Morphological Studies of Late-Stage Spinodal Decomposition in Polystyrene–Cyclohexanol System

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SYNOPSIS

We studied the late-stage spinodal decomposition of the polystyrene–cyclohexanol system in relation to membrane formation. Phase separation was effected by the removal of thermal energy from the homogeneous polymer solution. The ultimate morphology of the phase-separated systems has been studied using electron microscopy and has been found to be strongly affected by the quenching time. A shift from a highly interconnected open-cell structure to a closed-cell structure has been observed, indicating the transition of the spinodal decomposition from early to late stages. The cell growth in the late stage has been quantitatively analyzed and a power-law relationship between the cell size and quenching time has been found. The resulting exponent of 0.61 is consistent with literature values from light-scattering measurements, as well as from theoretical derivations. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Study of morphological characteristics of polymeric membranes is of great interest for membrane science.[1] It is known that one of the keys to better membrane performance lies in the structure of the membrane itself. In turn, the morphology of a particular membrane depends upon its processing conditions and the physical and chemical properties of the polymer system under consideration. Membranes from polypropylene,[2] high-density polyethylene,[2] and poly(vinylidene fluoride)[3,4] have been made via the thermal-inversion process. The structure was investigated for suddenly quenched systems as well as for systems where the temperature had been reduced at a controlled rate. In the case of systems suddenly quenched below the spinodal temperature, the membranes exhibited a highly interconnected "network" structure characteristic of systems that had undergone spinodal decomposition.[2-7] On the other hand, systems that had been subjected to a controlled decrease in temperature exhibited a cellular structure, characteristic of nucleation and growth.[2-4]

The current study is focused on later stages of spinodal decomposition of polymer solutions, with primary emphasis on its relation to membrane formation. Here, the network-type structure initially formed develops into spherical cells connected by pores. This has been noted by Laxminarayan,[7] Uriede and Uriede,[8] and Tsai and Torkelson.[9] It has been further observed that, at the beginning of the later stages of the spinodal decomposition, the spherical structure that is initially open tends to form closed spherical cells that increase in size with time. These changes are the result of a coarsening process in which smaller spherical cells of the solvent-rich phase tend to coalesce to form bigger cells. Apparently, this coarsening process consists of three steps: (1) approach of two such cells, also referred to as bubbles, toward each other; (2) breakup of the polymer-rich film between the approaching bubbles; and, (3) interfacial tension-induced coalescence between two smaller bubbles to form a larger one.

Considerable work has been devoted to study the dynamics of the late stages of spinodal decomposition. Siggia,[10] Langer et al.,[11] and Binder and Stauffer,[12] among others, have reported on their theo-

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retical work. Experimentally, Hashimoto and coworkers applied a light-scattering technique to study the kinetics of the late-stage spinodal decomposition in polymer blends,[13,14] whereas Lal and Bansil used its modification for polymer solutions.[15] Both theoretical and light-scattering studies have shown scaling behavior in the late stages of spinodal decomposition.

In this study, we tried a different approach. Polystyrene membranes were prepared from solution in cyclohexanol with different quenching times but the same quenching temperature, via the thermal-inversion method. The morphologies of these membranes were studied by scanning electron microscopy. Closed-cell structure was observed for membranes developed under late-stage spinodal decomposition conditions. The cell sizes of these membranes were measured and the relationship between the cell size and quenching time was analyzed to study the kinetics of the late-stage spinodal decomposition. These data and their comparison to the theoretical and light-scattering experimental results from the literature are discussed in this article.

EXPERIMENTAL

Materials

Polystyrene used in the experiments was a primary standard (MW = 400,000 g/mol) purchased from Pressure Chemical Co. Cyclohexanol, obtained from Aldrich, was fractionally distilled before use.

Membrane Preparation and Characterization

Solutions of 10 wt % polystyrene in cyclohexanol were prepared in a bath at 90°C and then maintained at this temperature for at least 1 day. This temperature is above the upper critical solution temperature of the polystyrene–cyclohexanol system.[16] The sample flask was then transferred into an oven maintained at temperatures between 90 and 100°C and kept there until needed for membrane casting.

The apparatus for preparing membranes includes a cell and an ethylene glycol bath fitted with a temperature controller. The cell (Fig. 1) consists of a Teflon cylinder, with a metal cover attached to the top. The bottom of the cylinder is formed by aluminum foil that is supported by a metal ring. Thus, the bottom of the cell is a very good thermal conductor, whereas the air space above the aluminum foil is a good insulator.

