Macromolecules 1994, *27*, 6389–6397

Coarsening Effects on Microstructure Formation in Isopycnic Polymer Solutions and Membranes Produced *via* Thermally Induced Phase Separation

Seung-Won Song[†] and John M. Torkelson[*,†,‡]

Departments of Chemical Engineering and of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208-3120

Received March 4, 1994; Revised Manuscript Received August 15, 1994[⊛]

ABSTRACT: The phase separation of *isopycnic* polystyrene–diethyl malonate solutions has been studied by investigating the microstructure of polymer membranes. Polymer solutions underwent spinodal decomposition and coarsening *via* a thermally induced phase separation procedure, and supercritical CO_2 extraction was employed to remove solvent, resulting in microporous membranes. At relatively short coarsening times, the coarsening rate of the cell size can be expressed as a power law in time with the exponent increasing with increasing quench depth; for deep quenches, the growth rate has an exponent of $^1/_3$ in agreement with the classic theories for coarsening by Ostwald ripening or coalescence. At longer coarsening times, there was a crossover to a much faster growth rate, yielding an exponent of 1.0 independent of phase separation temperature, consistent with expectations for the hydrodynamic flow mechanism of coarsening suggested by Siggia. This is the first experimental confirmation of the evolution of the coarsening mechanism from one mechanism with a growth rate consistent with Ostwald ripening or coalescence to a second mechanism with a faster growth rate. Comparisons were also made to coarsening observed in *nonisopycnic/low-viscosity* polystyrene–cyclohexane systems where strong gravitational effects dominate the phase separation process at relatively short times and crossover effects cannot be observed.

Introduction

Thermally induced phase separation of two-component mixtures has been studied extensively, especially the early stage processes such as spinodal decomposition.[1–17] In spinodal decomposition, phase separation occurs by an instantaneous and continuous process involving a diffusional flux against a concentration gradient, i.e., uphill diffusion. A characteristic bicontinuous morphology typically results from this phase separation process which can be used to advantage in designing materials with specific properties. After the early-stage development of microstructure, the two-phase system will continue to evolve in response to its tendency to reduce the surface energy associated with interfacial area. This process, called coarsening, often results in a reduction in the number of droplets and an increase in their size.

In the case of polymer–solvent systems, coarsening is of particular importance as it may come to dominate or overshadow spinodal decomposition effects within the first minute or few minutes of phase separation. While the early stage of phase separation associated with spinodal decomposition has been the subject of significant theoretical and experimental inquiry in polymer–solvent systems,[8,12–17] less emphasis has been placed on the study of the later stage of phase separation.[16–25] In 1982, Nose and co-workers[18] reported on coarsening of polystyrene (PS)–diisodecyl phthalate solutions by *in situ* microscopic observation. They observed droplets of one phase dispersed in a matrix of a second phase, with the average droplet diameter growing with time according to a power law with an exponent of 0.30 (±0.09) for the time frame less than 1000 min. In the following year, Kuwahara and co-workers[19] reported on coarsening in an *isopycnic* system consisting of poly(dimethylsiloxane) and diethyl carbonate. Using light scattering, they observed a coarsening stage after the early stage of spinodal decomposition in which the domain size grew in time with an exponent of 0.4 for the time scale less than 10 min. More recently, Kubota and Kuwahara[17] studied exactly the same system using a time-resolved light scattering technique and observed a $^1/_3$ power law dependence of the reduced wave vector up to coarsening time scale of 10 min, but the flow stage of coarsening was not studied. Krishnamurthy and Bansil[20] investigated coarsening in PS–cyclohexane solutions undergoing phase separation which they indicated was initiated by nucleation and growth rather than spinodal decomposition. Although they ignored the strong effects of gravitational sedimentation in their dilute polymer solutions, they concluded from photographic observation that the decrease in number density of polymer-rich droplets over a rather long time period (up to 130 min) could be attributed to the coalescence of polymer-rich droplets. Later Lal and Bansil,[16] studying the same system using time-resolved small-angle light scattering, found a growth rate exponent between 0.4 and 0.5 and suggested that hydrodynamic flow effects are important in the coarsening of their dilute polymer solutions.

In contrast to the studies made by observation in the solution state, coarsening in polymer solutions may also be characterized through the properties of microporous membranes made from phase-separated polymer solutions. Tsai and Torkelson qualitatively investigated coarsening effects for the poly(methyl methacrylate) (PMMA)–sulfolane system[21] and less viscous PMMA-*tert*-butyl alcohol system.[22] They reported that a lacy structure, which is a characteristic morphology for membranes produced by thermally induced phase separation *via* spinodal decomposition, could also develop over substantial coarsening times for nucleation and growth initiated phase separation. They suggested that flow properties could play a vital role during the later stage of phase separation. They also found *via* mercury intrusion porosimetry measurements that for the PMMA–sulfolane system the coarsening time dependence of the average pore size followed a power law with an exponent of

---

[*] To whom correspondence should be addressed.

[†] Department of Chemical Engineering.

[‡] Department of Materials Science and Engineering.

[⊛] Abstract published in *Advance ACS Abstracts*, September 15, 1994.

0024-9297/94/2227-6389$04.50/0

approximately $^1/_3$ during the first 100 min of phase separation at 13 °C below the cloud point temperature.[23] In a more extensive study, Aubert[24] investigated coarsening in the PS–cyclohexane system using scanning electron microscopy and BET surface area measurements. He showed that the growth rate of pore size follows a power law in time with an exponent in the range of 0.18–0.32 and that the structures remained highly interconnected throughout the coarsening experiments. In contrast to other studies which investigated solution coarsening by *in situ* techniques and indicated that coarsening occurred by coalescence and/or the hydrodynamic flow mechanism, Aubert concluded that the Ostwald ripening mechanism was consistent with his observations.

Given the disagreement in the conclusions drawn from the few coarsening studies reported on polymer–solvent systems, it is clear that a detailed understanding is lacking not only of the mechanisms responsible for coarsening in polymer solutions but also of how these mechanisms affect microstructure in solutions and in membranes produced from them. In the present study, we have specially selected a polymer–solvent system which is *isopycnic*, i.e., where the polymer and solvent densities are nearly perfectly matched, in order to extend the time scales accessible for coarsening studies in the absence of macroscopic phase separation due to buoyancy or gravitational effects.[26] In this manner, it is possible to comment on both how coarsening is initiated and how it evolves over time in polymer–solvent systems. Comparisons of coarsening studies in the *isopycnic* system, PS–diethyl malonate, are made to the commonly studied PS–cyclohexane system, where gravitational flow effects result in macroscopic phase separation on relatively short time scales.

Coarsening Background

Three different mechanisms have been described as being responsible for coarsening in the later stages of phase separation: Ostwald ripening, coalescence, and the hydrodynamic flow mechanism. In the first, Ostwald ripening, the total energy of the two-phase system composed of a dispersed second phase in a matrix can be decreased *via* an increase in the size of the second phase and thus a decrease in the total interfacial area. The classical theory of Ostwald ripening (widely referred to as the LSW theory or evaporation–condensation mechanism in materials science) was significantly developed by Lifshitz and Slyozov[27] and Wagner.[28] They examined the case of widely spaced domains of a second phase growing and shrinking in a matrix. The domains have asymptotic power-law growth behavior:[29]

$$\mathrm{d} \sim (D\xi)^{1/3}t^{1/3} \tag{1}$$

where d is the average domain size, D is the diffusion constant or thermal diffusivity, ξ is the correlation length, and t is the coarsening time. The driving force for the Ostwald ripening process is the curvature dependence of the chemical potential. Assuming an isotropic surface energy, the chemical potential per atom at a point of curvature K on the surface, $\mu(K)$, may be given by eq 2:

$$\mu(K) = K\gamma\Omega \tag{2}$$

where γ is the surface free energy per unit area and Ω is the molecular volume.[30] From eq 2, it is clear that material will diffuse from regions of high to low curvature. This results in the disappearance of surfaces possessing high curvature and an increase in the size scale of the dispersed second phase, which is consistent with the necessary decrease in the total energy of the two-phase system.

