The Kinetic Study for Asymmetric Membrane Formation via Phase-Inversion Process

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SYNOPSIS

The kinetics of membrane formation by phase inversion was studied emphasizing the rate of solvent diffusion from a polymer solution during the phase separation. Diffusional behavior of the solvent can be considered Fickian. Membrane morphologies were shown to be strongly dependent on the rate of solvent diffusion, indicating that mass-transfer rates of solvent and nonsolvent during phase separation are crucial for determining the final membrane structure for the following system: polysulfone (polymer), dimethyl acetamide (solvent), and ethanol (gelation medium). Specific reference to the mechanism of macrovoid formation was explored. Macrovoid formation was found to be proportional to the square root of time, suggesting that it is governed by a diffusion process. In addition, latex particles of coagulated polymer formed by the nucleation and growth of a concentrated polymer phase was observed inside the macrovoids. Such a result implies that the macrovoids grow by a diffusive flow which results from the growth of the polymer lean phase during binodal decomposition. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The phase-inversion process is a widely used method for making asymmetric, microporous polymer membranes. In this process, a viscous polymer solution is first spread into a thin film, then immersed in a gelation medium. Complicated phenomena are involved in this process such as thermodynamic phase separation of a homogeneous polymer solution into two phases, polymer-rich and polymer-lean, and diffusive interchange between the solvent and nonsolvent. The former is regarded as a thermodynamic effect while the latter is a kinetic one. Since the morphology and performance of membrane strongly depends on these two effects, which are closely related to preparation conditions, many authors have reported the mechanism of asymmetric membrane formation via the phase-inversion process.[1-8] The previous investigations have focused mainly on the thermodynamic terms, relating casting conditions to final morphologies of the membranes; however, it is known that pore-size distribution, in addition to skin and macrovoid formation, are controlled by kinetic effects.[9-11] This relationship between membrane morphology and kinetic effects suggests that a gelation medium mass transfer plays an important role in determining the structure of the membrane. Mass transfer occurs mainly at the interface between the polymer solution and gelation medium by a diffusion process. Exchange of solvent and nonsolvent across the interface introduces phase separation in the polymer solution, leading to various asymmetric structures. Recently, there have been several attempts to study the mass-transfer dynamics relating to the membrane morphologies.[12-18] One of the problems for the membrane scientists that have not been satisfactorily explained is the formation of macrovoids. It has been shown that the formation of macrovoids in membranes can be suppressed or eliminated through experimental procedures, but controversy still exists regarding whether the formation of macrovoids is a result of convective flow or diffusive flow.[19,20] In this article, the kinetic behavior affecting membrane preparation will be studied, especially the effect of the rate of solvent diffusing out from the polymer solution. Using this analysis, macrovoid formation will be discussed in terms of kinetic behavior, emphasizing the growth mechanism.
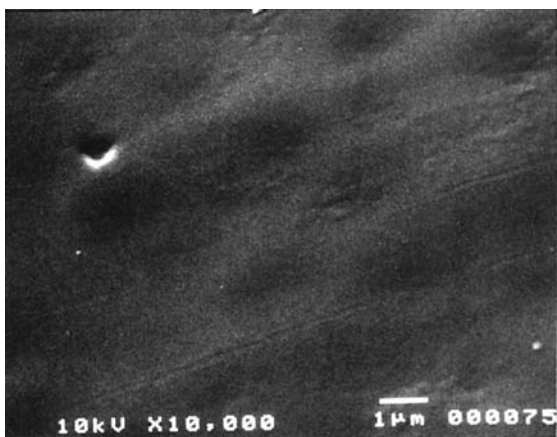
EXPERIMENTAL

