

# Formation of Polyurethane Membranes by Immersion Precipitation. II. Morphology Formation

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**ABSTRACT:** Polyurethane membranes were prepared by an immersion precipitation process. The effects of dope concentration, coagulation bath composition, and the chemical structure of the polyurethane on the morphology of the membranes were studied. The degree of contraction was measured by quenching freshly formed polyurethane membranes in liquid nitrogen. A mechanism for the formation of membrane morphology during immersion precipitation is proposed. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2124–2132, 1999

**Key words:** membrane formation; polyurethane membrane; degree of contraction; macrovoid; spinodal decomposition

## INTRODUCTION

When a homogeneous solution becomes thermodynamically unstable (e.g., by the introduction of a nonsolvent), the solution phase separates into two liquid phases of different composition to lower the free energy of the mixture. This process is responsible for the generation of the porous microstructure of a noncrystallizable polymer solution.<sup>1–3</sup> Liquid–liquid phase separation can occur either by nucleation and growth or by spinodal decomposition, depending on the kinetic path in the phase diagram. If the composition path stays at the metastable region for a sufficient time, nuclei can be formed that grow to form droplets of a polymer-poor phase in the polymer solution. Spinodal decomposition occurs if the

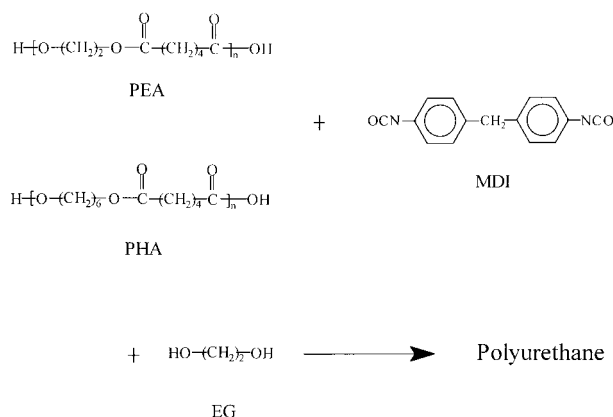
composition path rapidly passes the metastable region before stable nuclei are formed. The solution becomes unstable with respect to infinitesimal small concentration fluctuations and separates spontaneously into interconnected regions of high and low polymer concentration, ending up in cocontinuous networks of polymer-rich and polymer-poor phases.<sup>4</sup> The final morphology of the membrane is strongly influenced by the solidification process of the polymer-rich phase.<sup>5</sup> Solidification can be achieved by either gelation<sup>6</sup> or crystallization of the polymer-rich phase.<sup>6,7</sup>

In this work we prepared polyurethane (PU) membranes with various morphologies by varying the composition of the coagulation bath, dope concentration, and chemical structure of the PU. We considered liquid–liquid phase separation and solidification processes involved in the morphology formation during immersion precipitation.

Macrovoids are largely elongated pores that can extend over the membrane thickness. The causes for the generation of macrovoids during the formation of asymmetric membranes are the-

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**Figure 1** Reaction schemes for the synthesis of polyurethanes.

oretically interesting and practically important issues, because they cause mechanical weaknesses in the membrane but provide passage of permeate flow. However, there are still arguments about the origin and growth of macrovoids.<sup>8-12</sup> In this study we propose a mechanism for macrovoid formation by spinodal decomposition, and we also present detailed explanations of how the porous structures are formed during the immersion precipitation process.

## EXPERIMENTAL

### Preparation of PU Membrane

PUs with different polyol structures were used as described in detail in part I of this study.<sup>13</sup> The reaction schemes for the synthesis of PUs are shown in Figure 1. The molecular weights of the polyols and PUs are listed in Table I. The reaction was carried out by a single-step process with the molar ratio of 2.5 : 1 : 1.5 for 4,4'-diphenyl methane diisocyanate (MDI) : polyol : ethylene glycol. Notations of PHA/MDI-PU and PEA/MDI-PU in-

dicate that the polyol components are poly(hexamethylene adipate) diol and poly(ethylene adipate) diol, respectively. *N,N*-Dimethylformamide (DMF) was used as the dope solution and water was used as the nonsolvent. PU membranes were prepared by casting a dope solution onto a glass plate and then immersing this film into a coagulation bath containing various compositions of DMF and water.