In the coalescence mechanism, coarsening occurs by two or more droplets impinging on each other by translational diffusion and forming a single droplet. Binder and Stauffer explained the growth of clusters by simple molecular exchange as well as binary fission and fusion of droplets.[31] The coalescence mechanism is also diffusion controlled and has the power-law relation in time:[32]

$$\mathrm{d} \sim (k_{\mathrm{B}}T/\eta)^{1/3}t^{1/3} \tag{3}$$

where k_{B} is the Boltzmann constant, T is the separation temperature, and η is the viscosity. Interestingly, the power-law relation $d \propto t^{1/3}$ holds for the theoretical treatments in both Ostwald ripening and the coalescence mechanisms.

The third mechanism of coarsening is the hydrodynamic flow mechanism.[29,33] According to Siggia,[29] in the cylindrical part of the bicontinuous structure, the gradient of pressure along an axis of the cylinder causes a flow of inner fluid from a narrow to a wide region, which results in coarsening of domains. In this mechanism, the growth rate is linear in time:

$$d \sim (\sigma/\eta)t \tag{4}$$

where σ is the surface tension. As the basis of the hydrodynamic flow mechanism is an interfacial instability, phases of different size, and therefore different radii of curvature, have different pressures, which in turn cause flow.[24]

Siggia,[29] who considered theoretically a general two-component system undergoing phase separation, took into account both diffusive coalescence/Ostwald ripening and hydrodynamic flow effects in order to explain the accelerated growth rate beyond the initial stage. He estimated that the domain growth proceeds in three stages:

(i) intermediate stage (including coalescence)

$$d \sim (k_{\mathrm{B}}T/\eta)^{1/3}t^{1/3} \qquad \xi < d \le (k_{\mathrm{B}}T/\sigma)^{1/2} \tag{5}$$

(ii) flow state

$$d \sim (\sigma/\eta)t \qquad (k_{\mathrm{B}}T/\sigma)^{1/2} \le d \le (\sigma/(g\Delta\rho))^{1/2} \tag{6}$$

(iii) gravity-dominated state

$$d \ge (\sigma/(g\Delta\rho))^{1/2} \tag{7}$$

where g is the gravitational constant and $\Delta\rho$ is the density difference between the two phases. After the flow stage, the coarsening rate accelerates further due to gravity and the density difference of the two coexisting phases; in this last stage, coarsening does not follow a power law, and macroscopic layering is achieved.

More recently, Furukawa[34] formulated an asymptotic scaling function, indicating that there is only one length scale in the phase-separating system, and physical quantities depend on time only through this length scale. The scaling law is a more general form of the coarsening theory, and the asymptotic behavior of the characteristic length is depicted by

$$d \propto t^{a} \tag{8}$$

with the exponent a depending on the microscopic mechanism of particle growth. The scaling hypothesis is consistent with the results of a numerical simulation using the kinetic Ising model.[35] Hashimoto and co-workers[36,37] and Bates and Wiltzius[38] have demonstrated in the case

Table 1. Molecular Weight of Polystyrene

polystyrene	M_w	M_n	M_w/M_n
PS (1.9×10^6)	1 921 000	1 524 000	≤1.3
PS (6.5×10^5)	649 400	617 600	≤1.06
PS (2.9×10^5)	288 800	274 600	≤1.06

of polymer blends that *a* depends on time *t* over a broad time scale, with a crossover between coarsening processes which is consistent with the idea put forth by Siggia.[29] Such crossover effects have yet to be documented in the case of polymer–solvent systems.

Experimental Section

Atactic, monodisperse polystyrene (PS) standards (Pressure Chemical) were used. The molecular weight characteristics of PS samples under study are given in Table 1. Diethyl malonate (reagent grade), freezing point = −51 to −50 °C, and cyclohexane (reagent grade), freezing point = 6.5 °C, were obtained from Aldrich. All materials were used without further purification.

Phase diagrams for the PS–diethyl malonate and PS–cyclohexane solutions were determined using either differential scanning calorimetry (Perkin-Elmer DSC-7) or turbidimetry employing a UV–visible spectrophotometer (IBM 9410) as described in ref 21. Membranes of about 400 μm in thickness were produced *via* a thermally induced phase separation procedure also described in ref 21. In the case of membranes made from cyclohexane solutions, after coarsening, the solutions were fast-frozen in liquid nitrogen, and solvent removal occurred by freeze drying with a VirTis bench-top freeze dryer. For membranes made from diethyl malonate solutions, after fast-freezing, solvent removal occurred by supercritical CO_2 extraction. Diethyl malonate was first exchanged with methanol (typically lasting 5 h) followed by supercritical CO_2 extraction at 1100 psi.[39] Figure 1 shows a schematic diagram of the supercritical fluid extraction apparatus constructed for this study. The supercritical fluid extraction apparatus includes a gas booster system (Autoclave Engineers), which compresses CO_2 to the desired pressure, and a high-pressure extraction vessel (Parr Instrument). The extraction vessel is warmed at the bottom by a temperature-controlled water bath (at 35 °C) so that CO_2 is circulated inside of this vessel. The vessel has an internal condensing coil, and the sample is placed in a stainless steel syphon cup which hangs below the condensing coil.

Growth of cell size in membranes resulting from coarsening was studied quantitatively by scanning electron microscopy and, in limited cases, by mercury intrusion porosimetry. Cross sections of the resulting membranes were prepared by a freeze-fracturing method under liquid nitrogen, and membrane samples were gold sputtered before analysis by scanning electron microscopy (Hitachi S-570). Mercury intrusion porosimetry was performed employing a Quantachrome Autoscan-33 porosimeter in conjunction with Quantachrome supplied software. A mercury contact angle of 140° and an interfacial tension of mercury of 480 dyn/cm were used for all measurements.

Results and Discussions

(A) Isopycnic System: Polystyrene–Diethyl Malonate. In order to study the coarsening process in phase-separating polymer solutions without the influence of gravitational effects, which result in macroscopic phase separation on relatively short time scales, a nearly *isopycnic* system of PS and diethyl malonate was chosen. The density difference at 25 °C is very small for these materials,[40,41] about 0.002 g/cm^3, and as a result no macroscopic phase separation is observable for the conditions employed in this study for a period of at least 3 days.

The cloud points for the PS–diethyl malonate system are shown in Figure 2. For the 1.9×10^6 M_w system the critical concentration is about 5 wt % and the critical temperature is about 28.6 °C, while for the 2.9×10^5 M_w PS system the critical concentration is about 7.5 wt % and the critical temeprature is about 17.9 °C. It should be noted that these phase diagrams for the PS–diethyl malonate system are reasonably consistent with previous

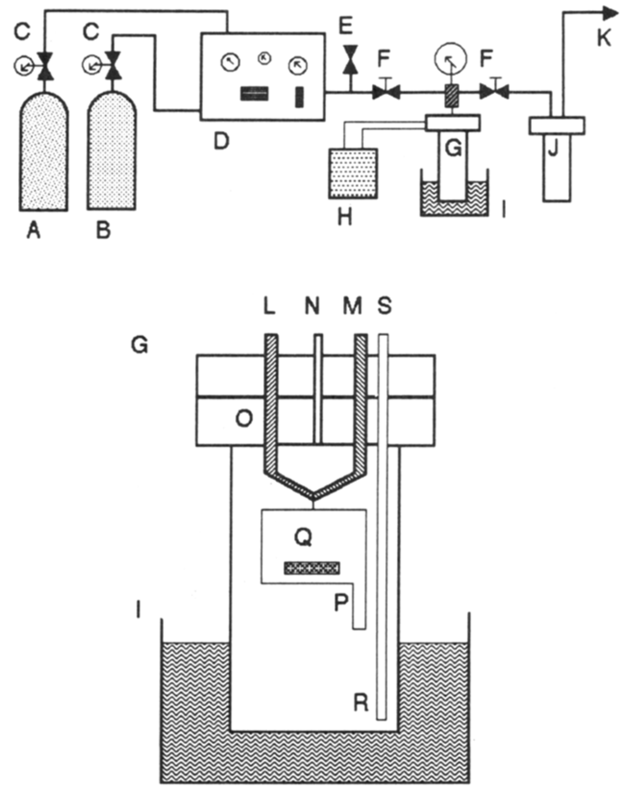

Figure 1. Schematic diagrams of the supercritical CO_2 extraction apparatus including a detailed description of the high-pressure extraction vessel: (A) air cylinder; (B) CO_2 cylinder; (C) line regulator; (D) gas booster system; (E) pressure relief valve; (F) needle valve; (G) high-pressure extraction vessel; (H) constant-temperature circulating bath; (I) constant-temperature water bath; (J) solvent recovery vessel; (K) vent to fume hood; (L) cooling water inlet; (M) cooling water outlet; (N) CO_2 inlet; (O) condensing coil; (P) syphon cup; (Q) sample; (R) dip tube; (S) CO_2 outlet.