~~Materials and Membrane Preparation~~

Polysulfone (PSF; Udel 1700, MW = 30,000) from Union Carbide was used for the membrane material.
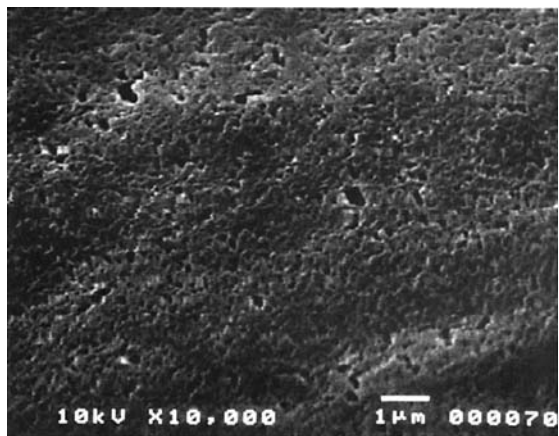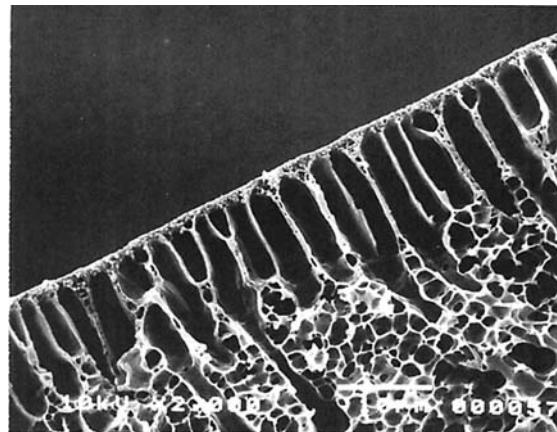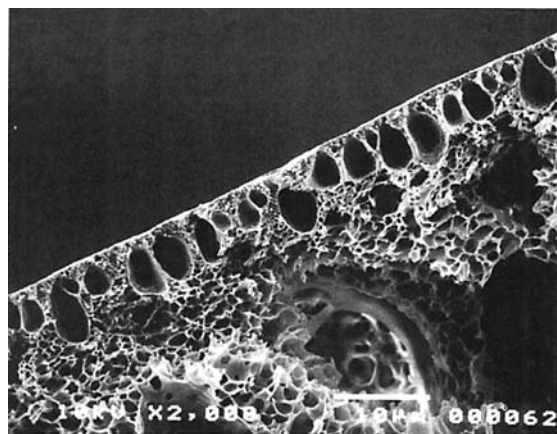

(a)

(b)

(c)
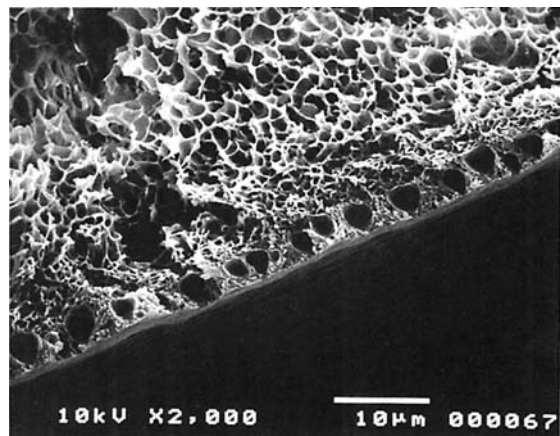
Figure 1   SEM micrographs of membrane surfaces of different polymer concentrations: (a) 15 wt %; (b) 20 wt %; (c) 25 wt %.
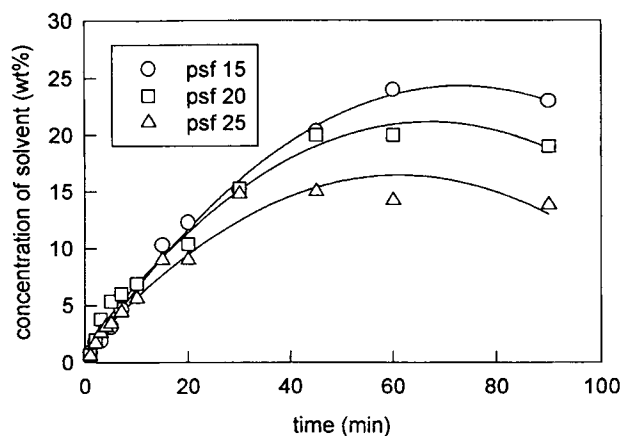

(a)

(b)

(c)

Figure 2   SEM micrographs of membrane cross sections of different polymer concentrations: (a) 15 wt %; (b) 20 wt %; (c) 25 wt %.