### Degree of Contraction

The degree of contraction was determined by measuring the change of the membrane thickness after immersion precipitation. After phase separation proceeded for about 10 min, the membrane was taken out of the bath and quenched in liquid nitrogen. The final thickness of the membrane was measured with an optical microscope. The degree of contraction was determined by the following equation:

$$\text{degree of contraction (\%)} = (t_d - t_f) \times \frac{100}{t_d}$$

where  $t_d$  is the thickness of the dope solution cast on the glass and  $t_f$  is the thickness of the final membrane after quenching.

### Membrane Morphology

Dried membranes were cut into a proper size and frozen in liquid nitrogen, then they were fractured to observe the cross section. The morphologies of the membranes were studied with a scanning electron microscope (Philips SEM 535M). The top surface and cross section of the membranes were observed.

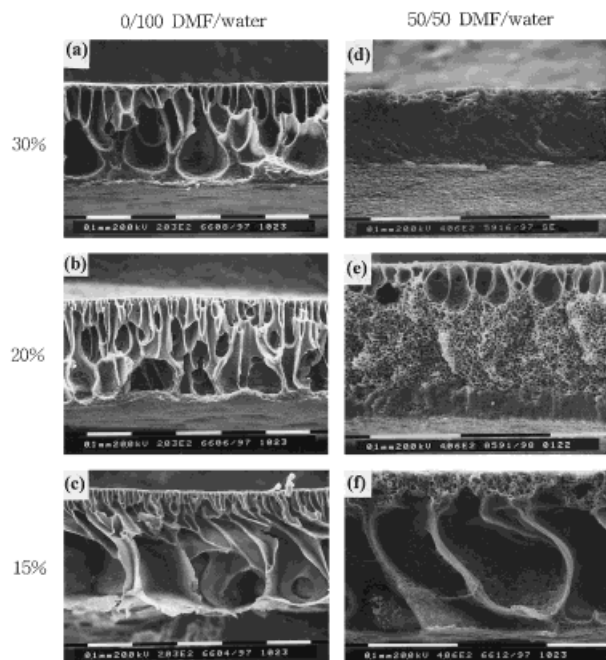
## RESULTS AND DISCUSSION

### Membrane Morphology

The SEM micrographs of the cross sections of the PHA/MDI-PU membranes prepared with various

**Table I** Molecular Weights of Polyols and Polyurethanes (PUs)

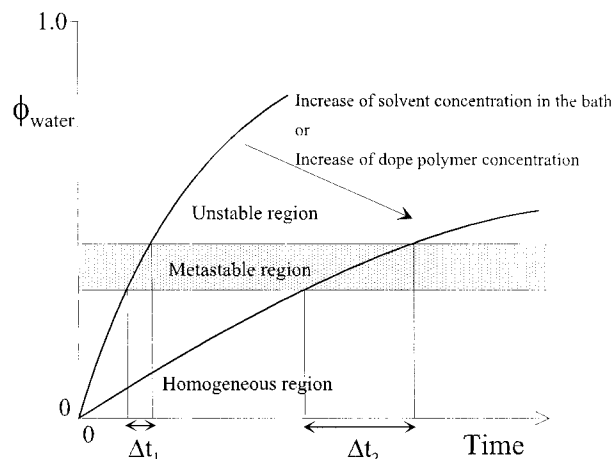
PU	Diisocyanate	Polyol	Chain Extender	$\bar{M}_n$ of		$\bar{M}_w/\bar{M}_n$
				Polyol	PU	
PEA/MDI-PU	MDI	PEA	Ethylene glycol	2008	34960	2.42
PHA/MDI-PU	MDI	PHA	Ethylene glycol	2016	33720	2.34



**Figure 2** SEM micrographs of the cross sections for the PHA/MDI-PU membranes; the dope polymer concentrations (30, 20, 15 wt % polymer in DMF) and coagulation bath compositions (0/100, 50/50 DMF/water) were varied.

