Microporous Poly(methyl methacrylate) Membranes: Effect of a Low-Viscosity Solvent on the Formation Mechanism

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Received January 22, 1990; Revised Manuscript Received April 20, 1990

ABSTRACT: The effect of a relatively low viscosity solvent, *tert*-butyl alcohol, on the formation of microporous poly(methyl methacrylate) (PMMA) membranes through the thermally induced phase separation (TIPS) method has been studied. Both cloud point and spinodal curves of a secondary standard PMMA (M_w = 93 300, M_n = 46 400) in *tert*-butyl alcohol were determined by optical density methods and thermal analysis. A rather flat cloud point curve was observed for this system which may be associated with hydrogen-bonding effects. In comparison to more viscous systems, it was determined that phase separation by nucleation and growth is more favorable during the quench through the metastable region into the unstable region of a low-viscosity system such as PMMA/*tert*-butyl alcohol. In the case of the PMMA/*tert*-butyl alcohol system studied here, except near the critical composition, it was not possible to avoid any effects of nucleation and growth during quenching into the unstable region until the PMMA concentration was increased to 25 wt %. In terms of designing a well-defined porous structure with good material strength through the TIPS process, this study illustrates the importance of choosing a system viscous enough to avoid phase separation by nucleation and growth during quenching to the unstable region.

Introduction

Microporous polymeric products have been developed for a variety of applications. These include preparation of targets for inertial confinement fusion,[1,2] catalyst supports,[3] controlled-release devices,[4] and asymmetric membranes as well as various medical uses such as artificial cells[5] and vascular replacements.[4] Since the early 1960s,[6] asymmetric membranes or microporous polymeric products for microfiltration, ultrafiltration, reverse osmosis, and gas separation have been commercially produced by the conventional phase inversion process. Recently, the thermally induced phase separation (TIPS) method for preparing microporous polymeric membranes was introduced by Castro.[7,8] This method has been reported[8-10] to allow for better process control, higher reproducibility, and production of higher void volume (about 80%) products compared to the phase inversion method. It has been demonstrated in a number of studies, including previous work by Tsai and Torkelson,[11] that the void volume of microporous products can exceed 90% when prepared by the TIPS method if an appropriate high-viscosity solvent is chosen. The basic idea behind this technique is to utilize heat as a latent solvent to induce phase separation; in contrast, in the phase inversion method, a nonsolvent is added to the system. Essentially, the TIPS process is comprised of three steps. First, an appropriate polymer/solvent system is heated if necessary to achieve a homogeneous solution. Next, the temperature of the polymer/solvent system is lowered to induce phase separation, i.e., a transition from a one-phase homogeneous solution to a two-phase heterogeneous system. Finally, the phase-separated structure is frozen in by an appropriate cooling medium followed by solvent removal through sublimation or liquid extraction.

By varying the composition and temperature, polymer solutions can be brought into different regions under the binodal envelope in a phase diagram exhibiting an upper critical solution temperature (UCST). The area below the binodal envelope can be demarcated by the spinodal curve into metastable and unstable regions. In the metastable region (the second derivative of the Gibbs free energy of mixing with respect to composition is greater than zero), the sample is believed to undergo phase separation by the nucleation and growth mechanism. For phase separation to take place in the metastable region, a large composition fluctuation is required. This activated process requiring an increase in the free energy to form initial fragments (nuclei) is referred to as nucleation. Once nuclei of sufficient size are formed, the system decomposes from the homogeneous region into the heterogeneous region with a decrease in free energy, and the nuclei grow in extent without changing composition, which is termed growth. The sizes of these nuclei increase initially by the growth mechanism and later by coarsening until two large phases are formed.

Growth of the nucleus has been monitored for polymer blends by both optical[12] and transmission electron microscopy.[13] Our previous study[11] was able to demonstrate a structure phase separated by nucleation and growth for a polymer solution. In that study,[11] a very weak structure composed of strings of small beads was obtained by quenching a polymer solution with the low polymer content (5 wt % PMMA/95 wt % sulfolane) into a metastable region. However, for a polymer solution of high concentration (usually with polymer concentration roughly equal to or greater than the critical concentration, C^*), a structure composed of nuclei of the practically pure solvent phase embedded among the polymer matrix is expected. In addition, the nucleation and growth mechanism needs time to initiate the formation of the nuclei. If the mobility of the system is low enough and if the polymer solution is quenched fast enough to a temperature within the unstable region, nucleation and growth can be avoided during quenching.