Dimethylacetamide (DMAc, Aldrich, 99+%) and ethanol (99.9%) were used as the solvent and gelation medium, respectively, for the polymer without further purification. Polymer solutions of 15, 20, and 26 wt % polysulfone solvated in DMAc were cast on

Figure 3   Change in concentration of solvent in the vicinity of polymer solution as a function of time during precipitation.

Figure 4   Schematic illustration of precipitation with time: (a) concentration profile of solvent at time $t = 0$; (b) concentration profile of solvent at time $t = t1$; (c) precipitated polymer solution; (d) gelation medium interface; (e) bulk gelation medium.
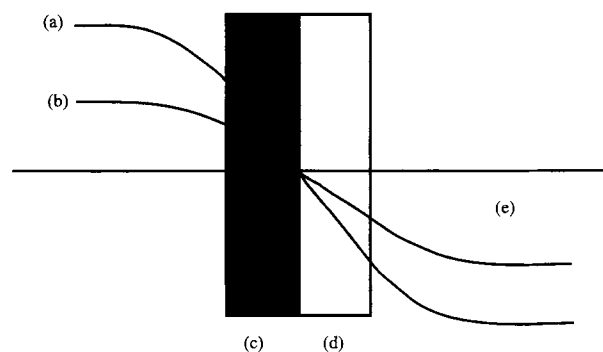
a glass plate, then immediately immersed into a gelation bath at room temperature without preevaporation. The resulting membrane was kept in the gelation bath at least for 1 day and then dried in a vacuum oven at 40°C.

The solvent concentration in the gelation medium was determined by pouring 30 mL of ethanol into 3 g of polymer solution. A 0.2 mL of the liquid near the surface of the precipitated polymer solution was sampled by a pipet and analyzed using a GC (Shimadzu GC-8A) equipped with a Porapak Q column. The procedure above was repeated at least three times.

The rate of precipitation was investigated using an optical microscope. The polymer solution was kept between two glass slides and observed under the microscope at magnifications of 25 and 90, during its precipitation in ethanol. The details of this experimental method were described elsewhere.[21] Membrane morphology was examined by scanning electron microscopy (SEM, Jeol ISM 5300) where both cross sectional as well as the surface images were prepared.

RESULTS AND DISCUSSION

Morphologies of the membranes studied are shown in Figures 1 and 2 as surface and cross surface images, respectively. As the polymer concentration in polysulfone/DMAc solution increases, Figure 1 shows that the number of surface defects decrease. The cross-sectional analysis shown in Figure 2 demonstrates that as the polymer concentration increased the number of macrovoids or cavities decreased. Thus, it can be generally stated that the

number and size of macrovoids strongly depends on the polymer concentration as reported by many authors.[7-11] Figure 3 shows the concentration of solvent near the precipitated polymer solution in the gelation medium as a function of time. It can be assumed that solvent molecules near the phase-separating polymer solution diffuse in two ways: diffusion of solvent from the polymer solution into the gelation medium interface and diffusion of solvent from the gelation medium interface into the bulk gelation medium, as described schematically in Figure 4. The concentration of solvent increased rapidly during early stages and decreased later on, which means that solvent diffuses out at a relatively higher rate in the initial period of precipitation (less than about 40 min), while the rate of solvent diffusion from the gelation medium interface into the bulk gelation medium increased in the later stage. In addition, it can be seen that the solvent concen-
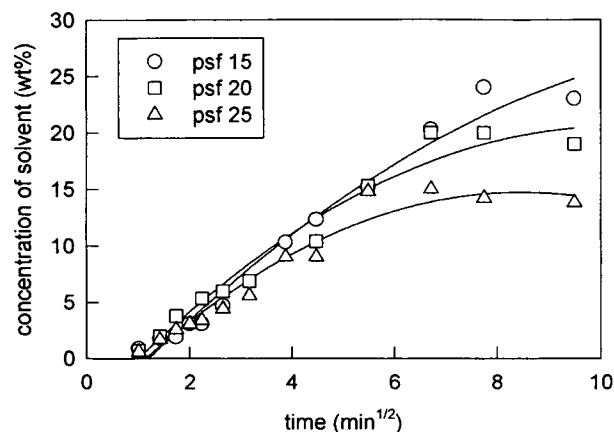
Figure 5   Change in concentration of solvent in the vicinity of polymer solution as a function of square root of time during precipitation.