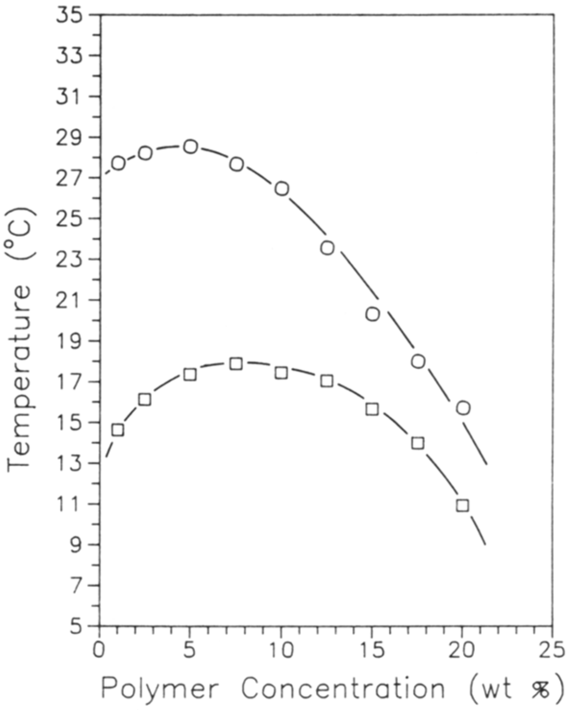

Figure 2. Cloud point curves of PS–diethyl malonate systems prepared from turbidimetry: (○) $M_w = 1.9 \times 10^6$; (□) $M_w = 2.9 \times 10^5$.

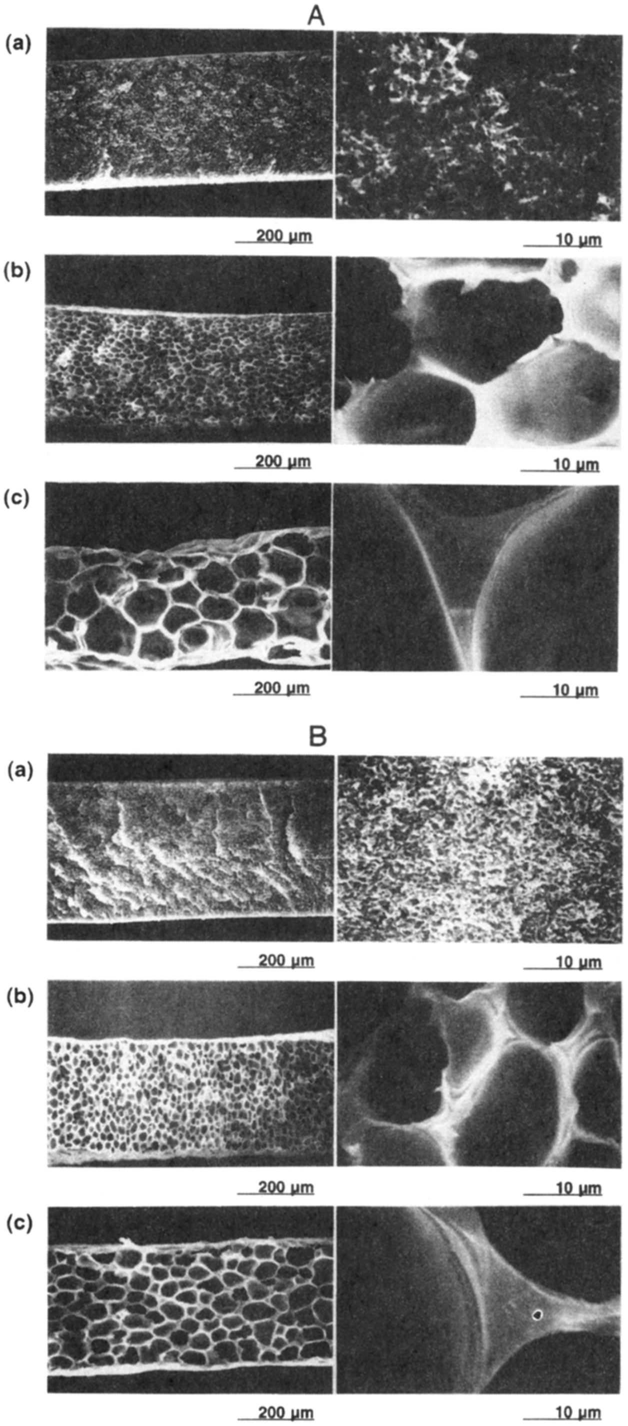

Figure 3. (A) Scanning electron micrographs of the cross section of PS membranes as a function of coarsening time: (a) 1 min; (b) 5 h; (c) 24 h. Membranes were prepared by quenching a 5 wt % PS–diethyl malonate ($M_w = 1.9 \times 10^6$) solution to 28 °C prior to supercritical CO_2 extraction. (B) Scanning electron micrographs of the cross section of PS membranes as a function of coarsening time: (a) 1 min; (b) 5 h; (c) 24 h. Membranes were prepared by quenching a 10 wt % PS–diethyl malonate ($M_w = 1.9 \times 10^6$) solution to 25 °C prior to supercritical CO_2 extraction.

studies by Orofino and Mickey[41] and Candau et al.,[42] who indicated that the θ-temperature for this system was 35.9 and 35.8 °C, respectively.

Figure 3 shows scanning electron micrographs for membranes produced from the 1.9×10^6 M_w PS solution at temperatures just slightly inside the two-phase region of the phase diagram; for a 5 wt % solution the phase separation occurred at 28 °C (Figure 3A), while for a 10 wt % solution the phase separation occurred at 25 °C (Figure 3B). The 5 wt % solution, with phase separation occurring near its critical composition, yields a major increase in cell size due to coarsening. At just 1 min into the phase separation process, the pore size is 2–3 μm, while after 24 h the pore size is over 100 μm.[43] Similar tends are observed in the membranes produced from the off-critical quench study using the 10 wt % solution. The 10 wt % solution system results in a smaller pore size at any coarsening time as compared to the 5 wt % solution, but the rate of growth is nevertheless dramatic; at 1 min into the phase separation process, the pore size developed in these membranes is slightly in excess of 1 μm, while at 24 h into the coarsening process the cell size has increased to approximately 40 μm. Apparent in both sets of micrographs is the well-interconnected morphology of nearly uniform pore size which is set up within 1 min and is maintained throughout the growth of the cell size due to coarsening. This morphology at short times is consistent with phase separation being initiated by spinodal decomposition rather than nucleation and growth.