Alternatively, when the system is in the unstable region (the second derivative of the Gibbs free energy of mixing is less than zero), any small fluctuations in composition will lower the free energy and continue to grow. Thus, phase separation should take place spontaneously without any thermodynamic barriers until equilibrium is reached. This mode of phase separation is known as spinodal decomposition. A mathematical treatment of the early

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0024-9297/90/2223-4983$02.50/0

stages of spinodal decomposition has been well developed by Cahn and Hilliard.[14,15] During the early stages of spinodal decomposition, it is believed that the composition departing slowly from the average changes exponentially with time whereas the volume fractions of the phases remain constant. A characteristic interconnected phase morphology is its main feature and has been reportedly observed in both polymer blends[16] and polymer solutions.[11,17] As equilibrium is reached, the system tends to minimize its interfacial free energy by decreasing the interfacial area. The interconnected structures may coarsen by one of two distinct mechanisms: an interfacial energy-driven viscous flow mechanism (coalescence) or Ostwald ripening. Coarsening results in formation of a spherically dispersed structure. However, if the viscosity of the system is relatively high, the final structure may still possess some resemblance to the initial interconnected structure.[18] This phenomenon has been observed in our previous study with a poly(methyl methacrylate) (PMMA)/sulfolane system.[11]

In order to freeze the resulting membrane structure at a desired point in time, the phase-separated system has to be quenched quickly to a temperature either below the glass transition temperature of the polymer-rich phase domain or the solidification point of the solvent-rich phase domain. Both *tert*-butyl alcohol, used in our present study, and sulfolane, used in our previous study, have high solidification temperatures which are convenient for freezing pore structures of the resulting membranes.

Our previous study[11] illustrates that an understanding of the formation mechanism of the microporous polymeric membranes is available through a detailed phase diagram. In the PMMA/sulfolane system,[11] excellent agreement between the conditions of phase separation (in either the metastable or the unstable region) and the membrane morphology observed by scanning electron microscopy was obtained. During the very early stage of phase separation by spinodal decomposition, a membrane with an interwoven structure results. In contrast, for membranes prepared from low polymer content solutions, a structure composed of strings of small beads is a consequence of the early stage of nucleation and growth.

Our current study investigates further the effect of solvent on the formation of asymmetric PMMA membranes. A much less viscous, hydrogen-bonding system, PMMA/*tert*-butyl alcohol, was chosen to compare with our previous results.[11] It is hoped that this work will contribute an understanding of the membrane formation mechanism, in particular as it relates to the system or solvent selection as well as the design of a structure with desired material strength. In our previous paper,[11] the importance of the phase diagram in designing a well-defined porous structure with good material strength is demonstrated. This current study will not only illustrate the importance of a detailed phase diagram but also emphasize the significance of choosing a system viscous enough to avoid phase separation by nucleation and growth during quenching to the unstable region.

Experimental Section

Secondary standard PMMA (M_w = 93 300, M_n = 46 400) was purchased from Scientific Polymer Products, Inc. Reagent grade *tert*-butyl alcohol was obtained from J. T. Baker Chemical Co. All materials were used as received.

Cloud points were determined by the optical density method with an IBM 9410 UV-visible spectrophotometer. A cooling rate of 0.29 °C/min was used for all cloud point measurements. The spinodal curve was determined with a Perkin-Elmer DSC2. The detailed experimental procedure for the determination of the phase diagram was described in our previous study.[11]

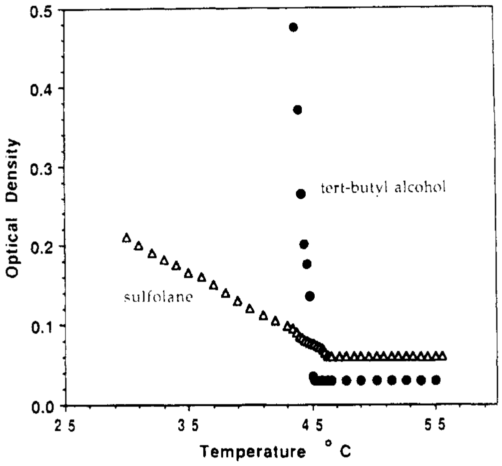

Figure 1. Variation of the relative optical density at 800 nm during cooling (●) a 15 wt % PMMA/*tert*-butyl alcohol solution and (△) a 15 wt % PMMA/sulfolane solution. The cooling rate is about 0.29 °C/min.

The thermally induced phase separation method[11] was used to prepare the asymmetric membranes. The initial homogeneous polymer solution was confined within a thin aluminum sheet and a Teflon block. A 5-in.-diameter compartment for holding the original polymer solution was inserted in an integrated manner on top of the Teflon block. The Teflon compartment is 500 μm in thickness. The casting cell was then held inside the cell assembly. (See ref 11 for a schematic diagram.) Temperature control was achieved by circulating water of the desired temperature through the inner chamber of the cell assembly. For freezing the membrane structure, liquid nitrogen can be introduced either into the annular space at the side of assembly or directly onto the top of the casting cell. The temperature of the polymer solution in contact with the aluminum sheet was monitored by placing a chromel-alumel thermocouple inside the cell assembly. The temperature of the aluminum surface can be controlled within ±0.1 °C fluctuation.

After the membrane was prepared by freezing the phase-separated PMMA/*tert*-butyl alcohol system, freeze-drying was used to remove the remaining *tert*-butyl alcohol in order to preserve the membrane microstructure. Freeze-drying was carried out with a VirTis bench top freeze-dryer at −55 °C for at least overnight. Cross sections of the resulting membranes were prepared by freeze-fracturing under liquid nitrogen. The surfaces of the resulting membranes were then coated by gold sputtering for scanning electron microscopy with a Hitachi S-570 SEM.