(a)
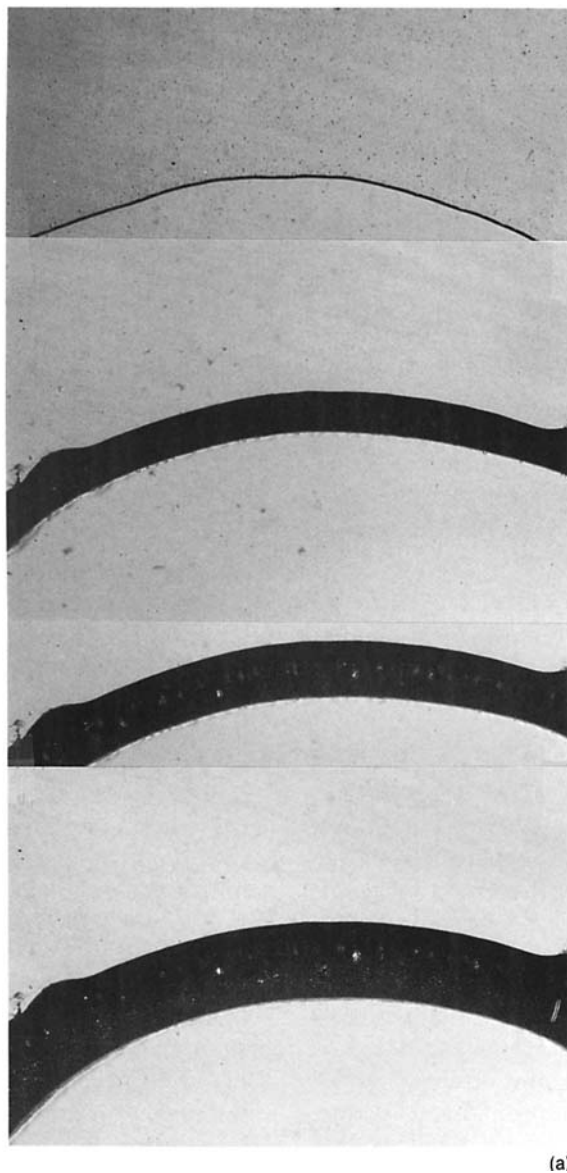
Figure 6 Optical micrographs of precipitation with time for polymer solutions containing different polysulfone concentrations: (a) 15 wt %; (b) 25 wt %.

tration in the gelation medium decreases as the polymer concentration increases, suggesting that polymer chains prohibit solvent molecules from diffusing through the phase-separated polymer solution.

Since during precipitation the diffusion of solvent molecule is controlled at the layer of the polymer solution in close vicinity of the solution/gelation medium interface, defined hereafter as the top layer, the mobility of the solvent molecules is likely restricted by polymer chains in the top layer. To investigate the diffusion behavior of solvent molecules through the top layer, the concentration of solvent in the gelation medium is plotted against

the square root of time in Figure 5. The concentration increases linearly and then reaches an equilibrium value, indicating that the solvent molecules demonstrate a Fickian behavior by diffusing through the top layer during precipitation. Based on the results shown in Figure 5, it may be considered that before equilibrium was reached the top layer through which solvent molecules diffuse was in a gel state made of a polymer/solvent mixture and thus allowed solvent molecules to move relatively freely as in above glass transition temperature condition, showing a Fickian behavior. Similarly, after the equilibrium condition is reached, it is postulated that the skin layer becomes nonflex-