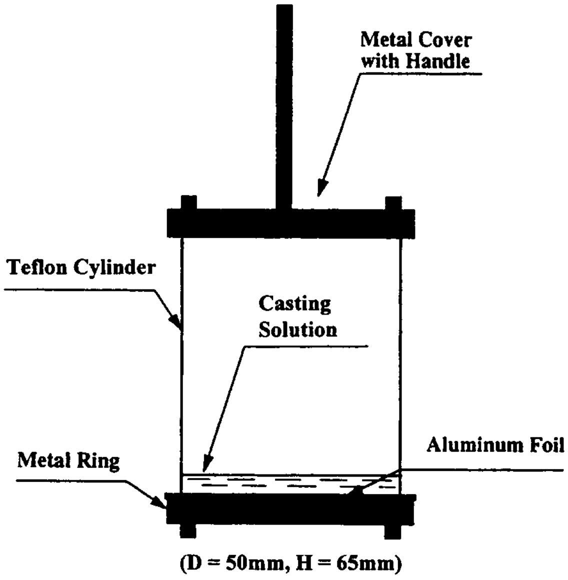

Figure 1 Cross-sectional diagram of the membrane casting cell.

Before use, the cell is first preheated in the oven. The homogeneous polystyrene solution is then poured into it to form a thin layer on the aluminum foil. The cover of the cell is replaced and the metal bottom of the cell is dipped into the ethylene glycol bath kept at 80.0 ± 0.1°C. Based on the work of Saxena et al.,[16] the system at this quench temperature should be thermodynamically unstable, i.e., below the spinodal temperature. After a predetermined quench time, the cell is put in dry ice for 20 min to freeze the structure (the freezing point of cyclohexanol is 22°C). The membrane is then taken out and immersed in ice-cold water to leach out the solvent; this step usually takes several days. Finally, the membrane is put into a vacuum oven at room temperature for 2 days to remove the water.

The dried membranes are then cracked in liquid nitrogen. A sample is cut and placed on a mounting cylinder with the fracture exposed for observation. It is coated with a gold–platinum sputter coater and observed using a scanning electron microscope (SEM). All the cross-sectional views that are displayed in the micrographs in the subsequent section show structures adjacent to the cooling aluminum-foil side of the thermal inversion cell.

RESULTS AND DISCUSSION

Figure 2 shows the scanning electron micrograph of the cross section of a polystyrene membrane that was quenched for 40 s. An interconnected network structure characteristic of the spinodal decomposi-

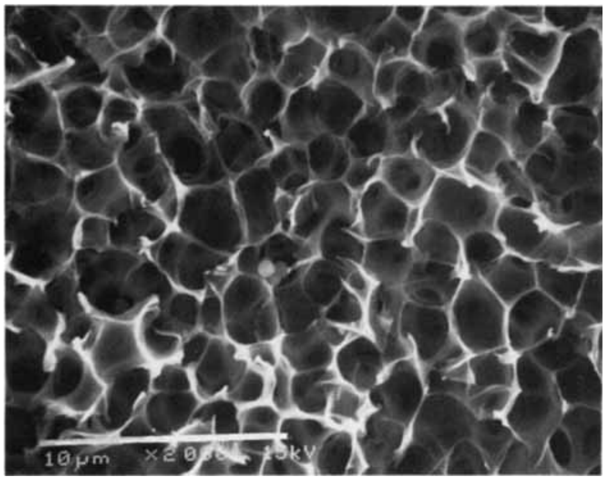

Figure 2 Scanning electron micrograph of a polystyrene membrane cast at 80°C from a 10 wt % polystyrene solution in cyclohexanol with a quenching time of 40 s.

tion process is observed. In Figure 3, the quenching time is 2 min. Here, spherical open cells (cells that are connected one to another by pores) have already been formed with an average cell size of about 1.8 µm in diameter. Figure 3(b) provides a close up of the structure. In Figure 4, for a quenching time of 5 min, the average cell size is about 2.4 µm in diameter. The membrane still maintains its open-cell structure, but with larger average size than that of the cells formed after 2 min. After 10 min of quenching (Fig. 5), the cells are already closed and their average size is about 37 µm in diameter. In Figures 6 and 7, the quenching times are 20 and 40 min, respectively. The cells are also closed and the average cell sizes are 56 and 87 µm, respectively.