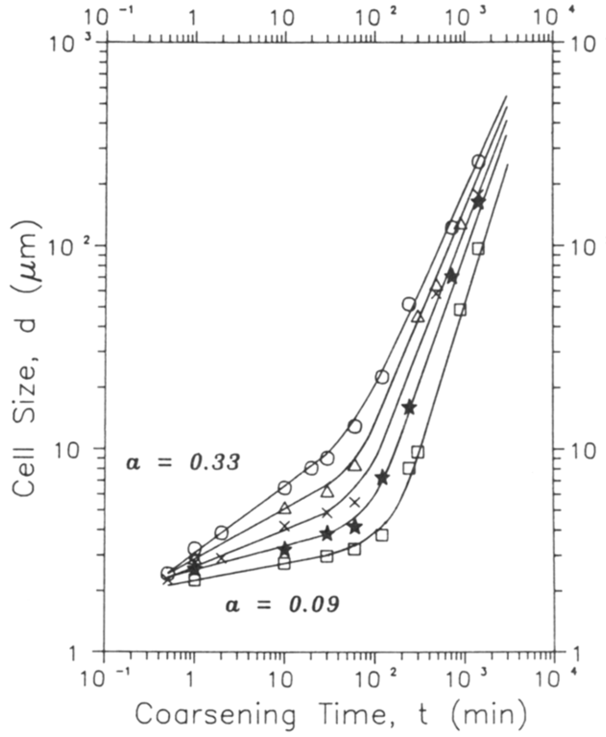

Figure 4. Coarsening time dependence of the average cell size for a 5 wt % PS–diethyl malonate ($M_w = 1.9 \times 10^6$) system obtained at various quench temperatures: (○) 20 °C; (△) 23 °C; (×) 25 °C; (★) 27 °C; (□) 28 °C. The cloud point determined by turbidimetry was 28.6 °C.

Figure 4 illustrates the growth of the cell size as a function of coarsening time and quench temperature for a near-critical composition of 1.9×10^6 M_w PS–diethyl malonate solution. Several points are obvious from this plot. At relatively short coarsening times, about 30 min and less for the 20 °C study and about 60 min and less for the 28 °C study, the growth rate of the cell size may be expressed as a power law in time, with the exponent increasing with increasing quench depth. Interestingly, at the deepest quench depth studied here, the growth rate has an exponent of $^1/_3$, in agreement with simple theories for coarsening by Ostwald ripening[27,28] or coalescence.[31] However, as the quench depth is decreased so that the phase separation is occurring just inside the two-phase region, the initial growth rate is much slower than that predicted by the simple theories of Ostwald ripening or coalescence; instead the growth rate has an exponent as low as 0.09 at a phase separation temperature of 28 °C.

Table 2. Cell Size (d) Determined by Mercury Intrusion Porosimetry (MIP) and Scanning Electron Microscopy (SEM)

membrane	surface area (m^2/g)	d_{MIP} (μm)	d_{SEM} (μm)
5 wt % Polystyrene–Diethyl Malonate (M_w = 1.9 × 10^6)			
1 min at 20 °C	12.3	4.07	3.2
2 min at 20 °C	12.8	3.90	3.9
10 min at 20 °C	7.0	7.11	6.5
10 wt % Polystyrene–Diethyl Malonate (M_w = 1.9 × 10^6)			
1 min at 25 °C	18.8	1.33	1.4
10 min at 25 °C	13.4	1.87	1.9

For all cases studied here, there was also a transition which occurred at intermediate times, approximately 30–60 min at 20 °C and 60–200 min at 28 °C, to a much faster growth rate which within experimental error yields an exponent of 1.0, independent of phase separation temperature. This higher growth rate is consistent with that expected for the hydrodynamic flow mechanism of coarsening.[29,33]

It is important to note that the conclusions reached about the growth rate of the cell size are independent of how the cell size was measured. In Table 2, examples of average cell sizes obtained by mercury intrusion porosimetry are compared to those from scanning electron micrographs for several solution conditions and are found to be in good agreement. Mercury intrusion porosimetry measurements have been employed to determine the surface area and cell size distribution of microporous membranes or microcellular foams.[23,44,45] The relationship between the surface area and the average spacing between phases as described by Aubert[24,46] was used to determine the average cell size:

$$d = 4/(\rho S) \tag{9}$$

where d is the average spacing between phases, ρ is the density, and S is the surface area per unit mass.

While the effects illustrated in Figure 4, showing an intermediate coarsening stage with a growth exponent of 0.09–0.33 followed by a transition stage and then finally a later coarsening stage with a growth rate exponent of 1.0, have not been observed previously in polymer solutions, as noted earlier, related effects have been documented in polymer blend systems. Hashimoto and coworkers[36,37] observed in time-resolved light scattering studies of PS–poly(vinyl methyl ether) that the phase separation process could be divided into three stages: early, intermediate, and late. In the early stage, the behavior was found to be approximated by the Cahn–Hilliard theory for spinodal decomposition,[1–4] and the growth in amplitude of the dominant concentration fluctuations occurred without change in wavenumber or size of the phase-separating regions. In the intermediate stage, both the amplitude and size of the concentration fluctuation increased but did not reach equilibrium values. In the late stage, the amplitude of the concentration fluctuation reached its equilibrium value and the fluctuation grew in size. In particular, Hashimoto and co-workers[37] found that in the intermediate regime the reduced wavenumber scaled with reduced time to a power of −0.2 to −0.3, while in the late stage it increased in magnitude to a value of −0.5 to −0.8. (As the wavenumber is inversely related to interdomain separation and thus the cell size, the exponent from time-resolved light scattering should be equal in magnitude but opposite in sign to those obtained for growth of the cell size.)

Bates and Wiltzius[38] performed time-resolved light scattering studies of spinodal decomposition and coarsening on a critical mixture of perdeuterated and protonated 1,4-polybutadiene. They described their time-dependent results with a four-stage model, which divided the phase separation into an early stage of spinodal decomposition accounted for by the Cahn–Hilliard theory, an intermediate stage in which the interdomain spacing growth occurs with a power-law exponent a varying from 0.099 to 0.260 which increases with quench depth and scales approximately as $a^2 \sim 1/T$, a transition stage which occurs when the composition fluctuation approaches the equilibrium values, and a final stage (when an equilibrium interfacial profile is achieved) where the interdomain separation increases, leaving the morphology unaffected as evidenced by a universal structure factor.

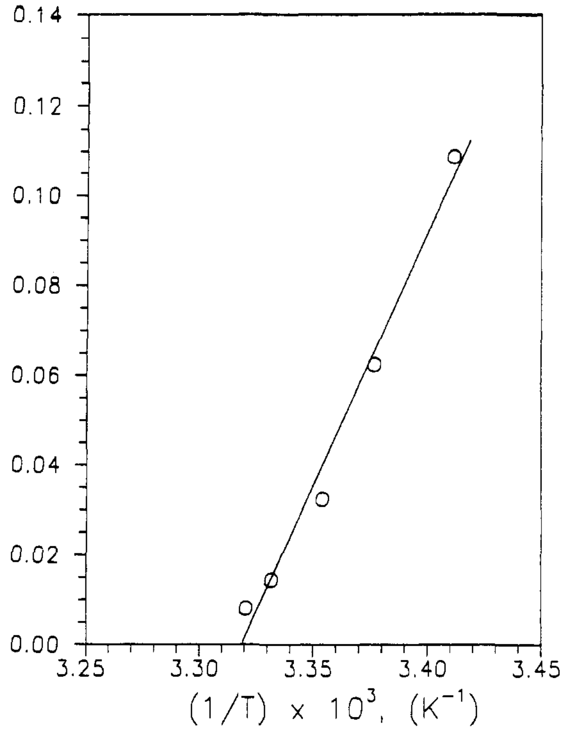

Figure 5. Phase separation temperature dependence of the power-law exponent a in the intermediate stage of phase separation.

It is noteworthy that Bates and Wiltzius[38] remarked that in the intermediate stage the quench depth dependence of the power-law exponent is "inexplicable", and they questioned whether such behavior is characteristic of all binary fluid mixtures, polymer mixtures, or strictly isotopic polymer mixtures and whether their choice of a nearly symmetric critical composition played any role in this phenomenon. (This may have resulted from the fact that previous studies[47] had suggested that, if time and length are properly scaled, then the coarsening dynamics are insensitive to the molecular details, i.e., small molecule liquids *vs* polymer blends *vs* inorganic glasses *vs* metallic alloys, of the system. Such a quench depth dependence of the growth rate exponent had not been reported previously in any systems.) On the basis of the results in Figure 4 (and later figures), it is clear that the quench depth dependence of the interdomain-spacing growth rate exponent is in fact not limited to polymer mixtures or strictly isotopic polymer mixtures and that a nearly symmetric critical composition is not necessary for such behavior to be observed. It is also of interest to note that the empirical observation by Bates and Wiltzius that $a^2 \sim 1/T$ in the intermediate stage also adequately approximates the behavior observed over the temperature range studied here in the PS–diethyl malonate solution system (see Figure 5).