(b)
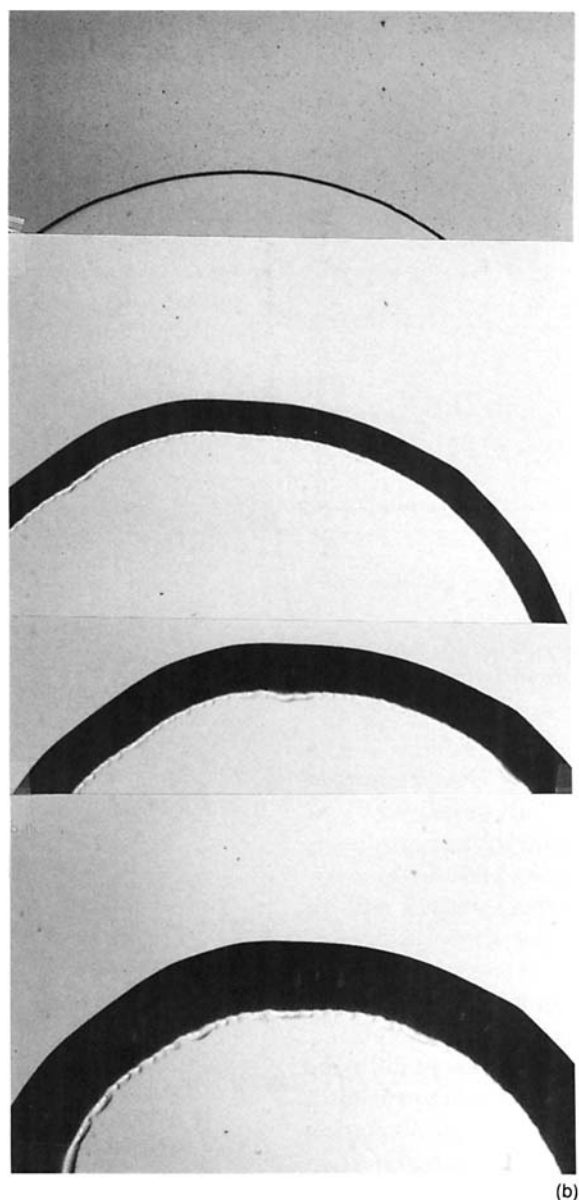
Figure 6   (*Continued from the previous page*)

ible and solidified and thus restricted the mobility of solvent molecules to be relatively immobile. Based on the fact that the equilibrium concentration of solvent at the gelation interface decreases as the polymer concentration of the casting solution increases, it can be stated that the gelled structure becomes too densely packed and inflexible for solvent molecules to diffuse through.

It has been proposed[3,21] that optical microscopy can be used to investigate precipitation kinetics in membrane preparation. The optical microscopic method was used in this work to measure the rate of nonsolvent penetration into the polymer solution. Figure 6 shows optical micrographs taken for the polymer solution containing 15 and 25 wt % of the polymer, respectively, as a function of time. The dark bands in the figure represent the precipitated region. As can be seen in Figure 6, the growth rate of the dark band is almost the same in both solutions. The width of the dark band is plotted against square root of time in Figure 7. The process of precipitation in a ternary system is very difficult to describe mathematically due to ternary diffusion, moving boundary, concentration change of medium, etc.; however, due to the fact that the penetration distance is linearly proportional to the square root of time in the initial stage of precipitation, the nonsolvent penetration can also be re-
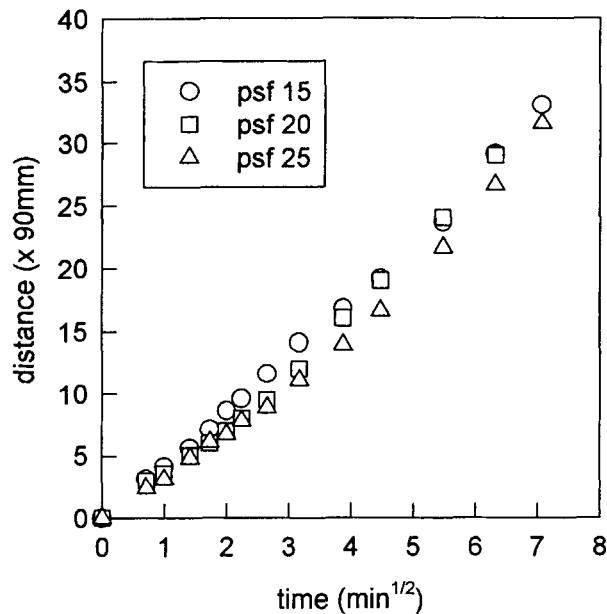
Figure 7 Precipitation distance vs. square root of time for polymer solutions containing different polysulfone concentrations.

garded as Fickian as reported by Strathmann et al.[3] and Kang et al.[21] Such an analysis suggests that the apparent diffusion coefficient of the nonsolvent can be calculated from the slope of the distance vs. time plot. The slopes of the three sets of data in Figure 7 are almost the same for all polymer concentrations, which indicates that there is not much difference in the diffusion coefficient and precipitation rate for different polymer concentrations. Further, it suggests that the rate of solvent diffusing from the polymer solution may be more crucial in the formation of a skin layer or initial formation of a precipitated structure than the rate of precipitation or diffusion of nonsolvent into the polymer solution.