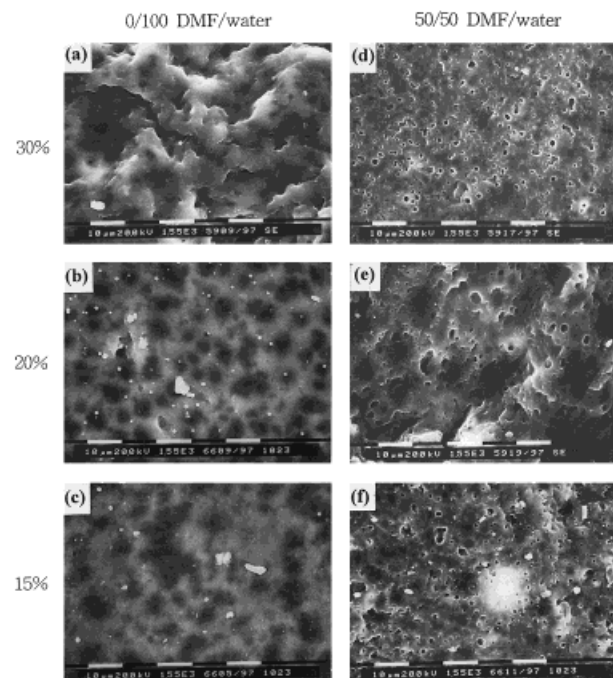
dope polymer concentrations and bath compositions are shown in Figure 2. With the increased solvent content in the coagulation bath, the number and size of the macrovoids were reduced and the cellular structure became dominant. A higher dope polymer concentration seemed to suppress the formation of macrovoids. As discussed in our light transmission experiment,<sup>13</sup> the addition of solvent to the coagulation bath or the increase of dope polymer concentration reduced the rate of water inflow, and the mixture stayed longer in the metastable region. This is depicted schematically in Figure 3. Thus, where  $\Delta t_2$  is larger than  $\Delta t_1$ , the dominant phase separation mechanism changes from spinodal decomposition to nucleation and growth with high solvent content in the coagulation bath or concentrated dope solution, resulting in the formation of the cellular structure.

Figure 4 shows the top surface of the PHA/MDI-PU membranes prepared with various dope polymer concentrations and coagulation bath compositions. Because the mass transfer rate is highest at the membrane–bath interface, one may expect the appearance of an interconnected structure due to spinodal decomposition at the top surface with appropriate conditions. When the



**Figure 3** Schematic figure showing the change of residence time in the metastable region at a certain point of the membrane solution with different conditions of the bath or dope solution.

coagulation bath contained pure water, spinodal structures appeared at the top surface of the membranes [Fig. 4(a–c)] because the metastable region could be surpassed. Spinodal demixing of the polymer solution that caused a cocontinuous

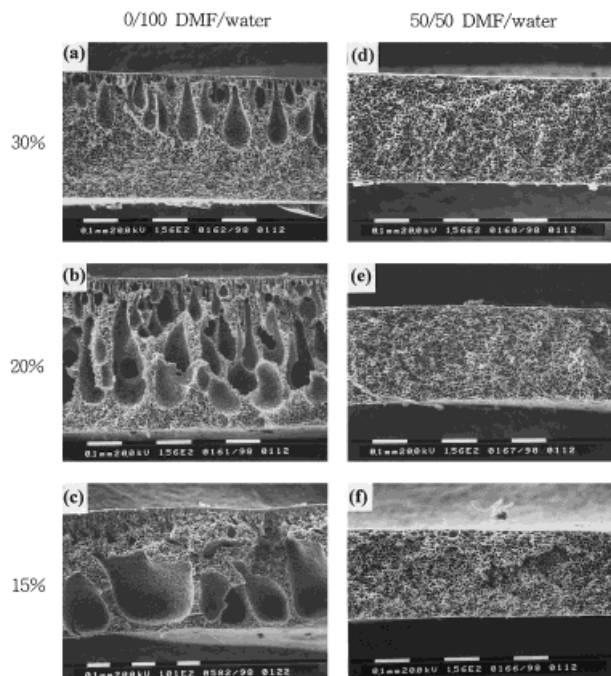


**Figure 4** SEM micrographs of the top surface for the PHA/MDI-PU membranes; the dope polymer concentrations (30, 20, 15 wt % polymer in DMF) and coagulation bath compositions (0/100, 50/50 DMF/water) were varied.