Results and Discussion

Phase Behavior and Phase Diagram Determination. *tert*-Butyl alcohol was chosen as the solvent mainly for its low viscosity and its high freezing temperature. As with sulfolane, which was used in our previous study,[11] *tert*-butyl alcohol has its solidification point near room temperature (around 26 °C), which is convenient for freezing the resulting membrane structure. Most importantly, the PMMA/*tert*-butyl alcohol solution is relatively mobile compared to the PMMA/sulfolane system. This distinct contrast in viscosity between sulfolane (6.5 cP at 50 °C) and *tert*-butyl alcohol (1.3 cP at 50 °C) allows us to investigate the effect of solvent viscosity on the resulting membrane structure. Additionally, in contrast to the PMMA/sulfolane system, the high mobility of the PMMA/*tert*-butyl alcohol system leads to a macrophase separation after annealing a certain period of time (about 30 min). Furthermore, hydrogen bonding formed between the hydroxyl group of the *tert*-butyl alcohol and the ester group of the PMMA molecules leads us to another interesting facet in studying the phase behavior of this system.

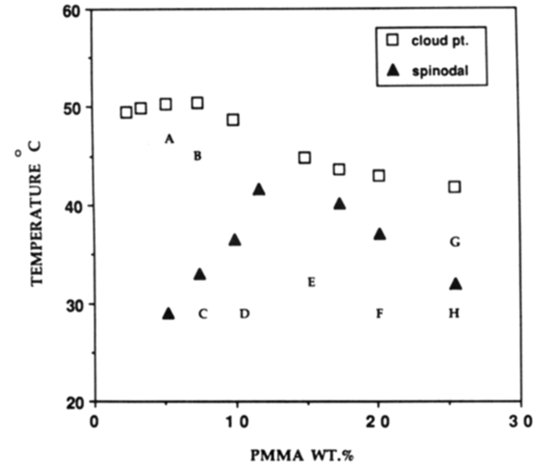

Figure 2. Phase diagram for a secondary standard PMMA (M_w = 93 300, M_n = 46 400)/*tert*-butyl alcohol system determined by the optical density method (cloud point curve) and thermal analysis with a DSC (spinodal curve).

Figure 1 shows a typical example for determining the cloud point by the optical density method. In Figure 1, variations of the apparent optical density during cooling 15 wt % PMMA/sulfolane and 15 wt % PMMA/*tert*-butyl alcohol solutions are compared. (The same cloud points can be obtained by heating a phase-separated system.) It should be noted that a cloud point curve does not coincide with the binodal curve for a polydisperse system. However, we believe that the cloud point curve determined through the optical density method for this system can offer a good basis for the SEM study in terms of dividing the homogeneous and heterogeneous regions. The increase in optical density at the cloud point for the PMMA/*tert*-butyl alcohol system is much sharper than in the PMMA/sulfolane system. This observation implies that the phase separation takes place much faster in the PMMA/*tert*-butyl alcohol system than in the PMMA/sulfolane system; this is expected based on the large differences in viscosity of the two solvents. Figure 2 shows a phase diagram including both cloud point and spinodal curves determined for the PMMA/*tert*-butyl alcohol system; a peculiar, flat cloud point curve was observed. This phenomenon is presumably due to hydrogen-bonding effects in the system. ten Brinke and Karasz[19] investigated the specific interaction effect on the phase diagram for polymer blend systems. In ten Brinke and Karasz's directional-specific model, they suggested that an extremely directional-specific interaction, hydrogen bonding, can be used to explain the very flat bottom of the closed-loop LCST phase diagram specifically observed for certain polymer blend systems. For the first time, a similar flat cloud point curve is observed for the polymer solution system. (The extreme broadness of the cloud point curve cannot be attributed to polydispersity of the PMMA or solvent viscosity as relatively narrow cloud point curves were determined for the PMMA/sulfolane system[11] and the PMMA/xylene system[17] using polymer identical with that used in this study.) It is also important to note that the flat cloud point curve in Figure 2 results in a much larger metastable regime than for the PMMA/sulfolane system. This, along with the lower solvent viscosity of *tert*-butyl alcohol, should enhance the likelihood of observing nucleation and growth during a quench to the metastable regime as compared to the PMMA/sulfolane study.

The spinodal curve shown in Figure 2 was determined by thermal analysis.[20,21] As shown with the PMMA/sulfolane system in our previous study,[11] this method has been proved to be a convenient way to determine the spinodal curve. However, this measurement must be carried out very carefully and patiently in order to be able to observe this transition. The basic idea behind this method is to observe the thermal transition due to the spinodal decomposition mechanism upon quickly quenching the sample into the unstable region. In the PMMA/sulfolane system,[11] we were able to observe easily the exotherm due to spinodal decomposition by using a cooling rate of 40 °C/min. However, owing to the higher mobility of the PMMA/*tert*-butyl alcohol system, we are not able to observe its thermal transition due to spinodal decomposition until the cooling rate is increased to 80 °C/min. In addition, due to the high volatility of the *tert*-butyl alcohol, these measurements need to be carried out in an extremely careful manner to avoid any leaking of the solvent vapor during measurement. This has been ensured by weighing the tested samples before and after each measurement and using hermetically sealed sample pans.