It is interesting to review the geometric shapes of cells shown in Figures 5–7. Basically, four kinds of cell shapes can be found: (1) smaller spherical cells, (2) larger double-ellipsoid cells with concave necks, (3) larger ellipsoid cells, and (4) larger spherical cells. Also, the matrix in which the cells are embedded is not homogeneous; rather, it shows porosity on a much smaller scale, as seen in Figures 6(b) and 7(b). This porosity may or may not be related to the small structures formed during the early stages of spinodal decomposition.

It has been reported that spinodal decomposition of a homogeneous polymer solution leads to a highly interconnected open network structure.[2-4] Theoretically, the structure is represented by a single predominant composition wavenumber.[17] Later-stage behavior resulting in the coarsening of structure has been cited to involve open-cell formation,[7] hydrodynamic flow,[10] and gravity flow.[10] Based on these considerations and our own experimental observation, we propose that the first step after thermal quenching is the formation of an interconnected network structure by diffusion. After the compositions of the solvent-rich and polymer-rich domains have attained the binodal values, further structure evolution is believed to occur on the basis of hydrodynamic flow. The driving force here is provided by differences in curvature at various locations of the interfacial boundaries. Since the migration of polymer molecules does not result in an increase in polymer concentration, the volume of the regions of migration should increase in the process. Ultimately,

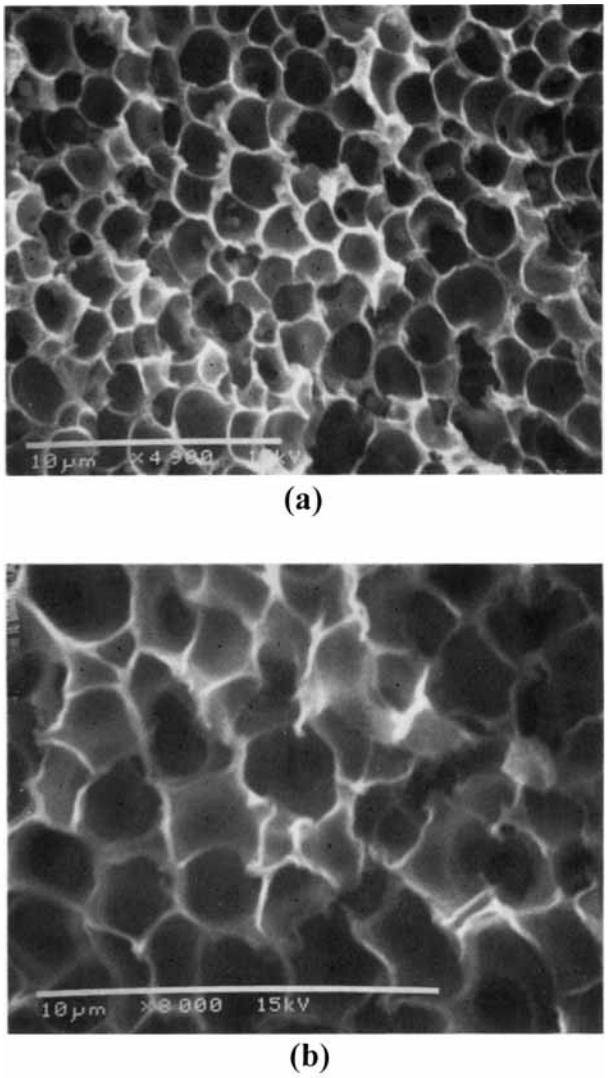

Figure 3 Scanning electron micrographs of a polystyrene membrane cast at the same conditions as in Figure 2, except that the quench time here is 2 min. (a) The cross-section of the membrane part adjacent to the thermal conductor side. (b) The close-up of the same sample.

