2D Coarsening in Phase-Separated Polymer Solutions: Dependence on Distance from Criticality

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Polymer solutions of various compositions have been phase separated in two dimensions in order to monitor the growth rate of the domain size d associated with coarsening in restricted dimensions. For off-critical solutions, d grows approximately as $t^{1/3}$, consistent with theory. For near-critical solutions, d grows approximately as $t^{1/3}$ at early times, followed by a crossover to a rate that is consistent with the $t^{2/3}$ growth rate reported in some numerical studies. The early-time coarsening of critical solutions is dominated by critical wetting and a highly bimodal size distribution, making measurements of d difficult to obtain.

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In the later stages of phase separation, the interfacial tension between phases, σ, drives the system to lower the interfacial area in a process known as coarsening, resulting in growth of phase domain sizes. Considerable interest [1–12] has been generated recently in the growth rate of the domain size in systems undergoing coarsening in two and three dimensions (2D and 3D). Recently, our group [2] determined the growth rates of domain size d for phase-separated critical and near-critical polymer solutions in a 3D geometry and found that for relatively deep quenches a crossover from a $d \sim t^{1/3}$ to a $d \sim t^1$ growth rate was observed, where t is coarsening time. This is in agreement with theoretical studies by Siggia [3] predicting that a crossover from a $d \sim t^{1/3}$ to a $d \sim t^1$ growth rate would occur when σ accelerates the early-time coarsening mechanism by causing currents (hydrodynamic flow). Related behavior has been observed experimentally in a 3D geometry using small molecule systems [4].

Numerical studies on coarsening in 2D have been performed on critical, near-critical, and off-critical systems [5–10]. While a $d \sim t^{1/3}$ rate is observed in off-critical coarsening with no crossover [5–8], in agreement with 2D Ostwald ripening theory [6], a higher growth rate ($d \sim t^{1/2}$ or $t^{2/3}$) is observed in the final stages of critical and near-critical coarsening [7,8]; however, this growth rate and the presence of a crossover are dependent on the molecular model used.

This issue is further complicated by the paucity of experimental 2D coarsening data. Tanaka performed 2D coarsening studies using oligomeric [11] and polymer-solvent systems [12]. He reported that the domain-size growth rate for the oligomeric system scaled as approximately $d \sim t^{1/3}$, while the rate for the polymer-solvent system scaled as approximately $d \sim t^{0.15}$. However, relatively few data were presented to support the growth rate determinations.

Experimental studies on 2D coarsening can be complicated by critical wetting [13]. For critical solutions in a 2D geometry that have been quenched into the two-phase region of the phase diagram, σ between the two liquid phases and between the liquid phases and the confining solid may cause one of the liquid phases to wet preferentially the solid surface to such an extent that a wetting layer is formed. This wetting layer accelerates domain-size growth due to the added interconnectivity [14]; therefore, comparison of experimental coarsening rates to theory can be much more difficult. Bodensohn and Goldburg [14] claimed that such wetting layers caused the very high initial domain-size growth rate ($d \sim t^{1.5}$) observed for their 2D coarsening experiments using small molecule systems.

In the present work, domain sizes of phase-separated polymer solutions in a confined geometry were monitored as a function of time. The domain-size growth rate was a strong function of distance from criticality and a crossover in growth rate was observed in near-critical solutions, in agreement with numerical studies [5–10]. The morphology of the critical systems was also a function of polymer molecular weight, due to the molecular weight dependence of σ [15].

Nearly monodisperse polystyrene (PS, Pressure Chemical) was dissolved in diethyl oxalate (DEO) [16]. The PS molecular weights and the approximate PS-DEO critical compositions (Φ_c) [17] and temperatures (T_c) [17] are given in Table I (conditions are given for both "dry" and "wet" solutions [16]). The solutions were sandwiched between two microscope slides; glass and quartz slides were used in order to test the wetting characteristics of the system. The slides were separated by a constant distance using 10 μm monodisperse glass beads (Duke Scientific). The samples were placed in a Mettler hot stage, and the phase separation was monitored using optical microscopy (Nikon Optiphot2.pol).

Typical micrographs following the coarsening of PS-DEO solutions of various compositions and quench depths are shown in Fig. 1. For circular, dispersed domains [Figs. 1(a) and 1(b)], d was determined as the mean of the diameters of circles. It should be noted that the

TABLE I. Molecular weight, T_c, and approximate Φ_c [17] values for PS-DEO systems [16].

PS sample (MW)	M_n[a]	M_w/M_n[a]	T_c (wet) (°C)	T_c (dry) (°C)	Φ_c[b] (wt %)
300×10^3	2.9×10^5	1.06	45	35	~7.5
2000×10^3	2.0×10^6	1.3	61	49	~2.5

[a] M_n is the number average molecular weight and M_w is the weight average molecular weight.

[b] These Φ_c values are similar for both dry and wet solutions [16,17].

experimental setup prevented accurate d measurements when $d < 6$ or $d > 100$ μm. A Fourier analysis was attempted for noncircular dispersed domains [Fig. 1(c)]; however, the fast rate of coarsening and irregular domain shapes prevented an accurate quantitative analysis. Since the average domain size of the dispersed phase was generally of the order of or larger than the gap width, 10 μm, and no overlap was observed for the coarsening times studied, the observed circles can be thought of as disks instead of spheres; therefore, the growth of the domains can be considered to be 2D coarsening.