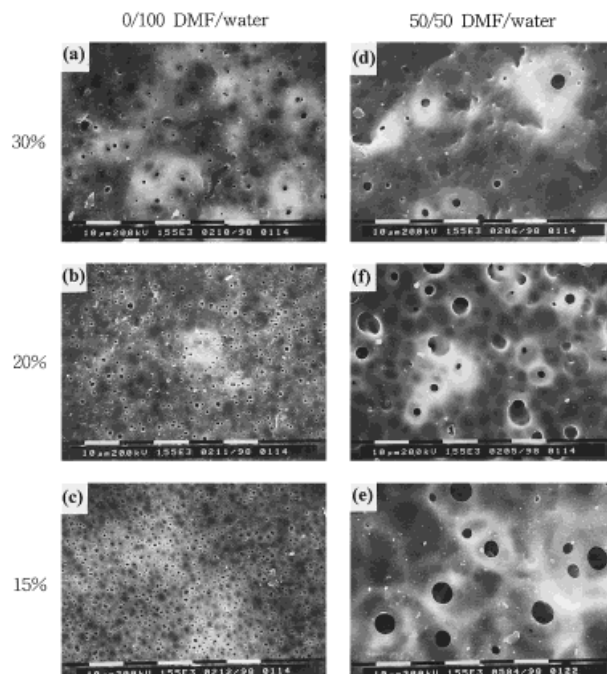


structure in the top layer of the ultrafiltration membranes was also reported by Wienk et al.<sup>14</sup> On the other hand, as the solvent content in the coagulation bath was increased, spinodal structures disappeared and porous structures appeared at the top surface. With a high solvent content in the coagulation bath, the mixture can stay for a longer time in the metastable region as illustrated in Figure 3 and porous structures of the top surface might originate from the phase separation by nucleation and growth. The number and size of pores are related to the solidification process that prevents the growth of pores. If the solidification rate is rapid, the number and size of the pores diminishes. This is demonstrated by the increase in the size and number of pores when lowering the dope polymer concentration or solvent content in the coagulation bath, which causes delays of the solidification process.

Figures 5 and 6 show the cross sections and top surfaces of the PEA/MDI-PU membrane prepared with various dope polymer concentrations and bath compositions. The macrovoid in the PEA/MDI-PU membrane was suppressed compared to the PHA/MDI-PU membrane and disappeared in the coagulation bath having 50 wt % DMF [Fig.



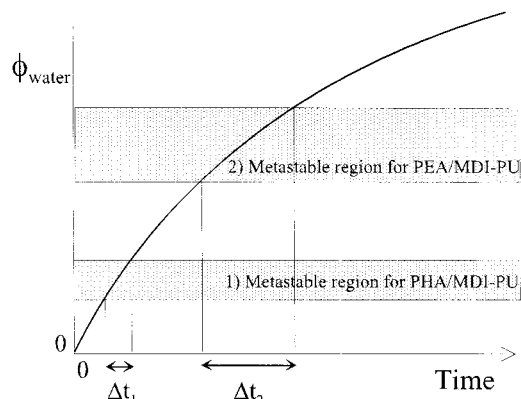
**Figure 5** SEM micrographs of the cross sections for the PEA/MDI-PU membranes; the dope polymer concentrations (30, 20, 15 wt % polymer in DMF) and coagulation bath compositions (0/100, 50/50 DMF/water) were varied.



**Figure 6** SEM micrographs of the top surface for the PEA/MDI-PU membranes; the dope polymer concentrations (30, 20, 15 wt % polymer in DMF) and coagulation bath compositions (0/100, 50/50 DMF/water) were varied.