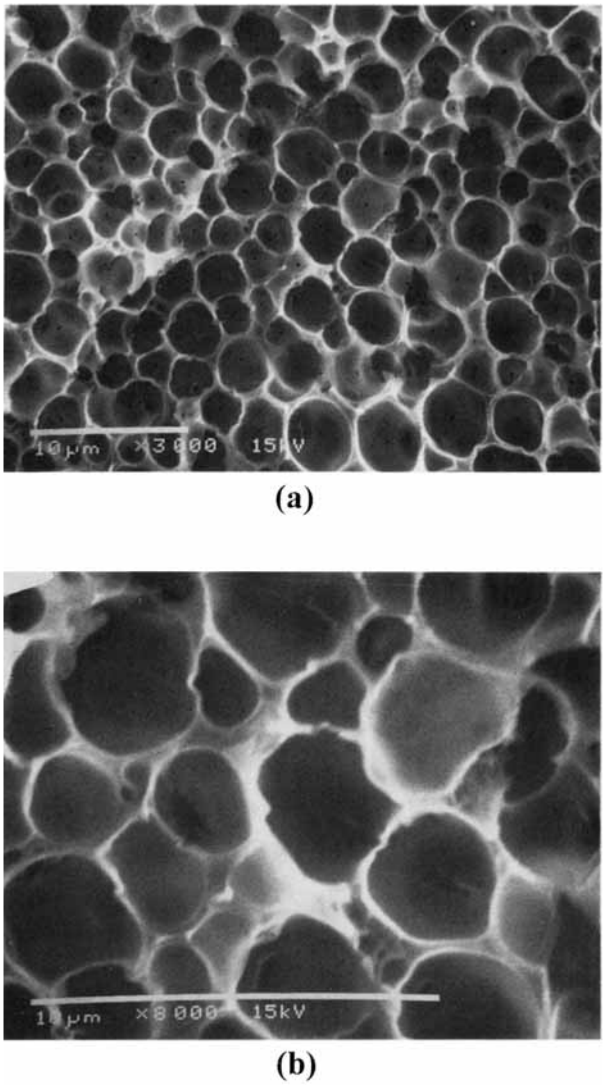

Figure 4 Scanning electron micrographs of a polystyrene membrane cast at the same conditions as in Figure 2, except that the quench time here is 5 min. (a) The cross-section of the membrane part adjacent to the thermal conductor side. (b) The close-up of the same sample.

these regions of migration will have enough polymeric material to fill up open pores, resulting in a closed-cell lattice structure. If this flow process evolves from a regular open-cell structure, then we should expect the resulting closed-cell structure to be regular as well, because regions of high and low curvature are also regularly spaced. After the spherical closed cells are formed, further coarsening primarily takes place by the approach of one closed cell to another, followed by rupture of the wall separating the cells.

Wall rupture would have to be preceded by wall thinning. The following factors can be identified as contributing to wall thinning:

1. The cells observed in these membranes obviously have nonuniform curvature, i.e., the cells are not perfectly spherical. This nonuniform curvature leads to a flow process that results in the migration of material from cell walls to cell junctions.
2. The second factor contributing to wall thinning is based on the hypothesis of Castro.[18] It assumes the possibility that, upon precipitation, the polymer phase would still be off its binodal composition. Slow diffusion of the solvent out of the polymer would then cause the walls to thin.

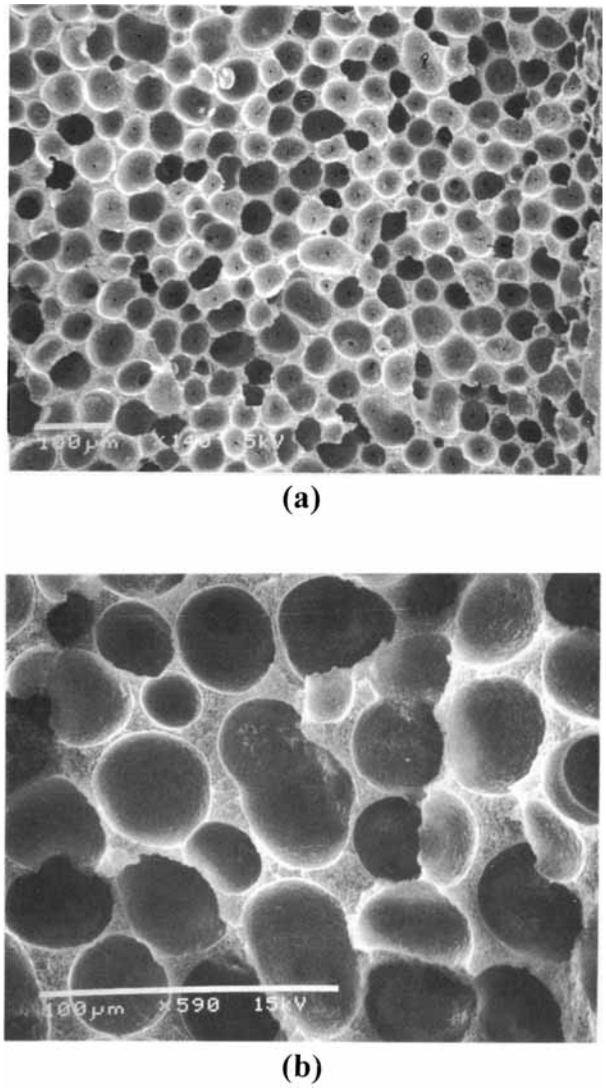

Figure 5 Scanning electron micrographs of a polystyrene membrane cast at the same conditions as in Figure 2, except that the quench time here is 10 min. (a) The cross-section of the membrane part adjacent to the thermal conductor side. (b) The close-up of the same sample.