Recently, Brown and Chakrabarti[48] investigated the nature of the quench depth dependence of the power-law exponent. In a numerical study of off-critical polymer blends, they determined that for deep quenches the exponent is $^1/_3$ independent of temperature, while for shallow quenches domain growth becomes progressively slower as the spinodal curve is approached. This effect is apparently associated with thermally induced fluctuations in local concentration which are important for polymer blends but irrelevant for small molecule systems. It will be important to determine in the future whether these same effects also explain the results observed here concerning the quench dependence of the growth rate exponent in polymer solutions.

The effect of a strong quench depth dependence of the coarsening growth rate exponent at time frames up to 60–100 min followed by a transition to a growth rate exponent independent of quench depth at long coarsening times is also revealed in parts a and b of Figure 6 which represent the growth of the cell size or interdomain spacing for far off-critical quenches of 10 wt % solutions of 1.9×10^6 M_w and 2.9×10^5 M_w PS, respectively, in diethyl malonate. In both systems, at quench depths of 1 °C or less below the binodal, the growth rate exponent at coarsening times of an hour or less is approximately 0.08–0.10, while at quench depths of 7 °C or more below the binodal curve, the growth rate exponent is approximately $^1/_3$. At long coarsening times, the growth rate is approximately linear in time.

The effect of solution concentration for the 1.9×10^6 M_w PS–diethyl malonate system can be observed by comparing Figures 4 and 6a which reveal that substantially smaller cell sizes are achieved at all coarsening times for the 10 wt % solutions as compared to the 5 wt % solutions. Similarly, while the growth rate exponents are in excellent correspondence for the two 10 wt % systems in parts a and b of Figure 6, there is a significant molecular weight dependence of the cell sizes achieved for a given quench depth. This point is made even more clear in Figure 7 which compares the growth rate of the cell size for three molecular weights of 10 wt % PS in diethyl malonate at equivalent quench depths below the cloud point curve (1.4–1.5 °C). Figure 7 reveals a nearly perfect symmetry in the growth rate–time dependence among the different molecular weights, with the only significant role played by molecular weight (for these off-critical quenches) apparently being to reduce the cell size as molecular weight is increased.[49]

The decreasing cell size with increasing polymer concentration, present even at the early stages of coarsening, may be rationalized qualitatively by the fact that according to eqs 5 and 6 cell size is always a decreasing function of viscosity, η, which increases with polymer concentration. The effect of polymer molecular weight on cell size is possibly more difficult to rationalize. Apparently even at very short phase separation times, less than 1 min, the cell size is a decreasing function of molecular weight. If one considers that the effect of the molecular weight on cell size should have its origin in the earliest stage of phase separation, spinodal decomposition, then van Aartsen's picture[8] of the fluctuation wavelength increasing with the polymer radius of gyration is inconsistent with the results of Figure 7. If one considers that the origin of the molecular weight effect on cell size as observed in Figure 7 should have its origin only in coarsening, the inverse relationship between d, the cell size, and $\eta^{1/3}$ in eq 5 and η in eq 6 are qualitatively consistent with the observation of a smaller cell size with increasing molecular weight. In order to gain a more quantitative understanding of how polymer concentration (for a given molecular weight and quench depth) and molecular weight (for a given concentration and quench depth) control cell size in coarsening polymer solutions and membranes made from them, further study will be required.

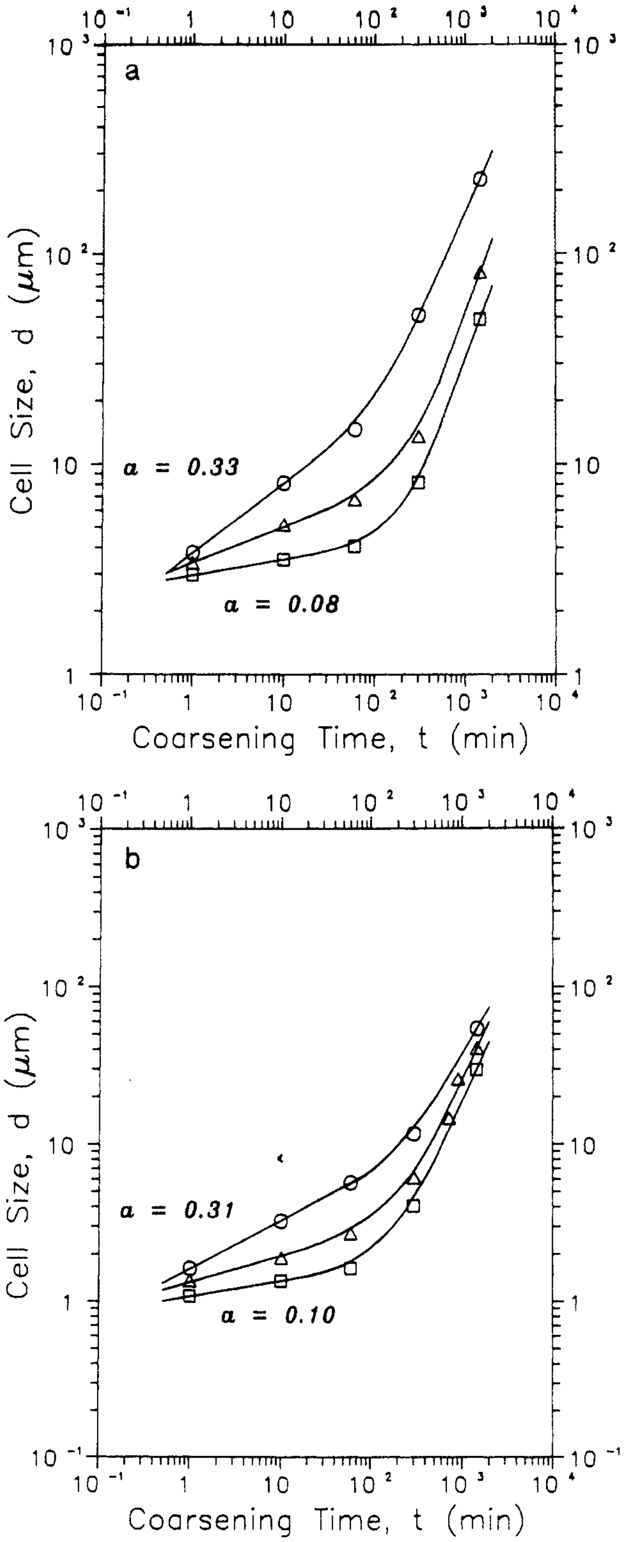

Figure 6. Coarsening time dependence of average cell size for a 10 wt % PS–diethyl malonate system obtained at various quench temperatures. (a) $M_w = 1.9 \times 10^6$: (○) 20 °C; (△) 25 °C; (□) 26 °C (the cloud point determined by turbidimetry was 26.5 °C). (b) $M_w = 2.9 \times 10^5$: (○) 10 °C; (△) 16 °C; (□) 17 °C (the cloud point determined by turbidimetry was 17.5 °C).