Numerous authors have reported on the importance of macrovoid formation in the preparation of asymmetric membranes by the phase-inversion process.[22] Frommer and Messalam[2] and Stevens et al.[23] suggested that surface tension gradients are the driving forces accounting for the initiation of macrovoids at the interfacial boundary of the film. Strathmann et al.[3] proposed that mechanical stresses cause the rupture of the thin top layer and this rupture point initiates the formation of macrovoids. Broens et al.[24] reported that loose local arrangements of polymer nodules in the top layer may set as initiation points for the macrovoids.

A controversy still surrounds the argument as to whether the macrovoids grow through a convec-

tive flow or a diffusional flow of solvent from the polymer solution into the nuclei of macrovoid. The convective flow is a result of an intrusion of non-solvent into the polymer solution through defects or a loose arrangement of nodules at the polymer solution–nonsolvent interface, whereas the diffusional flow of solvent is caused by thermodynamic phase separation in which the polymer solution tends to separate into a polymer-rich phase and a polymer-lean phase. Smolders et al.[19] reported that nucleated droplets of the polymer lean phase in the polymer solution through binodal decomposition are responsible for the initiation of macrovoids. The formation of macrovoids was observed in this work
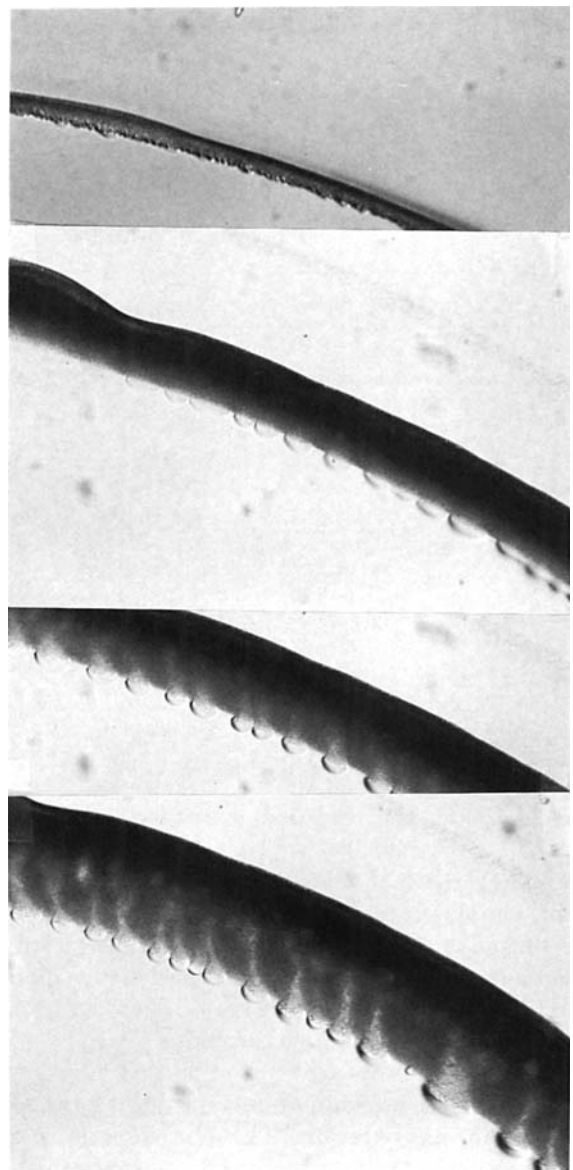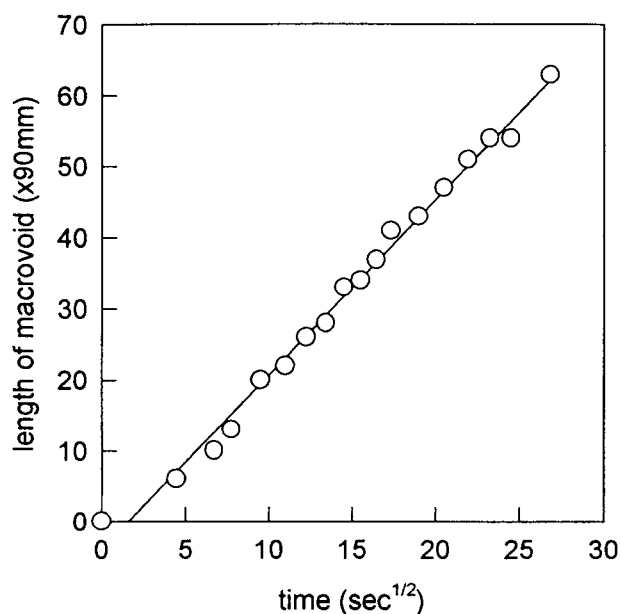

