim of this work is to produce a micro porous film from our blend. If the microporous film can be prepared from the 40/60 blend, we will have to reduce the size of the pore, namely the domain size below 1–10  $\mu\text{m}$ . The attempt for reduction of the size was done by changing the film-preparation condition. The evaporation rate of the solvent was forcibly increased by setting the cast solution under a reduced pressure. This attempt was based on an idea that the phase separation process can be frozen in a relatively early stage of coalescence by too much fast evaporation rate. If the polymer concentration was increased by evaporation of the solvent, the separation process ceased



**Figure 5** The percentage of the domains by surface area ( $x$ ) is plotted against the content of the A component.



**Figure 6** Optical microscopic photographs of the A/B (wt/wt) = 40/60 blend films that were prepared by various methods: (a) from the standard solution under a reduced pressure, (b) from the solution with triple weight and the same concentration as the standard one, and (c) from the standard solution in the Petri dish with its lid.

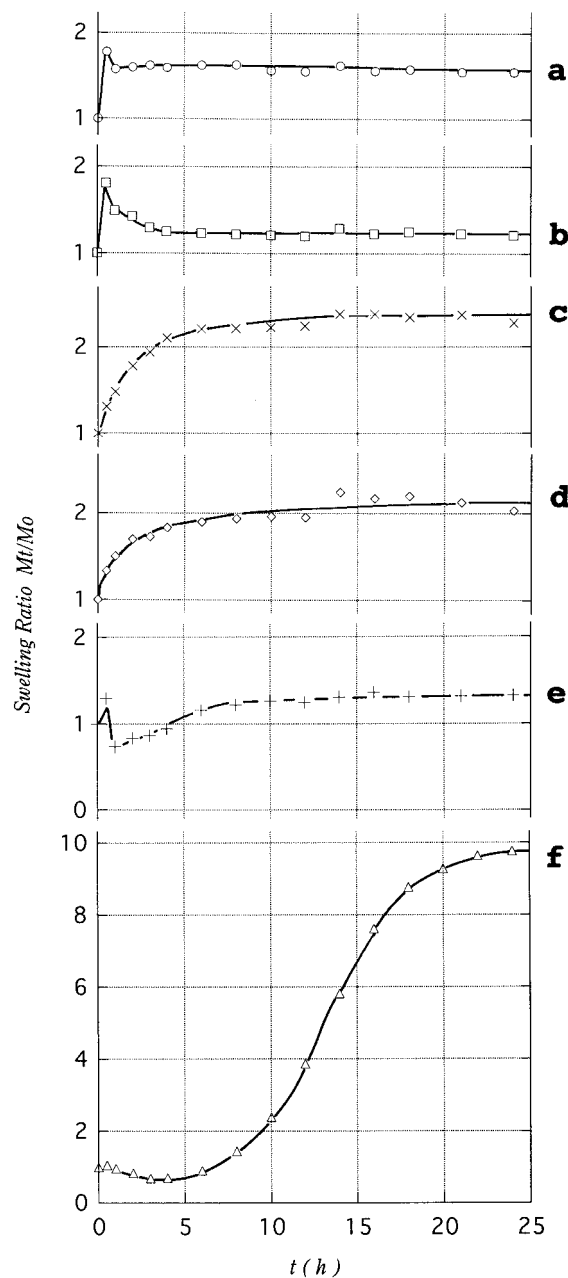
due to the limited mobility of the polymer. The film thus obtained had smaller size of the domains, but their shape was not circular in the plane, as shown in Figure 6(a). This figure shows the domains just coalescing with each other. The size is still bigger than that we aimed.

For a control experiment, the rate was decreased by the two ways described in the experimental section. As expected, the two films thus prepared have do-

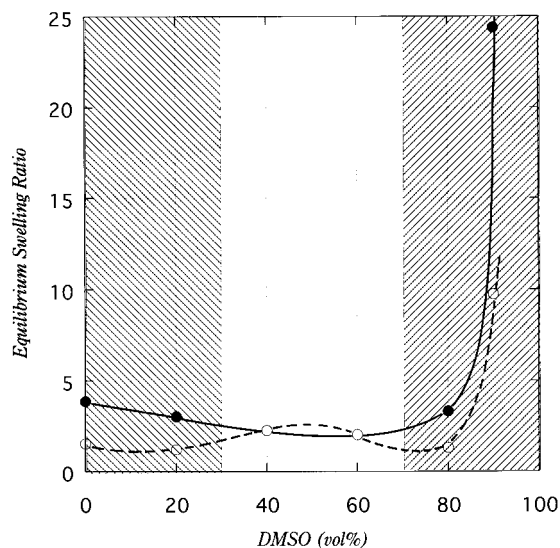
main with almost three or five times larger size than the standard film as shown in Figure 6(b) and (c). The relationship between the domain size and the evaporation rate has been clearly shown in Figure 6.