5(d–f)]. The spinodal structures are hardly observed at the top surface of the PEA/MDI-PU membranes, even when the coagulation bath contains pure water; the sponge structure is dominant instead as shown in Figure 6. With the use of relatively hydrophilic PEA/MDI-PU polymer, the homogeneous region and metastable region were enlarged as shown in part I of this study<sup>13</sup>; thus, the rate of water inflow upon inducing phase separation was lower and the mixture stayed longer in the metastable region. It can be seen in Figure 7 that a longer residence time in the metastable region is required with the use of more hydrophilic PEA/MDI-PU polymer, and the dominant phase separation mechanism is nucleation and growth that results in the cellular structure.

A comparison of Figures 4 and 6 reveals that the size of the pores in the top surface of the PEA/MDI-PU membrane in the coagulation bath containing 50 wt % DMF are bigger than that of the PHA/MDI-PU membrane. This phenomenon can be explained in terms of quench depth and the slope of the tie line in the phase diagram.<sup>15</sup> The spinodal structure of the PHA/MDI-PU membranes in Figure 4(a–c) suggests that a deep quench was attained during the immersion pro-



**Figure 7** Schematic figure showing the change of residence time in the metastable region at a certain point of the membrane solution with polyurethanes having different hydrophilicity.

cess, and the slope of the tie line is lower for the PHA/MDI-PU/DMF/water system than for the PEA/MDI-PU/DMF/water system as we showed in part I of this study.<sup>13</sup> A larger quench depth and lower slope of the tie line cause acceleration of solidification in the polymer-rich phase.<sup>5</sup> Bigger pores in the PEA/MDI-PU membrane are considered to result from the delayed solidification of the polymer-rich phase during the phase separation process.

### Contraction of Membrane on Coagulation

The degree of contraction of the final membranes is summarized in Tables II and III. The results show that the contraction ranges from 29 to 68%. The contraction of the membrane is due to the inequality in the magnitudes of the nonsolvent and solvent fluxes. If the solvent outflux is larger than the nonsolvent influx, the membrane solution will contract. The degree of contraction increased with the higher solvent content in the coagulation bath; thus, a thinner membrane was

obtained. The degree of contraction of the PEA/MDI-PU membrane was higher than that of the PHA/MDI-PU membrane. These phenomena can be interpreted with the phase separation mechanism during the immersion precipitation. As shown in figure 5 in part I,<sup>13</sup> the precipitation time decreased with lower solvent concentration in the coagulation bath and with a hydrophobic polymer. Thus, the dominant phase separation is spinodal decomposition, because the composition path stays in the metastable region for a very short time due to the high mass transfer rate. Once phase separation occurs via spinodal decomposition, a higher influx of water is expected due to the cocontinuous structure of the polymer-poor phase, giving rise to a lower degree of contraction of the membrane solution. This explains the smaller degree of contraction with a lower solvent content in the coagulation bath and with a more hydrophobic PHA/MDI-PU membrane, which is responsible for the macrovoid formation that will be discussed. If the dominant phase separation mechanism is nucleation and growth, the influx of water is not expected to be high through the dispersed polymer-poor phase. However, the solvent present in the still homogeneous matrix diffuses out easily into the coagulation bath, which results in the high degree of contraction.

The effect of the dope polymer concentration on the degree of contraction is not as obvious as that of the solvent content in the coagulation bath. It is complicated by the relaxation of the polymer component, as well as the phase separation mechanism. Because the nucleation and growth mechanism becomes dominant with a high polymer concentration due to a low water inflow rate, one may expect a high degree of contraction. In the concentrated polymer concentration, however, the relaxation of the polymer becomes difficult because of the increase of the intermolecular force and chain entanglements. Thus, the membrane solu-

**Table II** Degree of Contraction (%) of PHA/MDI-PU Membrane during Immersion Precipitation

Dope Polymer Concn (%)	Composition of Coagulation Bath			
	DMF/Water = 0/100	DMF/Water = 20/80	DMF/Water = 50/50	DMF/Water = 80/20
30	29	38	58	57
20	35	44	48	49
15	25	42	50	53

**Table III Degree of Contraction (%) of (PEA/MDI-PU) Membrane during Immersion Precipitation**

Dope Polymer Concn (%)	Composition of Coagulation Bath			
	DMF/Water = 0/100	DMF/Water = 20/80	DMF/Water = 50/50	DMF/Water = 80/20
30	30	53	58	63
20	48	56	65	67
15	38	56	66	68

tion cannot contract as much as the difference in the magnitudes of nonsolvent and solvent fluxes.