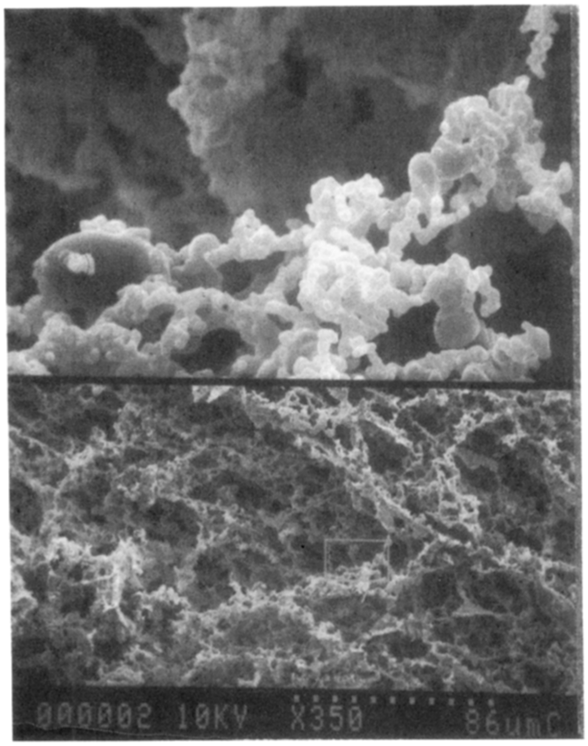

Figure 3. Scanning electron micrograph of the surface of the PMMA membrane in contact with the thermal-insulator plate. The membrane was prepared by quenching a 5 wt % PMMA/95 wt % *tert*-butyl alcohol solution to 47 °C (corresponding to the marker A in Figure 2) and holding for 2 min. (For the upper micrograph the scale bar represents 8.6 μm.)

Morphology Study of Phase-Separated Structure. In order to study the effect of the phase separation mechanism in the absence of coarsening on the resulting membrane morphology, we investigated the very early stage of phase separation by quickly quenching samples into the metastable region for nucleation and growth or into the unstable region for spinodal decomposition and then freezing the system after appropriate time periods. Various concentrations of PMMA/*tert*-butyl alcohol solutions were brought into different phase separation regions for study by employing the phase diagram displayed in Figure 2.

Figure 3 shows a membrane prepared by quenching a 5 wt % PMMA/95 wt % *tert*-butyl alcohol solution into the metastable region at 47 °C for 2 min. The structure appeared to be lacy under low magnification, but under much higher magnification it was revealed to be composed of many small beads on the order of 0.1 μm. The larger

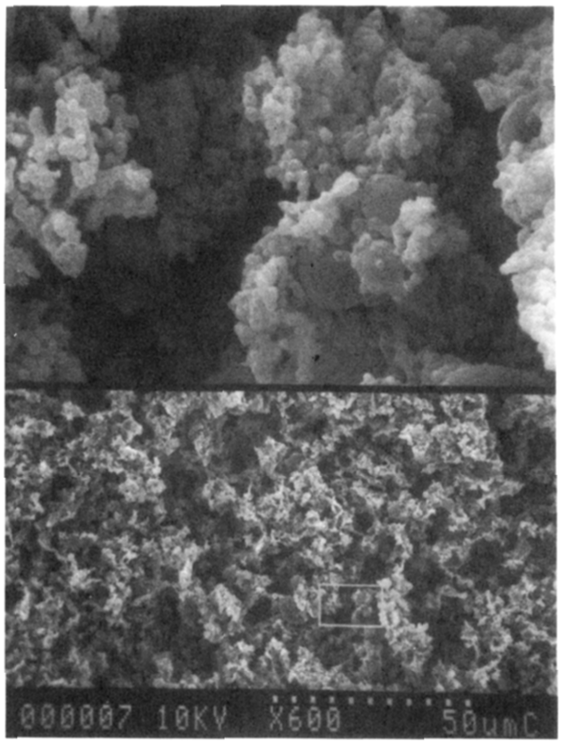

Figure 4. Scanning electron micrograph of the surface of the PMMA membrane in contact with the thermal-insulator plate. The membrane was prepared by quenching a 7.5 wt % PMMA/92.5 wt % *tert*-butyl alcohol solution to 45 °C (corresponding to the marker B in Figure 2) and holding for 5 min. (For the upper micrograph the scale bar represents 5 μm.)