### Swelling

Figure 7 shows swelling ratio vs. time curves for the initial 25-h swelling of the A/B (wt/wt) = 40/60 film



**Figure 7** Swelling ratio  $M_t/M_0$  vs. swelling time  $t$  curves for the A/B (wt/wt) = 40/60 blend film at 40°C in the DMSO/water solvent with different ratios (vol/vol): (a) 0/100 (water), (b) 20/80, (c) 40/60, (d) 60/40, (e) 80/20, and (f) 100/0 (DMSO).



**Figure 8** Equilibrium swelling ratio the A/B (wt/wt) = 40/60 blend film in the DMSO/water solvent at 40°C as a function of solvent composition (DMSO vol %). The ratio was calculated to the weight of the dried sample before (○) and after (●) swelling.

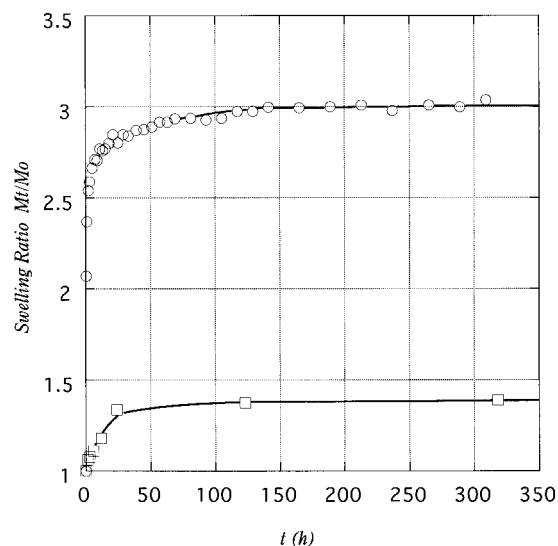
in the mixed solvents of DMSO/water with various mixing ratios. In all the solvents except the solvents with DMSO/water (vol/vol) = 40/60 and 60/40, the swelling ratio increased with time in the very initial stage of swelling, and then conversely began to decrease to a lower level of swelling ratio. The decreasing processes in the 80/20 and 90/10 solvents reach ratios lower than unity and then go into the increasing processes again. The appearance of peaks in the initial swelling stages means the weight loss of the film due to the dispersion of the domains into water, as described in Figure 3. The second increase stage observed in the 80/20 and 90/10 solvents is due to the Case II and the subsequent super Case II processes occurring in the matrix region. The Case II process very slowly proceeds compared with the dispersion of the domain.

The equilibrium swelling ratios are plotted by empty circles in Figure 8. As some of the films lost their weight on swelling, these ratios are the apparent ones. So they are recalculated for the films that lost their weight during swelling, assumed that the polymer weight in the equilibrium swelling state is equal to the polymer weight of the matrix region, and plotted by the solid circles in Figure 8. From the recalculated curve (solid line), the same dependence on the DMSO content as that reported for the neat PVA can be seen,<sup>3</sup> indicating that above assumption is correct. The shadowed region in Figure 8 coincides with the region where the neat B sample causes dispersion into water. The DMSO and water molecules is reported to most tightly form a com-

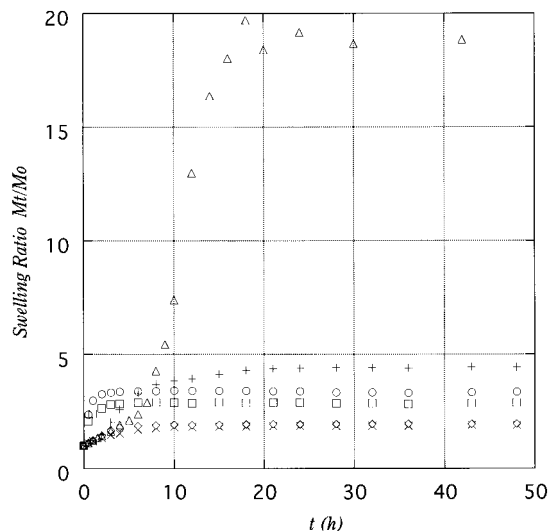
plex when the molar ratio DMSO/water is around 1/3, which corresponds to a volume ratio 57/43.<sup>9,10</sup> Our minimum position of the solid line coincides with that of their report. The tight interaction between the two solvent molecules means the weakest affinity of the PVA molecules and the solvent molecules. This is the reason why the films do not lose their weight in the DMSO/water (vol/vol) = 40/60 and 60/40 solvents.