It should be noted that, of the previously cited studies of polymer solution coarsening, only that by Nojima et al.[18] went to time scales approximating those of our PS–diethyl malonate study. Unlike the present study, they did not observe any crossover effect during the time scale of their experiment. This may be due to one of two factors. First, the system they chose for study, PS–diisodecyl phthalate, has a much higher viscosity than that of PS–diethyl malonate, even at the higher temperatures employed by Nojima et al. for phase separation. According

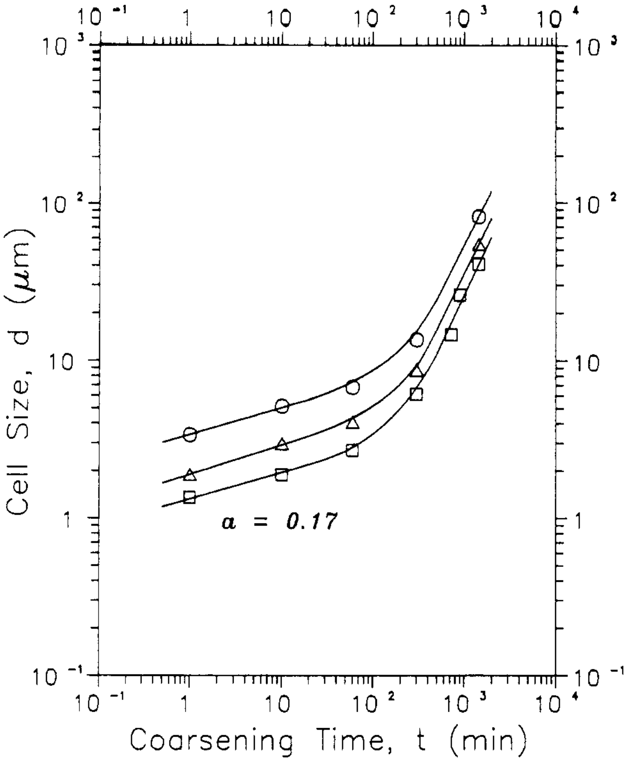

Figure 7. Coarsening time dependence of average cell size for 10 wt % PS–diethyl malonate systems at similar quench depth: (○) $M_w = 2.9 \times 10^5$ at 16 °C; (△) $M_w = 6.5 \times 10^5$ at 20 °C; (□) $M_w = 1.9 \times 10^6$ at 25 °C. Cloud points determined by turbidimetry were 17.5, 21.4, and 26.5 °C, respectively.

to eq 5, in the first stage of coarsening, $d \sim \eta^{-1/3}$, and thus it is possible that with the highly viscous nature of their system no crossover to the hydrodynamic flow regime was achievable on the time scales of their study. The fact they observed a growth rate exponent of $a = 0.30 \pm 0.09$ also lends credence to this explanation. Another possible explanation relates to the fact that since the study by Nojima et al. in 1982, it has been recognized that coarsening in two-dimensional binary fluids may proceed with different growth rate characteristics than those for a three-dimensional system (assumed for eq 5–7). It has been pointed out that Siggia's derivation for coarsening in three-dimensional systems may not be applicable to two-dimensional systems; instead a different coarsening dynamics has been predicted.[50–53] As the polymer solution observed microscopically by Nojima et al. was reportedly only 50 μm in thickness and average size scales of the droplets grew to 15 μm or larger, it may be possible that their observation of one growth rate for times approaching a day is related to the at least partially two-dimensional character of their coarsening system. Studies to investigate these effects are currently underway in various PS–solvent systems.[54,55]

(B) Nonisopycnic System: Polystyrene–Cyclohexane. Given that most studies of coarsening in polymer–solvent systems have involved conditions in which there is a great mismatch in polymer and solvent densities, a reinvestigation of a *nonisopycnic* system is necessary in order to comment fully on why a crossover between coarsening mechanisms, observed here in the PS–diethyl malonate system, has not been documented previously. Furthermore, as effects of quench depth on coarsening have not been previously reported in polymer–solvent systems, some investigation of this issue under *nonisopycnic* conditions is also warranted. The system chosen was PS–cyclohexane, used earlier by Bansil and co-workers[16,20] and Aubert.[24]

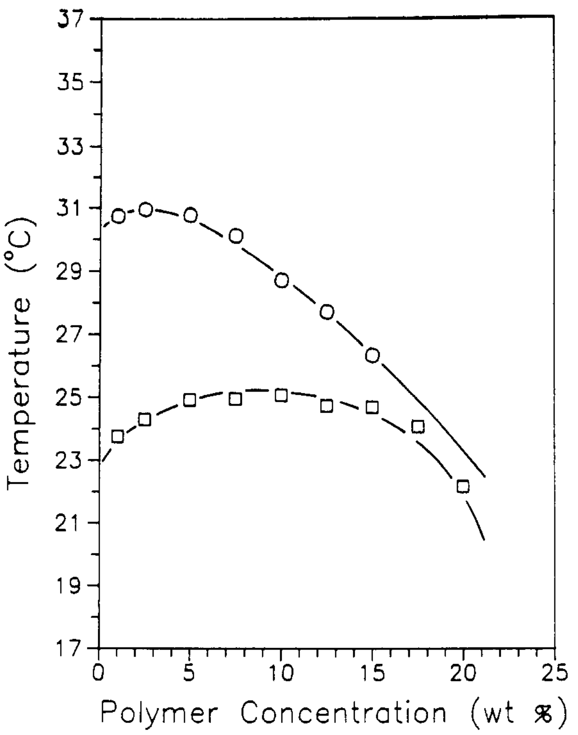

Figure 8. Cloud point curves for the PS–cyclohexane system prepared from differential scanning calorimetry measurement: (○) $M_w = 1.9 \times 10^6$; (□) $M_w = 2.9 \times 10^5$.

The cloud point curves for the PS–cyclohexane systems used in this study are given in Figure 8 and are consistent with others[24,41] reported in the research literature. It must be noted that attempts to prepare membranes useful for characterization of coarsening phenomena over a reasonable range of time scales (10 min or longer) were not successful using the 2.9×10^5 M_w PS system, even at a concentration of 10 wt %. Macroscopic layering of the nearly pure solvent phase on top of the polymer-rich phase, due to gravitational effects, led to an effective shrinkage in the thickness of the membranes obtained in this study. Even on phase separation time scales of 1–2 min, the achievable membrane thickness with the 2.9×10^5 M_w PS was significantly smaller than the thickness achieved using our membrane casting cell with the PS–diethyl malonate system. Furthermore, simple visual observation of macroscopic layering of the solvent-rich phase on top of the polymer-rich phase for a solution of 2.9×10^5 M_w PS in cyclohexane undergoing phase separation in a cuvette confirms that gravitational effects may dominate phase separation at very short times (10 min) in this system. This brings into question conclusions drawn by Lal and Bansil[16] on the phase separation of PS–cyclohexane systems of lower molecular weight and concentrations.

By using a much higher molecular weight PS sample, $1.9 \times 10^6 M_w$, at a concentration of 7.5 wt %, it was possible to avoid these significant gravitational effects on relatively short time scales and effectively to repeat the investigation performed earlier by Aubert[24] on how coarsening time affects solution or membrane microstructure. Additionally, we also considered the effect of quench depth. Figure 9 shows the effects of coarsening time on the microstructure developed over a period of 1 h at phase separation temperatures of 29 and 27 °C. For membranes produced by phase separation at 29 °C, which is very close to the cloud point temperature in the system, the micrographs suggest that the predominant mechanism of phase separation is spinodal decomposition rather than nucleation and growth, as the latter mechanism would result in either a stringy, beady, poorly interconnected structure or in an interconnected structure with highly nonuniform pore