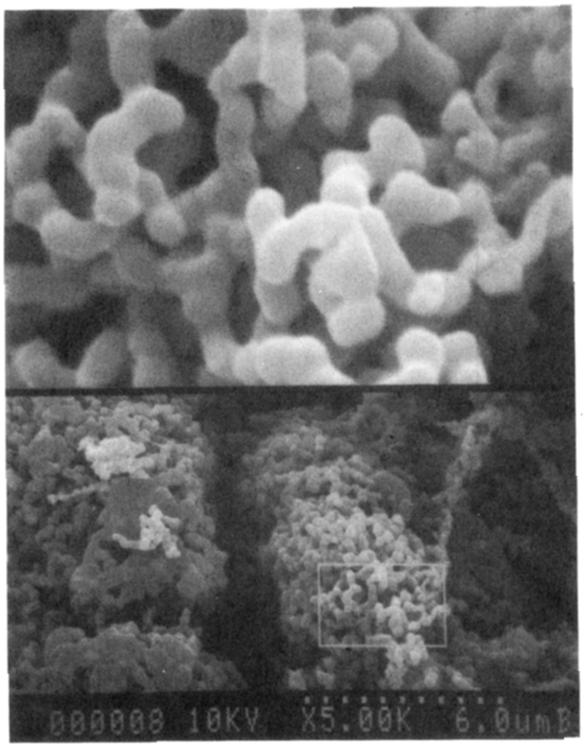

Figure 5. Scanning electron micrograph of the surface of the PMMA membrane in contact with the thermal-insulator plate. The membrane was prepared by quenching a 7.5 wt % PMMA/92.5 wt % *tert*-butyl alcohol solution to 45 °C (corresponding to the marker B in Figure 2) and holding for 30 min. (For the upper micrograph the scale bar represents 1.2 μm.)

bead observed under higher magnification in Figure 3 might be an indication of the phase-separated remnant of the polymer components with higher molecular weight fractions. In addition, this structure is very fragile. These features are consistent with what is expected for nucleation and growth. Furthermore, this observation is similar to the result[11] for a 5 wt % PMMA/95 wt % sulfolane solution quenched into the metastable region for 30 min. This similarity in structure implies that coarsening may already be occurring significantly in the PMMA/*tert*-butyl alcohol system even in the annealing time frame of 2 min. It is believed that the higher mobility of this system should allow coarsening to take place in a much shorter time frame than that in a viscous system like PMMA/sulfolane.

Figure 4 shows a membrane prepared by quenching a 7.5 wt. % PMMA/92.5 wt % *tert*-butyl alcohol solution into the metastable region at 45 °C for 5 min. A structure with many beadlike particles knitted together to form a lacy structure was observed. On the basis of the result shown in Figure 3, it is believed that this structure is a consequence of nucleation and growth followed by coarsening. Figure 5 shows a membrane prepared by the same quenching procedure and from a starting concentration as above but holding for 30 min. Apparently, the beadlike particles present at short annealing time merge together and form a multitude of regular, triangular-like clusters. It is believed that this structure is associated with macrophase separation or a precipitation process.

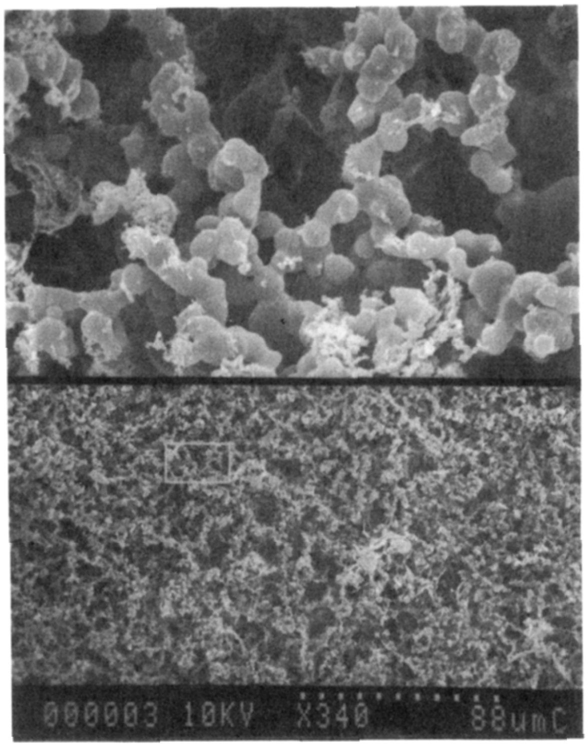

Figure 6. Scanning electron micrograph of the surface of the PMMA membrane in contact with the thermal-insulator plate. The membrane was prepared by quenching a 7.5 wt % PMMA/92.5 wt % *tert*-butyl alcohol solution to 29 °C (corresponding to the marker C in Figure 2) and holding for 1.5 min. (For the upper micrograph the scale bar represents 8.8 μm.)

Figure 6 shows a membrane made from a solution with the same composition as in Figure 5 but quenched into the unstable region at 29 °C for 1.5 min. At lower magnification, a lacy structure appears to be the feature of phase separation by spinodal decomposition. However, at higher magnification, we can see the structure is actually composed of some small beadlike particles. There are two possible reasons for this observation. One is that the polymer concentration is not high enough to form an interconnected structure. However, in the previous study employing sulfolane as the solvent,[11] a sound bicontinu-