### Macrovoid Formation Mechanism

Strathman explained that macrovoids are the result of the rapid penetration of nonsolvent at certain weak spots in the top layer of the membrane.<sup>16</sup> However, large defects were hardly observed at the surface of the membrane. Smolders et al.<sup>10</sup> suggested that macrovoid growth is controlled by diffusional flows, and they focused on the relative kinetics of the growth of the droplets of the polymer-poor phase and the exchange rate of solvent and nonsolvent. They suggested that macrovoids are formed just beneath the skin layer from freshly formed nuclei of the diluted phase. Due to the large amount of solvent present in the polymer-poor droplets, the droplets can be considered as a coagulation bath with a lot of solvent. Thus, delayed demixing occurs and a net solvent inflow from the surroundings into the droplets is the result. Their explanation is elegant and complete for the origin and growth of macrovoids. However, considering that macrovoids grow very rapidly, one may wonder how rapid growth is possible by the inflow of solvent with a relatively low concentration gradient between the surroundings and the macrovoids. McKelvey and Koros proposed recently that the macrovoid formation is driven by osmotic pressure forces generated in the nucleated polymer-lean phase.<sup>11</sup> They assumed that the polymer-rich nucleus wall between the moving front and the nucleus is a semipermeable membrane, depending on the solvent type and the degree of plasticization of the nucleus wall. However, they did not explain the semipermeability in terms of membrane morphology. Cheng and Gryte<sup>17</sup> showed that spinodal decomposition does not occur in an isothermal-precipitation process. That may result from the basic assumptions they adopted. One of the assumptions is that diffusional mass transfer, even with

strong concentration gradients, is sufficiently slow so that the higher order terms in the variational expansion of free energy are neglected. This assumption may not be realistic in actuality, because higher order terms can be neglected in only small concentration gradients. Spinodal decomposition is believed to occur when the mass transfer rate is fast enough to pass the metastable region without allowing the formation of stable nuclei.

Before discussing our proposal on the origin of macrovoids, we briefly present literature experimental observations in membrane morphology on the formation of macrovoids.<sup>1,10,18,19</sup>

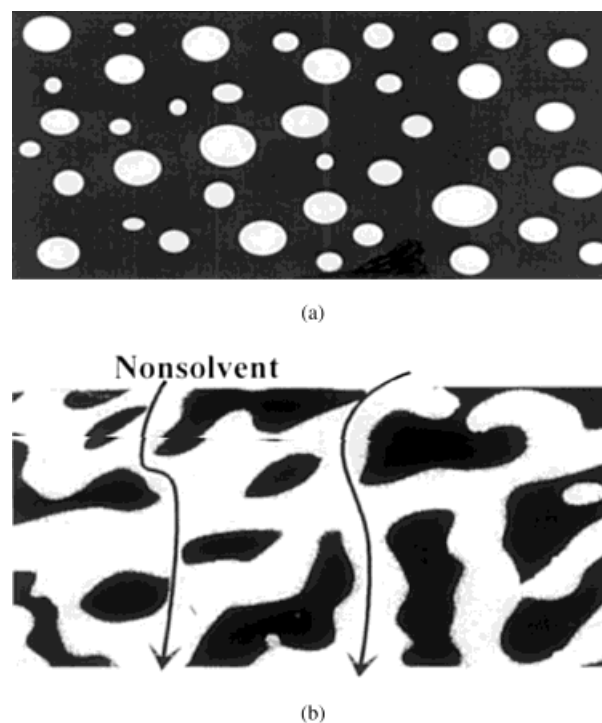
1. Macrovoids are usually associated with instantaneous precipitation (spinodal decomposition). Thus, the tendency toward macrovoid formation is increased with the increase of miscibility in a solvent/nonsolvent pair. Conversely, delayed demixing will usually result in the disappearance of macrovoids.
2. The tendency toward macrovoid formation will increase with a decrease in the dope polymer concentration and viscosity of the dope solution.
3. The walls of macrovoids are porous.