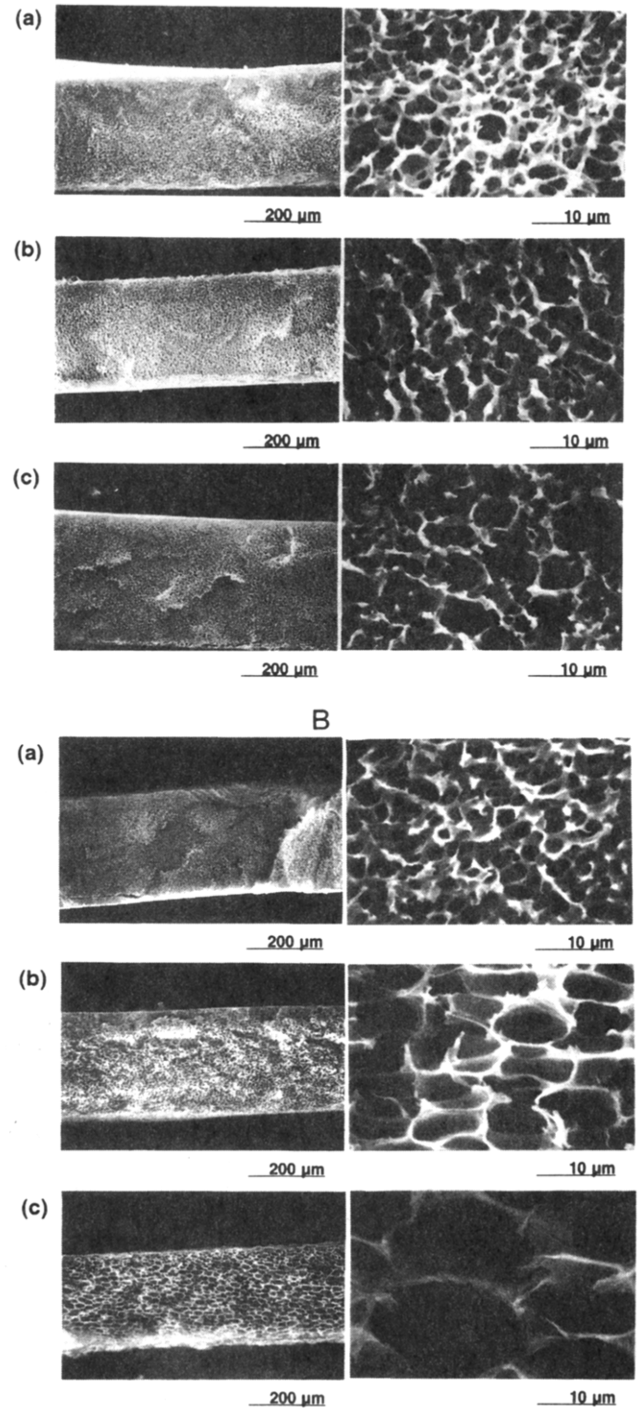

Figure 9. (A) Scanning electron micrographs of the cross section of PS membranes as a function of coarsening time: (a) 1 min; (b) 2 min; (c) 60 min. Membranes were prepared by quenching a 7.5 wt % PS–cyclohexane ($M_w = 1.9 \times 10^6$) solution to 29 °C prior to freeze-drying. (B) Scanning electron micrographs of the cross section of PS membranes as a function of coarsening time: (a) 2 min; (b) 10 min; (c) 60 min. Membranes were prepared by quenching a 7.5 wt % PS–cyclohexane ($M_w = 1.9 \times 10^6$) solution to 27 °C prior to freeze-drying.

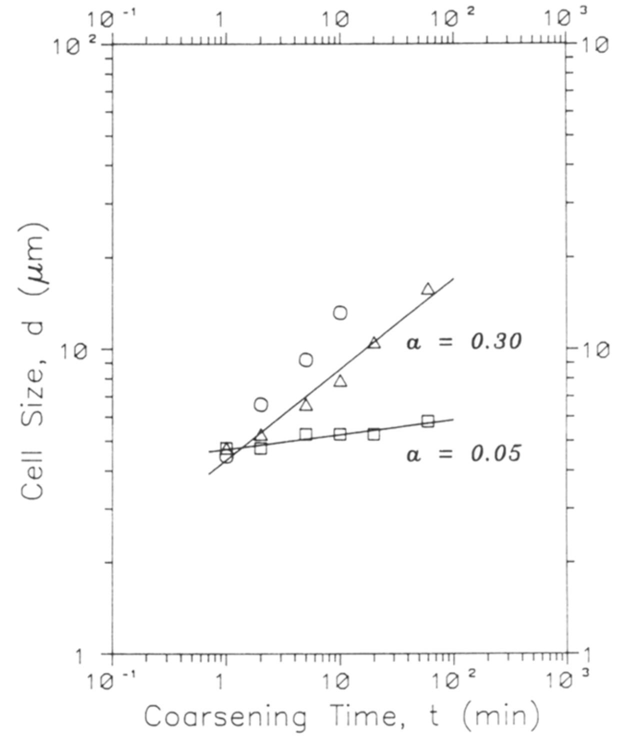

Figure 10. Coarsening time dependence of average cell size for a 7.5 wt % PS–cyclohexane ($M_w = 1.9 \times 10^6$) system obtained at various quench temperatures: (○) 20 °C; (△) 27 °C; (□) 29 °C. The cloud point determined by differential scanning calorimetry measurement was 30.1 °C.

sizes.[21,22] As coarsening proceeds at 29 °C, there is at most a modest increase in cell or pore size over the first hour. In contrast, with a slightly deeper quench to 27 °C, the same quench temperature used in Aubert's study[24] of 2.2×10^6 M_w PS in cyclohexane, a much more substantial growth in cell size with coarsening time is observed.

Figure 10 shows the quench temperature dependence of the cell size growth rate for a 7.5 wt % solution of 1.9×10^6 M_w PS in cyclohexane as determined from scanning electron microscopy. For the highest quench temperature examined, the growth rate exponent is 0.05, close to the values obtained at short coarsening times in the PS–diethyl malonate system when phase separation occurred very close to the cloud point. As the quench temperature is decreased to 27 °C, the growth rate exponent at short time increases to 0.30, consistent with previous observations in the PS–diethyl malonate system and also in Aubert's study[24] at 27 °C which yielded growth rate exponents of 0.18–0.32 for solutions varying from 3 to 10 wt %. Also consistent with Aubert's study, the experiments became invalid on time scales longer than an hour due to significant gravitational sedimentation effects.

Noteworthy in Figure 10 is that at 20 °C the growth rate exponent at "short" coarsening times (less than 10 min) apparently exceeds the value of $1/3$, considered by some[48] to be a limiting exponent at short coarsening times. The apparently high value of the short time growth rate exponent may be due to a variety of factors. First, on time scales exceeding 10 min gravitational effects dominate at 20 °C and characterization of cell size is not meaningful, leaving conclusions to be drawn from few data points. Second, it is possible that the observed growth rate, even at these short times, is some combination of a $t^{1/3}$ growth rate at short times followed by a crossover to a faster growth rate prior to the domination of gravitational sedimentation. Shinozaki et al.[56–58] have shown that surface tension in demixed polymer solutions increases significantly with increasing quench depth, suggesting that the three stages of domain growth delineated in eqs 5–7 could be compressed into a very short time scale for this system at 20 °C, thus making a clear determination of any one growth rate exponent difficult at best.

From the measurements made in the PS–cyclohexane system in this study, it is not clear that it would ever be possible to observe the same crossover effects seen in the PS–diethyl malonate system. The results in the PS–cyclohexane system may be deemed consistent with those in the PS–diethyl malonate system if it noted that the quantity of $(\sigma/(g\Delta\rho))^{1/2}$, which indicates when gravitational effects dominate, is orders of magnitude smaller in the PS–cyclohexane system. In fact, this may compress the "flow stage" to a time scale so small as to be almost impossible to characterize with techniques employed here and in other studies. In contrast, in PS–diethyl malonate, gravitational effects can be delayed for days relative to the time scales observed in PS–cyclohexane, and thus a crossover from one coarsening mechanism to a second can be easily observed.

Finally, the studies by Shinozaki et al.[56-58] on the molecular weight dependence of σ in polymer solutions make it abundantly clear that decreasing molecular weight significantly increases σ and thus reduces the time scale at which gravitational sedimentation dominates the coarsening procedure. Given that the results of both this study and the one by Aubert[24] have demonstrated that the coarsening time scales in the absence of gravitational effects are very limited in high molecular weight PS–cyclohexane solutions, systems different from PS–cyclohexane should be considered for any further study, especially if a lower molecular weight polymer is to be employed. Such a study[59] on a high-viscosity PS–cyclohexanol system has recently been completed, giving further support to the effects observed here in the lower viscosity but *isopycnic* PS–diethyl malonate systems.

Acknowledgment. We gratefully acknowledge the financial support of the Dow Chemical Co. We thank Dr. William Mickols and Dr. Richard Fibiger of Dow Chemical for valuable discussions. We also thank Professor Barbara-Ann Lewis of Northwestern University for the valuable technical advice regarding mercury intrusion porosimetry and Dr. James Aubert of Sandia National Laboratories, who kindly provided us with information necessary for constructing a supercritical CO_2 extraction apparatus.

References and Notes

(1) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1958**, *28*, 258.

(2) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1959**, *31*, 688.

(3) Cahn, J. W. *J. Chem. Phys.* **1965**, *42*, 93.

(4) Cahn, J. W. *Trans. AIME* **1968**, *242*, 166.