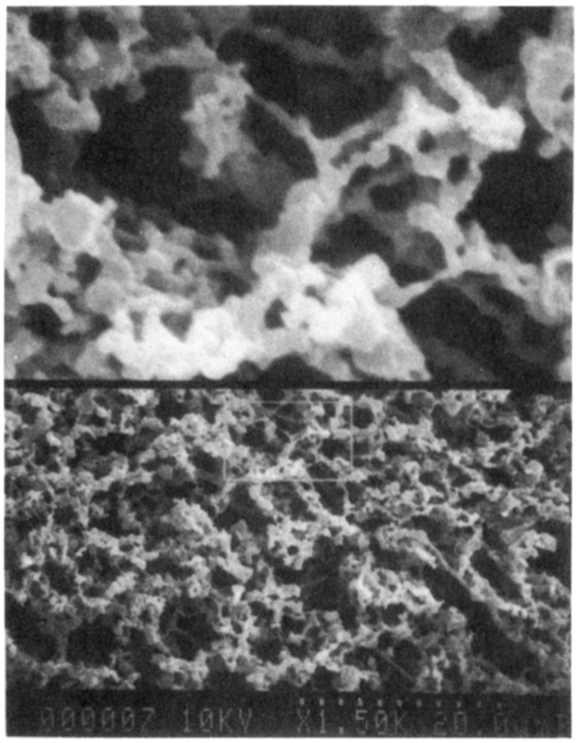

Figure 7. Scanning electron micrograph of the surface of the PMMA membrane in contact with the thermal-insulator plate. The membrane was prepared by quenching a 10 wt % PMMA/90 wt % *tert*-butyl alcohol solution to 29 °C (corresponding to the marker D in Figure 2) and holding for 1.5 min. (For the upper micrograph the scale bar represents 4 μm.)

ous, interwoven structure due to spinodal decomposition could be prepared even from a 5 wt % PMMA/95 wt % sulfolane solution. Thus, this suggests that the polymer concentration itself may not be responsible for the observed noncontinuous structure. The second possible reason might be associated with both the polydispersity of the polymer and the flow properties of the system. According to the phase diagram in Figure 2, before this 7.5 wt % PMMA sample reaches the unstable region, it has to travel through a large area of the metastable region. Combined with the fact that this system is highly mobile, it is believed that during the quench the higher molecular weight fractions may start to form nuclei. On the other hand, the lower molecular weight fractions might still undergo a spinodal decomposition process after the solution finally reaches the unstable region.

Figure 7 shows a membrane prepared by quenching a 10 wt % PMMA/90 wt % *tert*-butyl alcohol solution into the unstable region at 29 °C for 1.5 min. In Figure 7, the presence of a lacy, interwoven structure is more pervasive than in Figure 6 although some beadlike particles are embedded within this structure. This difference observed in morphology between Figures 6 and 7 is presumably due to the fact that the higher viscosity of the 10 wt % PMMA sample is able to prevent the phase separation from nucleation and growth during the quench more effectively than that of the 7.5 wt % PMMA sample. Additionally, the beadlike particles embedded within the lacy structure in Figure 7 suggest that nucleation and growth might still influence the phase separation to some extent but does not play as significant a role in phase separation as for the membrane shown in Figure 6. Furthermore, the morphology shown in Figure 7 also supports our hypothesis for the 7.5 wt % PMMA results that the higher molecular weight fractions may phase separate by nucleation and growth during the quench.

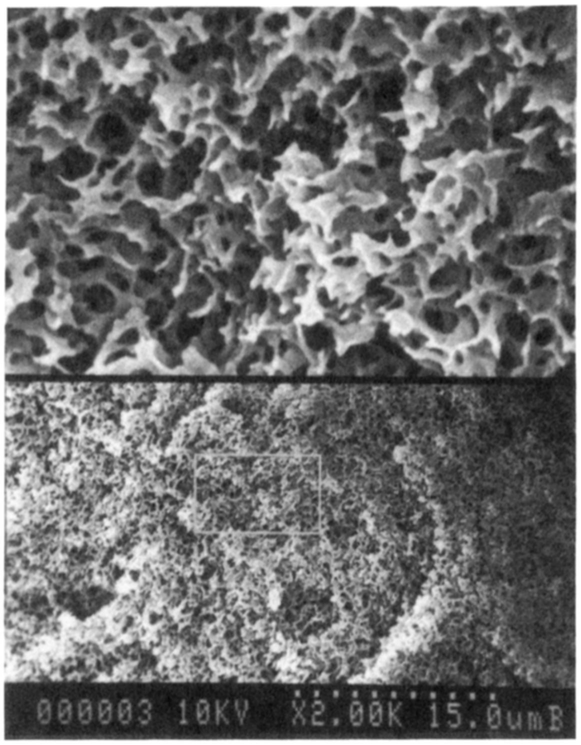

Figure 8. Scanning electron micrograph of the cross section of the middle portion of a PMMA membrane. The membrane was prepared by quenching a 15 wt % PMMA/85 wt % *tert*-butyl alcohol solution to 32 °C (corresponding to the marker E in Figure 2) and holding for 1.5 min. (For the upper micrograph the scale bar represents 3 μm.)