Figure 8 Optical micrographs of precipitation with time for polymer solution containing 15 wt % polysulfone.
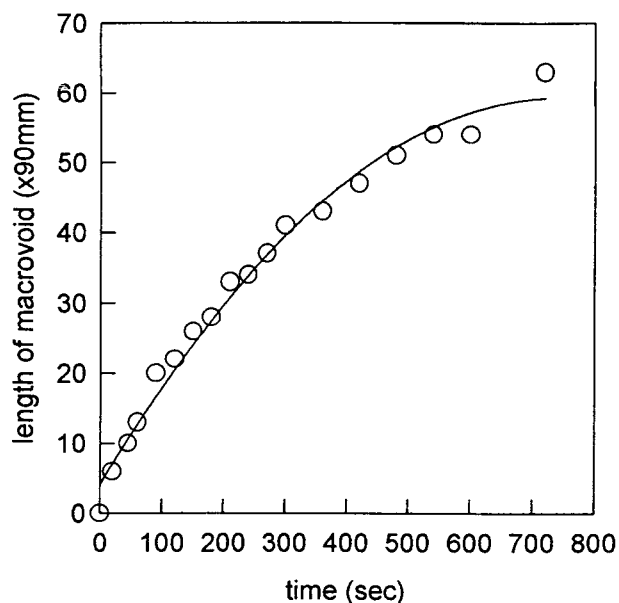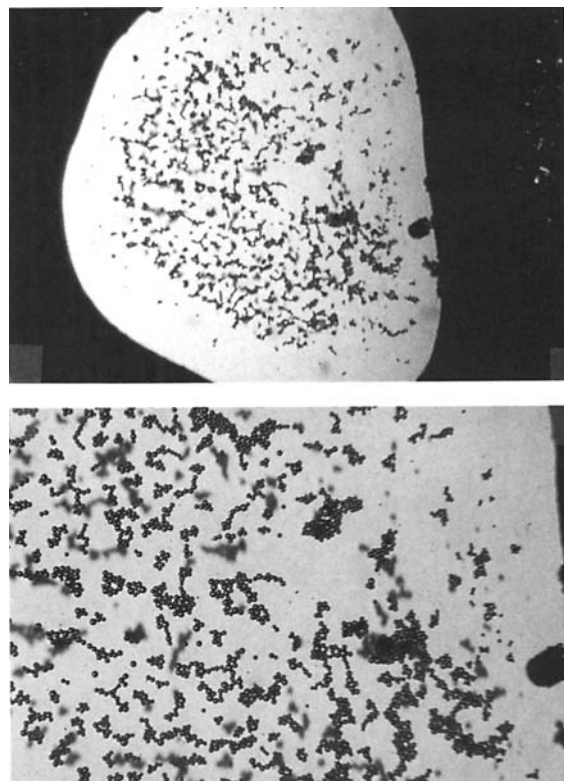
Figure 9 Longitudinal length of macrovoid vs. time for
polymer solution containing 15 wt % polysulfone.

with the aid of an optical microscope and the ki-
netics of macrovoid growth will be discussed in the
following section.