(5) Cook, H. E. *Acta Metall.* **1970**, *18*, 297.

(6) Langer, J. S.; Bar-on, M.; Miller, H. D. *Phys. Rev. A* **1975**, *11*, 1417.

(7) Kawasaki, K.; Ohta, T. *Prog. Theor. Phys.* **1978**, *59*, 362.

(8) van Aartsen, J. J. *Eur. Polym. J.* **1970**, *6*, 919.

(9) de Gennes, P.-G. *J. Chem. Phys.* **1980**, *72*, 4756.

(10) Pincus, P. *J. Chem. Phys.* **1981**, *75*, 1996.

(11) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.

(12) van Aartsen, J. J.; Smolders, C. A. *Eur. Polym. J.* **1970**, *6*, 1105.

(13) Smolders, C. A.; van Aartsen, J. J.; Steenbergen, A. *Kolloid Z. Z. Polym.* **1971**, *243*, 14.

(14) Hamano, K.; Tachikawa, M.; Kenmochi, Y.; Kuwahara, N. *Phys. Lett.* **1982**, *90A*, 425.

(15) Kuwahara, N.; Tachikawa, M.; Hamano, K.; Kenmochi, Y. *Phys. Rev. A* **1982**, *25*, 3449.

(16) Lal, J.; Bansil, R. *Macromolecules* **1991**, *24*, 290.

(17) Kubota, K.; Kuwahara, N. *Phys. Rev. Lett.* **1992**, *68*, 197.

(18) Nojima, S.; Shiroshita, K.; Nose, T. *Polym. J.* **1982**, *14*, 289.

(19) Kuwahara, N.; Hamano, K.; Aoyama, N.; Nomura, T. *Phys. Rev. A* **1983**, *27*, 1724.

(20) Krishnamurthy, S.; Bansil, R. *Phys. Rev. Lett.* **1983**, *50*, 2010.

(21) Tsai, F.-J.; Torkelson, J. M. *Macromolecules* **1990**, *23*, 775.

(22) Tsai, F.-J.; Torkelson, J. M. *Macromolecules* **1990**, *23*, 4983.

(23) Tsai, F.-J. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1990.

(24) Aubert, J. H. *Macromolecules* **1990**, *23*, 1446.

(25) Kuwahara, N.; Kubota, K. *Phys. Rev. A* **1992**, *45*, 7385.

(26) Although Kuwahara and co-workers (refs 17 and 19) did coarsening studies on the *isopycnic* system of poly(dimethylsiloxane)–diethyl carbonate, they limited measurements to coarsening times of 10 min or less and consequently were not able to observe the effects reported in this manuscript. It should also be noted that Guenoun et al. (Guenoun, P.; Gastaud, R.; Perrot, F.; Beysens, D. *Phys. Rev. A* **1987**, *36*, 4876; Guenoun, P.; Beysens, D.; Robert, M. *Physica A* **1991**, *172*, 137) have used *isopycnic* solutions of lower molecular weight fluids for studying spinodal decomposition in the absence of gravitational effects. For very short duration experiments, phase separation studies under microgravimetry conditions have been performed employing sounding rockets (Beysens, D.; Guenoun, P.; Perrot, F. *Phys. Rev. A* **1988**, *38*, 4173; Garrabos, Y.; Le Neindre, B.; Guenoun, P.; Khalil, B.; Beysens, D. *Europhys. Lett.* **1992**, *19*, 491; Schmitz, G.; Klein, H.; Woermann, D. *J. Chem. Phys.* **1993**, *99*, 758).

(27) Lifshitz, I. M.; Slyozov, V. V. *J. Phys. Chem. Solids* **1961**, *19*, 35.

(28) Wagner, C. *Z. Elektrochem.* **1961**, *65*, 581.

(29) Siggia, E. D. *Phys. Rev. A* **1979**, *20*, 595.

(30) Mullins, W. W. *J. Appl. Phys.* **1957**, *28*, 333.

(31) Binder, K.; Stauffer, D. *Phys. Rev. Lett.* **1974**, *33*, 1006.

(32) Chou, Y. C.; Goldburg, W. I. *Phys. Rev. A* **1979**, *20*, 2105.

(33) Voigt-Martin, I. G.; Leister, K. H.; Rosenau, R.; Koningsveld, R. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 723.

(34) Furukawa, H. *Adv. Phys.* **1985**, *34*, 703.

(35) Marro, J.; Lebowits, J. L.; Kalos, M. H. *Phys. Rev. Lett.* **1979**, *43*, 282.

(36) Hashimoto, T.; Itakura, M.; Hasegawa, H. *J. Chem. Phys.* **1986**, *85*, 6118.

(37) Hashimoto, T.; Itakura, M.; Shimidzu, N. *J. Chem. Phys.* **1986**, *85*, 6773.

(38) Bates, F. S.; Wiltzius, P. *J. Chem. Phys.* **1989**, *91*, 3258.

(39) No "melting" or evidence of coarsening as a function of methanol-exchange time was observed in the PS–diethyl malonate systems processed by supercritical CO_2 extraction.

(40) Richardson, M. J.; Savil, N. G. *Polymer* **1977**, *18*, 3.

(41) Orofino, T. A.; Mickey, J. W., Jr. *J. Chem. Phys.* **1963**, *38*, 2512.

(42) Candau, F.; Strazielle, C.; Benoit, H. *Macromol. Chem.* **1973**, *170*, 165.

(43) It should be noted that while the structure across a membrane thickness (in Figure 3) appears quite uniform, the membranes do exhibit some asymmetry as a fairly dense skin is formed on one side and a very porous structure is formed on the other side. The significant degree of uniformity across the membrane is the result of the rapid quench; this is in contrast to the huge asymmetry often observed in phase inversion membranes where the phase separation occurs by the slow exchange of solvent and nonsolvent.

(44) Aubert, J. H.; Sylwester, A. P. *J. Mater. Sci.* **1991**, *26*, 5741.

(45) Gabriel, E. M.; Gillberg, G. E. *J. Appl. Polym. Sci.* **1993**, *48*, 2081.

(46) Aubert, J. H. *J. Cell. Plast.* **1988**, *24*, 132.

(47) Snyder, H. L.; Meakin, P. *J. Chem. Phys.* **1983**, *79*, 5588.

(48) Brown, G.; Chakrabarti, A. *J. Chem. Phys.* **1993**, *98*, 2451.

(49) A more complete investigation of molecular weight effects is underway which will include comparisons of critical quenches.

(50) Marqusee, J. A. *J. Chem. Phys.* **1984**, *81*, 976.

(51) Rogers, T. M.; Elder, K. R.; Desai, R. C. *Phys. Rev. B* **1988**, *37*, 9638.

(52) Rogers, T. M.; Desai, R. C. *Phys. Rev. B* **1989**, *39*, 11956.

(53) Farrell, J. E.; Valls, O. T. *Phys. Rev. B* **1991**, *43*, 630.

(54) Song, S.-W. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1994.

(55) A reinvestigation by us of PS–diisodecyl phthalate solutions using optical microscopy to perform *in situ* monitoring of coarsening has resulted in data in good agreement with previous studies on the same system by Nose and co-workers.[18] As with other systems studied by us in the solution state (in ~40-μm-thick samples) by optical microscopy, including PS–diethyl malonate and PS–cyclohexane, preliminary results indicate no evidence of either a crossover in coarsening mechanism or a strong quench depth dependence of coarsening growth rate in these very thin solution-state samples. The difference in the coarsening behavior, as compared to that observed in the 400-μm-thick membrane systems described in this manuscript, may be due to the at least partially two-dimensional character of the coarsening in these very thin samples. This work will be described more fully in a forthcoming manuscript.

(56) Shinozaki, K.; Abe, M.; Nose, T. *Polymer* **1982**, *23*, 722.

(57) Shinozaki, K.; van Tan, T.; Saito, Y.; Nose, T. *Polymer* **1982**, *23*, 728.

(58) Shinozaki, K.; Saito, Y.; Nose, T. *Polymer* **1982**, *23*, 1937.

(59) Song, S.-W.; Torkelson, J. M. *J. Membr. Sci.*, in press.