According to the phase diagram, the 15 wt % PMMA/85 wt % *tert*-butyl alcohol solution is the starting solution most likely in the neighborhood of the critical composition for this quasi-binary phase diagram. It is expected that nucleation and growth can be easily avoided during quenching for this composition because the metastable region disappears. The membrane made from the 15 wt % PMMA sample was quenched to 32 °C and stored for 1.5 min prior to being frozen in. Figure 8 shows the cross-section view of the middle portion of the resulting membrane. In contrast to the previous structures shown in Figures 3–7, an interconnected, lacy structure with uniform pore size on the order of 0.3 μm was seen. In addition, this membrane has a much better material strength than that of the membranes shown in the previous figures. Furthermore, in comparison with the structure prepared from a 13.5 wt % PMMA/sulfolane sample (a composition close to the critical composition of this system) and annealed for approximately same time period,[11] the structure shown in Figure 8 seems to possess a thicker wall among the cells. This is presumably due to the fact that the starting solution concentration of the PMMA/*tert*-butyl alcohol system is higher than that of the PMMA/sulfolane system.[11]

Figure 9 shows a membrane prepared by quenching a 20 wt % PMMA sample into the unstable region at 29 °C for 1.5 min. Instead of an interwoven structure with well-defined pore size obtained with the spinodal decomposition, a structure with voids of various sizes randomly dispersed among the PMMA matrix was observed. In addition, this structure possesses a certain degree of regularity. It should be noted that as nucleation takes place in the low-concentration region, the nucleus is mainly comprised of polymer molecules, dispersed among the continuous solvent-rich phase. This is shown in Figures 4–6. In contrast, in the high-concentration region (usually at the

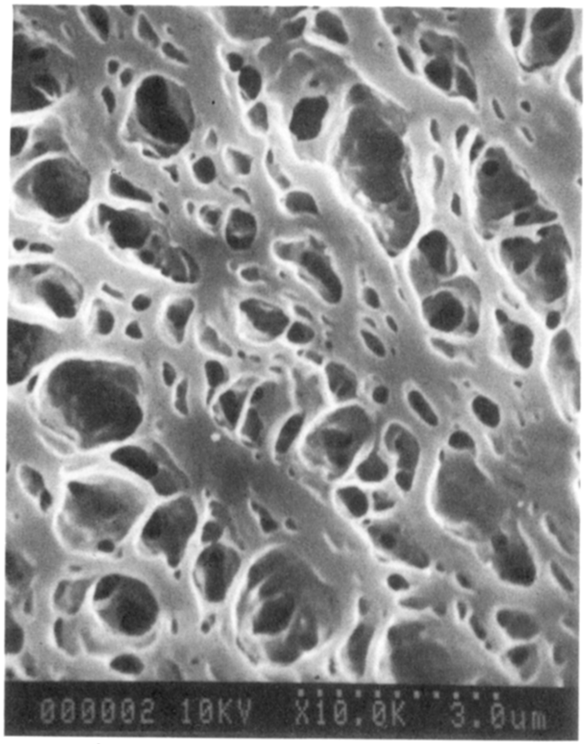

Figure 9. Scanning electron micrograph of the surface of the PMMA membrane in contact with the thermal-insulator plate. The membrane was prepared by quenching a 20 wt % PMMA/80 wt % *tert*-butyl alcohol solution to 29 °C (corresponding to the marker F in Figure 2) and holding for 1.5 min.

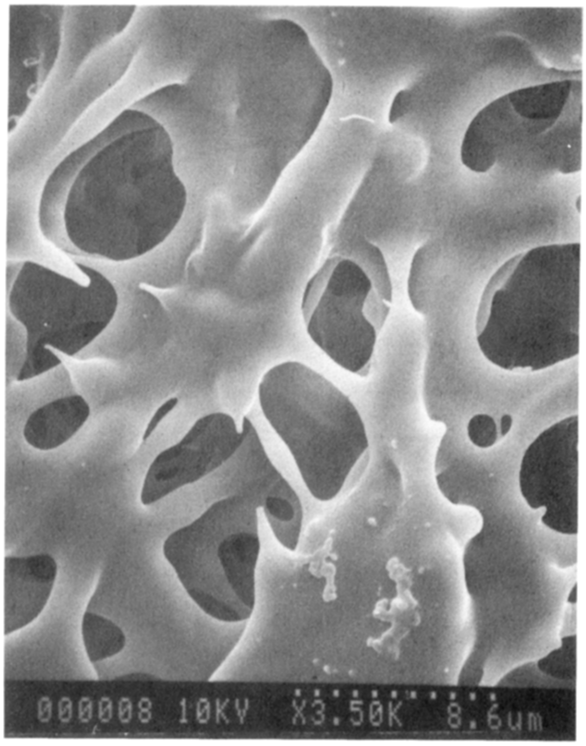

Figure 10. Scanning electron micrograph of the surface of the PMMA membrane in contact with the thermal-insulator plate. The membrane was prepared by quenching a 25 wt % PMMA/75 wt % *tert*-butyl alcohol solution to 35 °C (corresponding to the marker G in Figure 2) and holding for 1.5 min.

right-hand side of a binary phase diagram), the nucleus droplet is mainly comprised of solvent molecules, embedded in the continuous polymer-rich phase. Accordingly, some of the voids appearing in Figure 9 might originally be occupied by the solvent-formed nuclei due to the nucleation and growth of the higher molecular weight fractions during the quenching. On the other hand, some of the regularity can presumably be attributed to the remnant phase separated by the spinodal decomposition of the lower molecular weight fractions as the sample eventually entered into the unstable region. In other words, the morphology shown in Figure 9 may be a combination of a structure phase separated by the nucleation and growth of the higher molecular weight fractions and a structure phase separated by the spinodal decomposition of the lower molecular weight fractions. Additionally, this result suggests that the viscosity of this starting solution is still not high enough to avoid the nucleation and growth mechanism during quenching, at least for the polymer fractions with higher molecular weight.