The fact that macrovoids are usually associated with instantaneous precipitation<sup>10</sup> indicates that the formation of macrovoids is related to the fast mass transfer process. Fast mass transfer can cause the mixture to reach the unstable region instantly, resulting in the occurrence of spinodal decomposition. The porous walls of macrovoids also indicate the occurrence of phase separation by the solvent/nonsolvent exchange between macrovoids and the surrounding polymer solution. Based on the above experimental observations, we suggest that macrovoids are formed via a spinodal decomposition mechanism, and



small cells around the macrovoids are formed via a nucleation and growth mechanism in the secondary phase separation. The detailed descriptions for macrovoid formation are as follows with imaginary multilayers of the whole thickness of the polymer solution.

The first layer (top layer contacting the coagulation bath) is separated into a polymer-rich phase and a polymer-poor phase via spinodal decomposition at the beginning of immersion due to a deep quench. Once phase separation occurs, it is expected that mass transfer becomes dominant in the polymer-poor phase rather than in the polymer-rich phase. Thus, as the mass transfer progresses through the polymer-poor phase, the second layer is also separated into two phases by the spinodal decomposition. The third layer, fourth layer, and fifth layer, and so forth, were separated via a mechanism similar to the former cases. This would be possible due to the formation of channeling morphology by the succession of the polymer-poor phase by spinodal decomposition, which provides the route for easy penetration of nonsolvent. The size of the channel can be related to the wavelength of the concentration fluctuation at the early stage. The wavelength at the early stage becomes small in a deep quench.<sup>20–22</sup> Thus, if the size of the concentration fluctuation is sufficiently small in a deep quench condition such as in the coagulation bath with pure water, channeling morphology may act as a semipermeable membrane for the generation of osmotic pressure. This fact can be a complementary explanation for the McKelvey and Koros proposal for the origin of osmotic pressure in macrovoid formation.<sup>11</sup> Because the polymer-rich phase solidifies very fast near the membrane–bath interface, the coalescence of the polymer-poor phase is difficult at this position. The polymer-poor phase begins to grow by coalescence at a certain point beneath the membrane–bath interface where solidification of the polymer-rich phase is slow enough for coalescence. In addition, the rapid ingress of nonsolvent through the channel into the polymer-lean phase should account for the large size of the macrovoids in the longitudinal direction. On the other hand, if the phase separation occurs by a nucleation and growth mechanism the channeling morphology is infrequent, which indicates that macrovoids rarely appear. A schematic representation of the morphology expected from the different phase separation mechanisms is shown in Figure 8. The cells around the macrovoids are considered to form by secondary phase separation. After pri-