Figure 8 shows the growth of macrovoids with
time. The macrovoid front is almost the same as
the precipitation front, which indicates that the
mechanism of macrovoid formation may be the
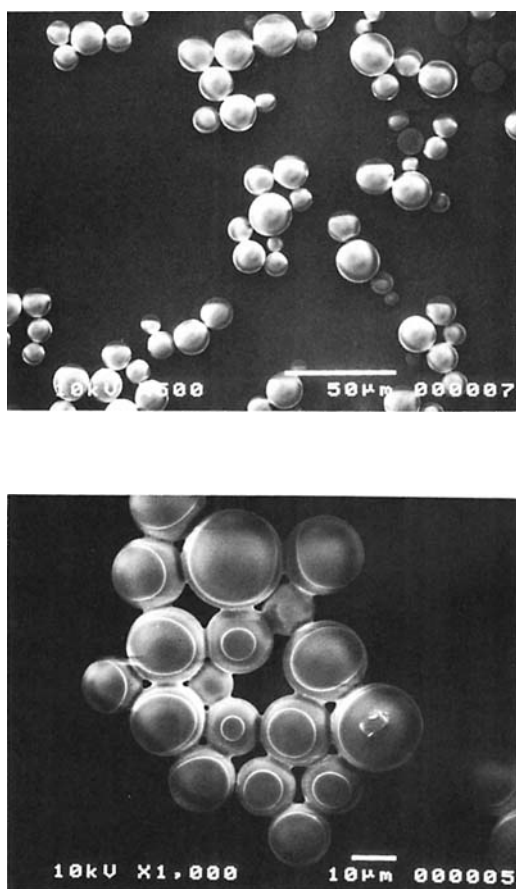same as that of precipitation. In Figures 9 and 10,

Figure 11 Optical micrographs of morphology inside
macrovoid for polymer solution containing 15 wt % poly-
sulfone.

Figure 10 Longitudinal length of macrovoid vs. square
root of time for polymer solution containing 15 wt % poly-
sulfone.

the longitudinal length of the macrovoids is plot-
ted against time. It suggests that the macrovoid
grows proportionally with the square root of time,
which means that the growing macrovoid can be
considered as a result of diffusional flows rather
than of convective flows. In other words, the ini-
tiation and growth of macrovoids can be explained
thermodynamically in terms of phase separation
of the polymer solution as described by Smolders
et al.[19]: Macrovoids are formed by a change in pre-
cipitation conditions from instantaneous to de-
layed onset of demixing at a certain distance from
the film interface and the growth of the macrovoids
is caused by solvent being expelled by the sur-
rounding polymer solution during phase separa-
tion. Hence, macrovoids can be regarded as the
result of the growth of the polymer lean phase
during binodal decomposition.

From the slope of line in Figure 10, the apparent
diffusion coefficient for the macrovoid growth could
be calculated by the equation suggested by Kang
et al.[21] and Strathmann et al.,[3] resulting in 1.874
$\times 10^{-6}$ cm^2/s, which is in accordance with diffusion
coefficient in liquid. To verify it visually, the mor-

Figure 12 SEM micrographs of morphology inside macrovoid for polymer solution containing 15 wt % polysulfone.

phology inside of the macrovoids formed between two slide glasses was examined at high magnification after precipitation for 1 week. Figures 11 and 12 are photographic pictures inside the macrovoid taken by an optical micrograph and SEM, respectively, where a morphology typical of that resulting from the phase separation of a polymer solution with a very low polymer concentration (0.5 wt %) and below the critical polymer concentration as reported by Koenhen et al.[25] is shown. They presented an SEM photograph of the product of the coagulation process at very low (0.5%) polymer concentration. At such a polymer concentration, nucleation and growth of the concentrated phase has occurred and then latex particles of coagulated polymer were observed. Such an observation can be explained by the following: Macrovoids consist of a polymer lean phase of very low polymer concentration, and, thus, their initiation and growth can be attributed to the diffusion of solvent from the polymer solution into the polymer lean phase,

the nuclei for macrovoids, during the phase-inversion process.

CONCLUSIONS

1. In studying the kinetic effect in the phase-inversion process for preparing asymmetric membranes, it is concluded that the diffusional behavior of solvent in the polymer solution during precipitation can be regarded as Fickian.
2. The rate of diffusion of the solvent from the polymer solution, relative to the rate of diffusion of the nonsolvent into the polymer solution, plays an important role in determining the membrane structure.
3. It can also be concluded from the kinetic observation of the formation of macrovoids that macrovoids are caused by a diffusional flow resulting from the growth of the polymer lean phase during binodal decomposition. It is confirmed by the existence of latex particles of coagulated polymer in macrovoids which is thought to be the result of the nucleation and growth of the concentrated phase.

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