In order to support further our hypothesis regarding the 20 wt % PMMA sample, we quenched a 25 wt % PMMA sample into a metastable region. Except for lacking the degree of regularity present in Figure 9, Figure 10 shows a structure reasonably similar to the one obtained by quenching the 20 wt % PMMA sample into the unstable region. This result supports our hypothesis relating to nucleation and growth still influencing the phase separation mechanism to some extent for the 20 wt % PMMA sample. Further, we prepared a membrane by quenching this 25 wt % PMMA sample into an unstable region at 29 °C for 1.5 min. Interestingly, a sound lacy, interconnected structure with pore size on the order of 2 μm and a good material strength was observed. The surface view of the membrane is shown in Figure 11. This structure exhibits all the main features of the spinodal decomposition mechanism.

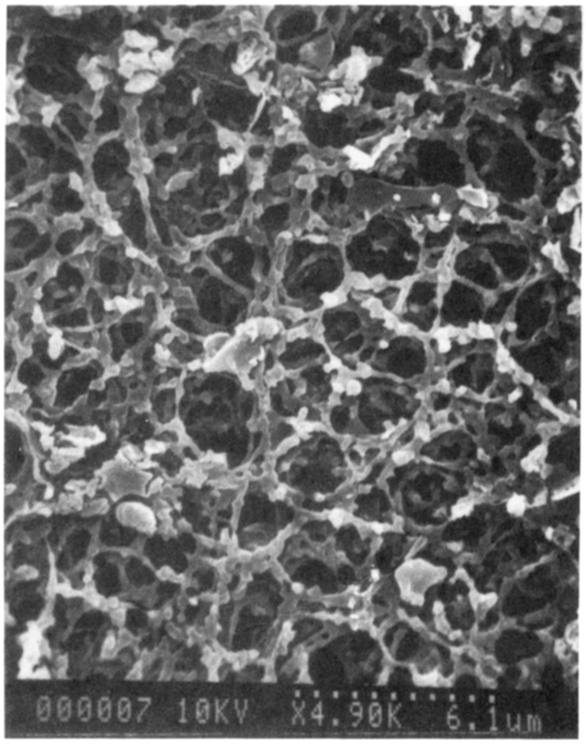

Figure 11. Scanning electron micrograph of the surface of the PMMA membrane in contact with the thermal-insulator plate. The membrane was prepared by quenching a 25 wt % PMMA/75 wt % *tert*-butyl alcohol solution to 29 °C (corresponding to the marker H in Figure 2) and holding for 1.5 min.

For this 25 wt % PMMA sample, the excellent agreement between the conditions of phase separation (either in the metastable or in the unstable region) and the membrane morphology observed by SEM suggests that the nucleation and growth mechanism during the quenching can be retarded or completely avoided. Intuitively, it is believed that this observation is associated with the increase in viscosity simply due to the increase of polymer content in the starting solution. Furthermore, we also measured the intrinsic viscosity of this system. The intrinsic viscosity, $[\eta]$, of the PMMA/*tert*-butyl alcohol system at 55 °C was determined to be about 0.041_8 dL/g. On the basis of this information, we further calculated the overlap concentration C^*. C^* is an important scaling property of polymer coils in solution, believed to be associated with a transition region separating dilute solutions (nonoverlapping coils in solvent) from semidilute solutions (polymer coils interpenetrate one another). In other words, at C^*, it is possible for polymer coils in solution to interpenetrate one another. According to Graessley,[22] C^* for linear chains in solution can be obtained from the expression $0.77/[\eta]$. In this case, C^* was calculated and was roughly equivalent to a $21._9$ wt % PMMA solution sample. For a relatively low viscosity system like PMMA/*tert*-butyl alcohol, this investigation implies that below C^*, the nucleation and growth mechanism might easily occur during quenching. As the concentration is above C^*, nucleation and growth might be avoided due to the fact that a longer time frame is required to initiate the nucleation process. It should be noted that the increase in viscosity above C^* may be important in avoiding the occurrence of nucleation and growth during quenching. However, we do not exclude the possibility that the increase in viscosity unrelated to C^* and simply due to the increase in polymer content is responsible for the suppression of nucleation and growth during the quench of the 25 wt % PMMA sample to the unstable region of the phase diagram. Further investigation of this issue is underway.

Summary

Through the thermally induced phase separation method, the resulting membrane morphology can be affected by various parameters such as modes of phase separation (nucleation and growth vs spinodal decomposition), coarsening effect (Ostwald ripening vs coalescence), solution viscosity, quenching rate, and the polydispersity of polymer. In our previous paper,[11] we demonstrated the importance of the phase diagram in designing a well-defined porous structure with good material strength. In addition to reinforcing this argument, this study suggests further that the choice of a system viscous enough to prevent phase separation from nucleation and growth during quenching to the unstable region is also critically important.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation through a Presidential Young Investigator Award and Northwestern University. We also thank the Materials Research Center at Northwestern University for use of the scanning electron microscope.

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