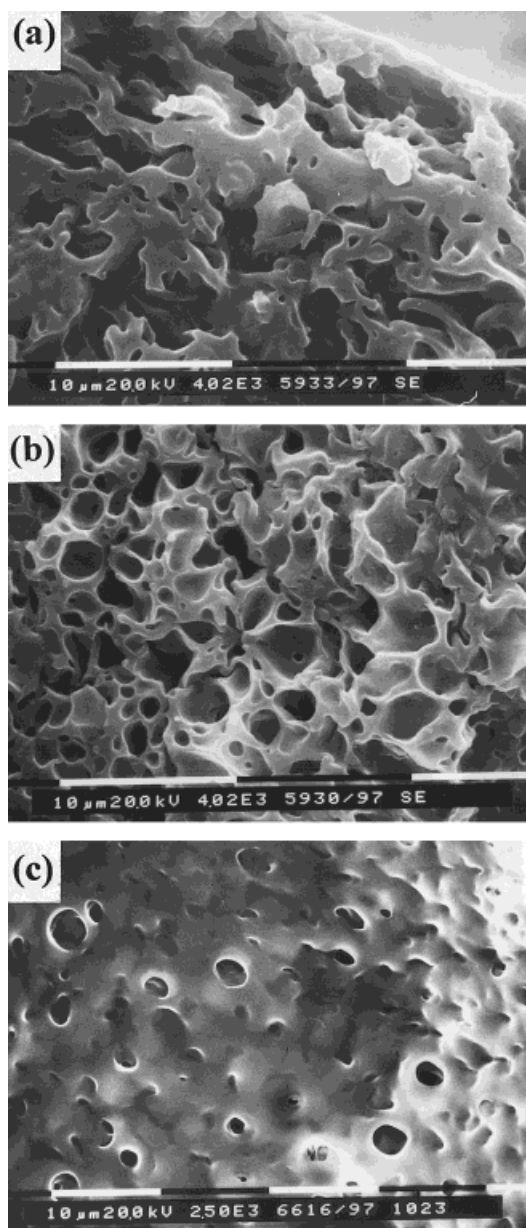


**Figure 8** Schematic representation of the morphology by different phase separation mechanisms: (a) nucleation and growth and (b) spinodal decomposition.

mary phase separation, the polymer-rich phase between the macrovoids separates again into polymer-rich and polymer-poor phases via a nucleation and growth mechanism. In other words, macrovoids (primary polymer-poor phase) act as a local coagulation reservoir with high solvent content. The polymer-poor phase can grow further before solidification occurs, and it would also be possible for them to coalesce with each other to form open pores.

In our proposal a large difference in the nonsolvent mass transfer rate through the polymer-rich and polymer-poor phases is crucial for the formation of macrovoids. This is supported by the fact that the tendency to form macrovoids increases when using a relatively hydrophobic polymer, which is shown in Figures 2 and 5. This is due to the fact that the polymer-rich phase formed by the hydrophobic polymer can be a stronger barrier against the nonsolvent.

Cross-sectional morphologies of different parts of the PHA/MDI-PU membranes are shown in Figure 8. The upper part of the membrane shows the spinodal structure with holes in Figure 9(a), which seems to be the channel morphology from successive spinodal decompositions. The middle part of the membrane between the macrovoids



**Figure 9** SEM micrographs of the PHA/MDI-PU membrane with 30 wt % dope polymer concentration in DMF and a coagulation bath composition of 0/100 DMF/water: (a) the upper part of the membrane, (b) the middle part of the membrane between macrovoids, and (c) the wall of the macrovoid.

seems to have cell structure by the secondary phase separation [Fig. 9(b)], which is manifested by the porous structure in the wall of the macrovoids as shown in Figure 9(c).

## CONCLUSIONS

A variety of membrane structures were obtained in this work, depending on the type of PU, the

polymer concentration of the dope solution, and the coagulation bath compositions. An increase of dope polymer concentration or the solvent content in the coagulation bath suppressed the formation of macrovoids, and the use of relatively hydrophilic polymer also suppressed the formation of macrovoids. The interconnected structure due to spinodal decomposition was dominant at the top surface of the PU membrane when either the coagulation bath contained pure nonsolvent or more hydrophobic PHA/MDI-PU was used.

The degree of contraction of the membrane solution increased with the solvent content in the coagulation bath. The degree of contraction was about 10–20% lower in the PHA/MDI-PU membrane than in the PEA/MDI-PU membrane, which is responsible for the delays in phase separation in the hydrophilic PEA/MDI-PU membrane, providing a longer time for the solvent outflux.

We propose that the macrovoid formation occurs via the spinodal decomposition mechanism and the cellular structure between the macrovoids results from the secondary phase separation by nucleation and growth. Channeling morphology can be formed by successive spinodal decompositions that would otherwise hardly be formed by the nucleation and growth mechanism. The formation of macrovoids is attributed to the growing of the polymer-poor phase by coalescence after spinodal decomposition, as well as the ingress of nonsolvent into the polymer-poor phase through the channel. The macrovoids with rather high solvent content act as a local coagulation bath, and the cellular structure is formed by secondary phase separation via a nucleation and growth mechanism.

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