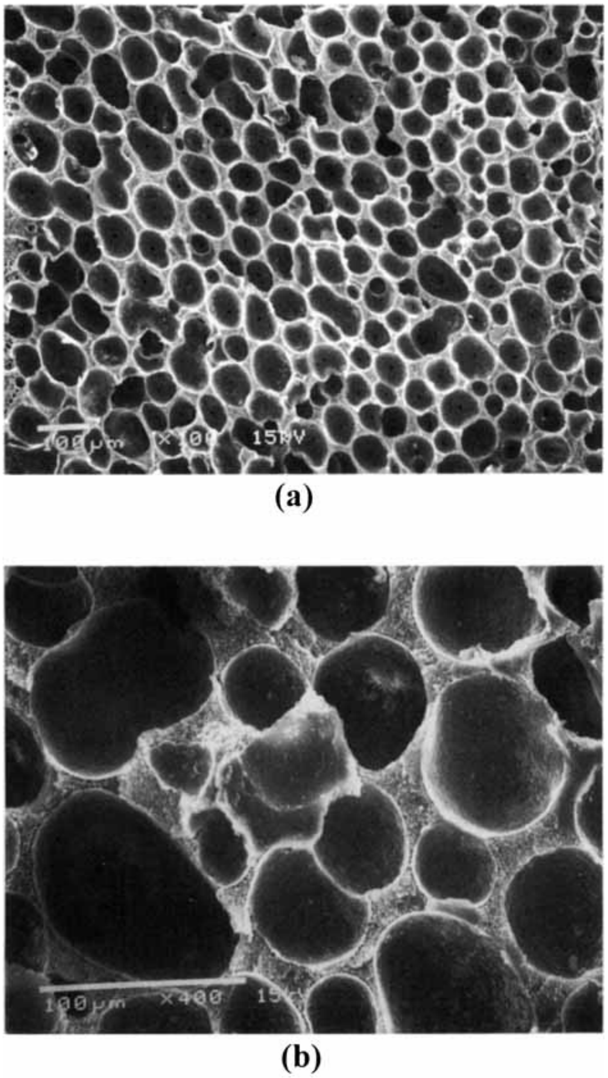

Figure 6 Scanning electron micrographs of a polystyrene membrane cast at the same conditions as in Figure 2, except that the quench time here is 20 min. (a) The cross-section of the membrane part adjacent to the thermal conductor side. (b) The close-up of the same sample.

A quantitative analysis of the cell sizes has been carried out. The diameters of all the cells in Figures 3(a), 4(a), 5(a), 6(a), and 7(a) were measured using a micrometer, and their mean value plotted against quenching time, as shown in Figure 8. It is apparent that the cell diameter generally increases with time. However, between 5 and 10 min of quenching, the time dependence seems to change functionality.

The closed-cell structure of the membrane quenched at 10 min or later (Figs. 5–7) indicates that the spinodal decomposition taking place in the system is already in its late stages. The time dependence of the closed-cell sizes can be linearized by replotting them on a logarithmic scale (Fig. 9). In Figure 9, a practically linear function is obtained with a slope of about 0.61. This result suggests that, in the late stages of our system, the relationship of the domain size and quench time obeys a power-law function with an exponent of 0.61.