The swelling ratio vs. time curves for the two neat PVA films, A and B, in the DMSO/water (vol/vol) = 60/40 at 40°C are shown in Figure 9 (the curve for A is from our previous paper<sup>3</sup>). The solvent with this mixing ratio is one of the solvent in which all of the blend films we used cannot be dissolved. The curve for the 40/60 blend film (not shown in Fig. 9) is located between the two curves. The equilibrium swelling ratio (2.1) of the 40/60 blend is a reasonable value, because the ratio for the two neat PVAs are 1.4 for the A sample and 3.0 for the B sample from Figure 9. The difference in the equilibrium swelling ratio between the three samples can be related to that in the crystallinity, 45.7% for A, 21.2% for B, and 34.6% for the 40/60 blend.

The reincreasing process observed in the late stage of swelling in the 80/10 and 90/10 solvents shown in Figure 7 is due to the Super Case II process. The diffusion of the DMSO-rich solvent through the neat A film is in the early stage of swelling obeyed the Case II process and followed by Super Case II process.<sup>3</sup> After the Case II diffusion proceeds for a while, the swelling ratio abruptly increases. This is called Super Case II process. In the previous article, we attributed the Super Case II to



**Figure 9** Swelling ratio  $M_t/M_0$  vs. swelling time  $t$  curves for two types of the neat films in the DMSO/water (vol/vol) = 60/40 solvent at 30°C: for A (○) and for B (□).



**Figure 10** Swelling ratio  $M_t/M_0$  vs. swelling time  $t$  curves for the A/B (wt/wt) = 60/40 blend film at 40°C in the DMSO/water solvent with different ratios (vol/vol): (O) 0/100 (water), (□) 20/80, (×) 40/60, (◇) 60/40, (+) 80/20 and (Δ) 100/0 (DMSO).

the appearance of craze in the film. Once the unswollen core of the film is released by cracking from the expansion force due to the swollen layer, the swelling ratio abruptly increases. However, the Super Case II process in the matrix did not accompany cracking in the blend system. Because the matrix involves a number of pores as traces of the domains, the stress gradually elevated by swelling would be dispersed in the film. It is shown that the appearance of crack is not necessary for starting the super Case II process.

The swelling ratio vs. time curves are also shown for the A/B (wt/wt) = 60/40 blend film at 40°C in Figure 10. This blend film has no cylindrical domain. The peak figure observed in the case of the 40/60 blend films in Figure 7 cannot be detected in Figure 10, indicating that the B molecules in the A/B (wt/wt) = 60/40 blend film are so compactly contacted with the A molecules that it would not cause the partial dissolution of the B molecules from the film. Moreover, the observation of the swelling process is indicated to be a useful tool for detection of molecular compatibility.

## CONCLUSIONS

Our A/B blend systems shows the sub mm-sized cylindrical domain-containing structure in the range from 36 to 43 wt % content of A. Because the domain penetrates the film in the thickness direction and can be selectively dissolved away by soaking in water, we aimed to prepare the film as the porous membrane filter. The selective dissolution of the

domain is due to the B-rich regional composition. The size of the pore, namely the domain, of the A/B (wt/wt) = 40/60 film could not be reduced under 10  $\mu\text{m}$ , by reducing the evaporation rate during film casting. However, it is shown that the size of the domain decreased with the increase of the evaporation rate, indicating that the domain is coalescing with each other in our film preparation stage. It was also shown that the phase structure of the blend film can be investigated by observing its swelling behavior in the DMSO/water solvents. The selective dissolution of the domain is detected by the peak figure in the swelling ratio vs. time curve. The reincrease of the curve in the late stage of swelling in some DMSO-rich solvents means the case II or super case II diffusion of the solvent through the matrix. The structure not containing cylindrical domains in the A/B (wt/wt) = 60/40 did not show the peak figure.

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## APPENDIX

Here, the equation is induced, which relates the mol fraction of the VA unit in the blend and those of the component polymers or those of the phases. The component polymers are the PVAs that are composed of the vinyl alcohol (VA) and the vinyl acetate (VAc) repeating units. The total weight fraction of the VA unit in a specific region such as the matrix and the domain in the blend or in the whole region of the blend,  $Y_{VA}^{12}$  can be related to the weight fractions of the polymer components or the regions,  $Y_{VA}^1$  and  $Y_{VA}^2$  as follows.

$$Y_{VA}^{12} = Z_1^{12}Y_{VA}^1 + Z_2^{12}Y_{VA}^2 \quad (1)$$

where,  $Z_1^{12}$  and  $Z_2^{12}$  are the weight fractions of the components (or regions) 1 and 2 in the system 12, respectively, and the following relation holds.

$$Z_1^{12} + Z_2^{12} = 1 \quad (2)$$

The weight fraction of  $Y_{VA}^{12}$  can be transformed into the mol fraction,  $X_{VA}^{12}$ , through the following equation.

$$(X_{VA}^{12})^{-1} = 1 - (M_{VA}/M_{VAc})[1 - (Y_{VA}^{12})^{-1}] \quad (3)$$

where  $M_{VA}$  and  $M_{VAc}$  are the molecular weight of the repeating units VA and VAc, respectively.



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