Power-law relations have been predicted by Siggia,[10] Langer et al.,[11] and Binder and Stauffer,[12] among others, in their theoretical studies of the kinetics of the late-stage spinodal decomposition. Whereas Langer et al. suggested an exponent of 0.21, Binder and Stauffer's droplet coalescence growth mechanism, as well as Lifshitz and Slyozov's evaporation–condensation mechanism,[19] all predicted an

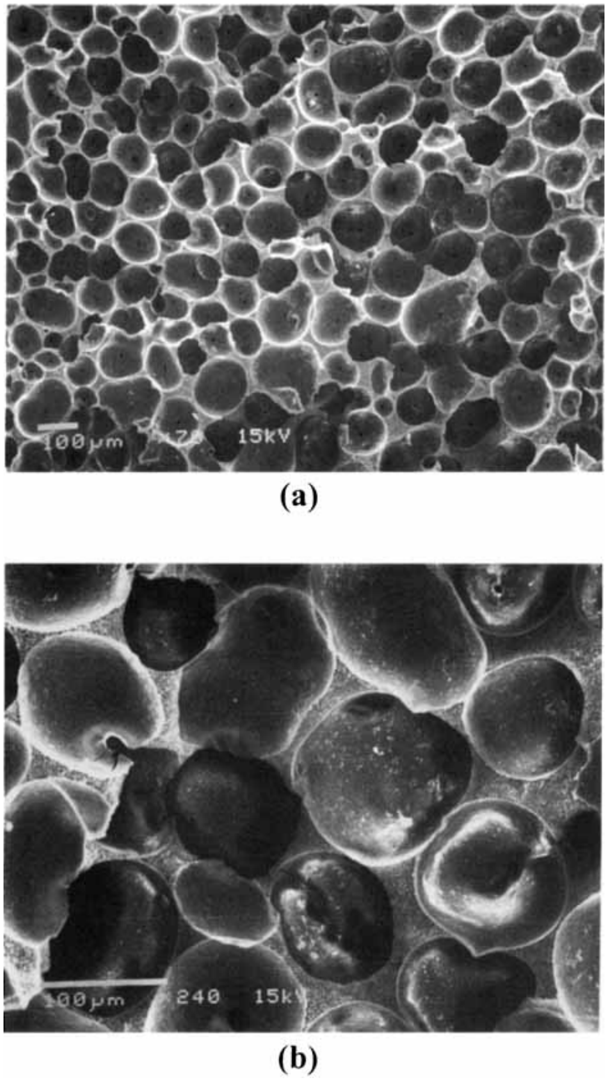

Figure 7 Scanning electron micrographs of a polystyrene membrane cast at the same conditions as in Figure 2, except that the quench time here is 40 min. (a) The cross-section of the membrane part adjacent to the thermal conductor side. (b) The close-up of the same sample.

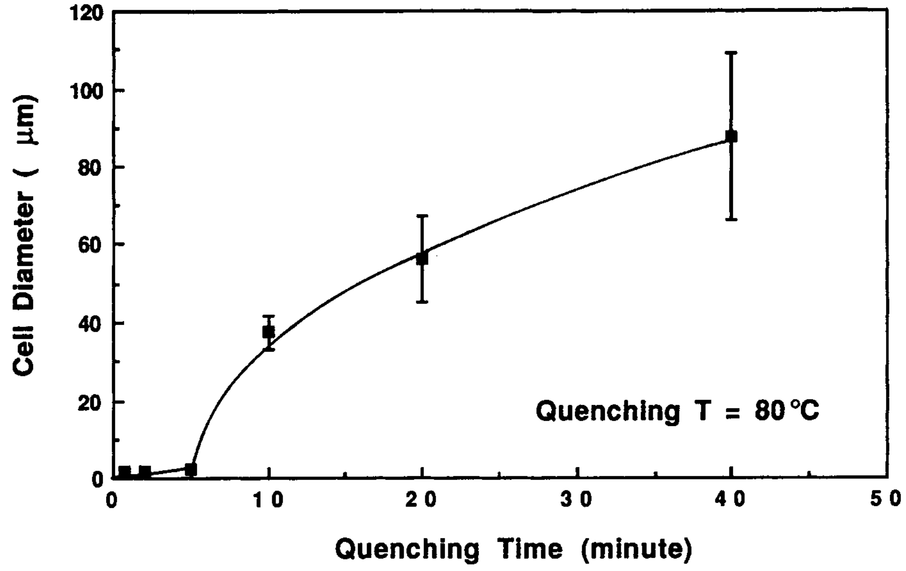

Figure 8 Plot of the diameter of the membrane cells as a function of quenching time.

exponent of $\frac{1}{3}$. On the other hand, if hydrodynamic effects are included, one should expect exponent values larger than $\frac{1}{3}$. Siggia suggested that in a quench for polymer blends at the critical concentration, where the minority phase is continuous, the surface tension effects increase the exponent value from $\frac{1}{3}$ to 1. Therefore, the value of 0.61, derived from Figure 9, should be feasible if the surface tension effects play important roles in our polymer solution system.

It should be noted that experimental exponents higher than $\frac{1}{3}$ were also obtained by two other groups. Hashimoto and co-workers studied the kinetics of spinodal decomposition for a binary mixture of polystyrene and poly(vinyl methyl ether) by using the time-resolved light-scattering technique.[14] By plotting the wavenumber (q_m) and the peak scattered intensity (I_m) as a function of time and fitting them with a power-law expression, they obtained exponent values of 0.39 and 0.42 for two dif-

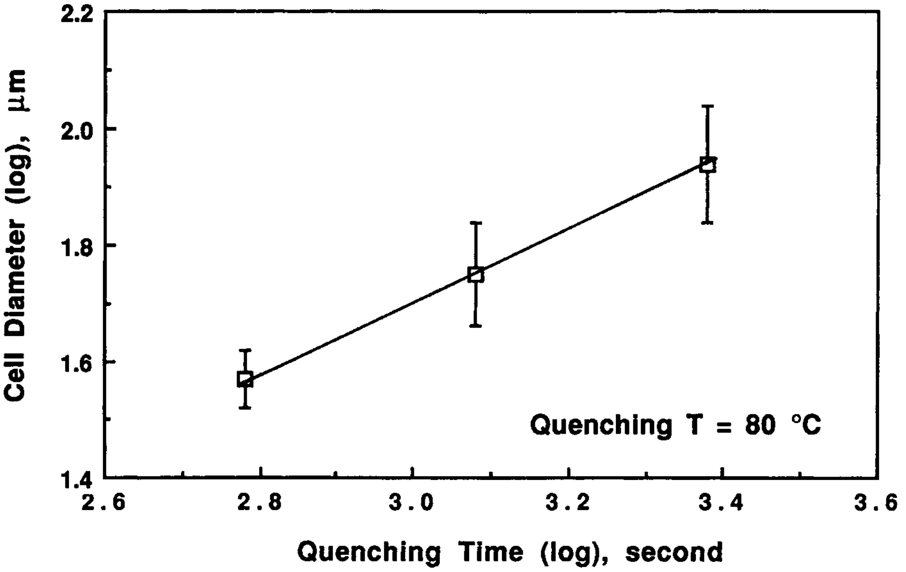

Figure 9 Plot of the logarithm (base 10) of the membrane cell diameter vs. that of the quenching time for structures with closed cells only. The slope of a line drawn through the data is about 0.61.

ferent temperatures. Their values are also higher than $\frac{1}{3}$ predicted by most theories, although not as high as ours are. This difference is not unexpected, since, in a highly viscous polymer–polymer blend, the hydrodynamic effects should play a less dominating role and therefore lower the exponent. On the other hand, the polystyrene-cyclohexane system, recently studied by Lal and Bansil using the small-angle light-scattering technique,[15] should have results similar to those that we had obtained. By plotting the peak position (k_m) as a function of time, they also obtained a power-law relationship with exponents ranging from 0.43 to 0.59, depending on the sample and quenching temperature, in reasonable agreement with our exponent value of 0.61.

In membrane formation, it is desirable to have open cells in order to maximize the flux of fluid through the separating barrier. It is therefore important to note that closed cells might form after a certain period of quenching time, and one must be able to effectively freeze the open-cell or network structure at the right time. In the thermal-inversion preparation of high-density polyethylene and polypropylene membranes, the occurrence of closed cells is minimized by the formation of crystalline domains.[2] In amorphous polymer systems, however, the open cells seem to be readily obtainable at reasonably low quenching temperatures or by using highly viscous solvents. Here, the viscosity of the polymer-rich phase could be high enough to result in a lower rate of interfacial tension-induced flow.

CONCLUSIONS

Based on our morphological study of polystyrene membranes prepared by the thermal inversion process, we conclude the following:

1. The structure of a polymer membrane made by thermal inversion is strongly affected by the processing time, i.e., the quenching time. The morphology of a membrane, formed by phase separation via spinodal decomposition, shifts from an open-cell structure to a partially closed-cell structure as the quenching time increases.
2. The partially closed cells tend to coalesce and form closed cells.
3. A power-law relationship has been found between the closed-cell size and the quenching time, with an exponent of about 0.61. This value is in reasonable agreement with some reported theoretical and light-scattering experimental results on the late-stage spinodal decomposition of other polymer systems.

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