The morphology of all phase-separated off-critical solutions featured dispersed circles in a continuous matrix [see Fig. 1(a)]; due to the large average distance between droplets, coarsening occurred primarily through an evaporation-condensation mechanism, i.e., there was little coalescence between droplets. The average circle diameter, equal to d for the dispersed phase, is presented as a function of time in Fig. 2. The dispersed phase grows as t^a, where $0.22 \leq a \leq 0.35$, slightly dependent on quench depth, for several decades in time. The growth rate does not appear to depend on substrate, i.e., changing the cross-sectional curvature of the droplets does not change the coarsening rate. The growth-rate results are consistent with the theoretical work of Yao *et al.* [6]; their application of 3D Ostwald ripening to 2D coarsening of off-critical systems featured a domain-size growth rate of $d \sim t^{1/3}$. The area fraction of the dispersed phase, F_A, as a function of time for a typical off-critical sample, is also given in Fig. 2. Since F_A remains roughly constant over all but the earliest times studied, it can be assumed that there is no wetting layer and proper coarsening is observed.

The morphology of phase-separated near-critical solutions was similar to that for the off-critical case, and the average d as a function of time is given in Fig. 3. Because of the greater concentration of droplets, coalescence was observed much more frequently than in the off-critical case; however, the system coarsened mainly via apparent Ostwald ripening. The dispersed phase grows as approximately $t^{1/3}$ at early times, then accelerates to an approximately $t^{2/3}$ growth rate; this behavior is similar to that predicted numerically by Farrell and Valls using Langevin fluid models [8] and is the first reported experimental crossover in 2D coarsening. From Fig. 3 it is apparent the crossover domain size depends slightly on quench depth and sample molecular weight (MW) and in cases studied here occurred when $d \sim 12$ μm. The similarity between the dry and wet DEO data at equivalent quench depths shows that the presence of water in the system has little effect on the coarsening behavior and that the crossover does not depend on the dry or the wet nature of the solvent. This crossover has been predicted theoretically for 2D systems by Furukawa [18] and has been attributed to hydrodynamic flow.

The morphology of phase-separated critical solutions [17] is strikingly different from noncritical solutions. While some critical systems feature dispersed droplets

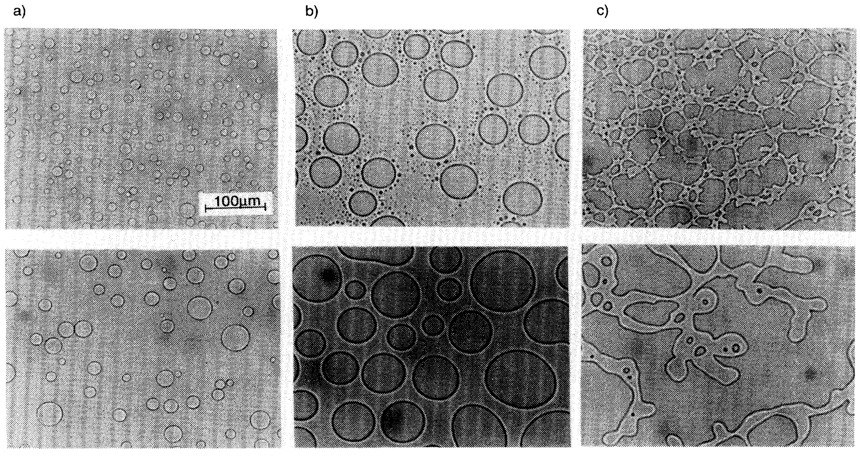

FIG. 1. Optical micrographs for various phase-separated PS-DEO (wet [16]) solutions using a 10 μm gap width: (a) 300×10^3 MW PS-DEO, 2.5 wt % (off-critical), quench depth (ΔT = distance from cloud point curve) = 4 °C, coarsened for 24 (upper) and 133 (lower) min with glass substrate; (b) 300×10^3 MW PS-DEO, 7.5 wt % (critical), ΔT = 0.5 °C, coarsened for 1.2 (upper) and 10 (lower) min with quartz substrate; (c) 2000×10^3 MW PS-DEO, 2.5 wt % (critical), ΔT = 2 °C, coarsened for 75 (upper) and 300 (lower) sec with glass substrate.

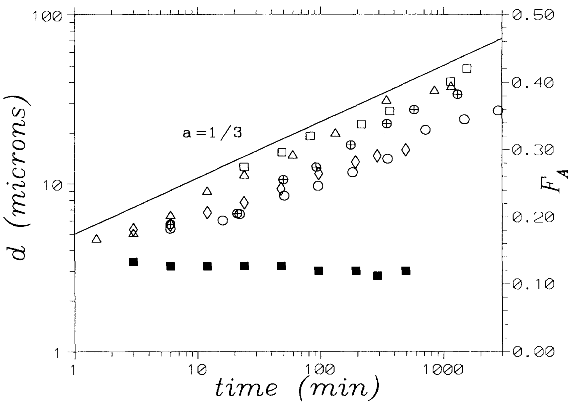

FIG. 2. Average domain size (d) and area fraction (F_A) of minority phase as a function of coarsening time for 2.5 wt % 300×10^3 MW PS-DEO (wet [16]) solutions (off-critical) with either quartz or glass substrates and a gap width of 10 μm. Glass: ○, $\Delta T = 2$ °C; △, $\Delta T = 4$ °C; □, $\Delta T = 6$ °C; ◇, $\Delta T = 8$ °C. Quartz: ⊕, $\Delta T = 2$ °C. ■, F_A for sample with symbol ◇. The slope is not a fit, only a guide for $d(t)$ growth.

with a highly bimodal distribution [see Fig. 1(b)], by increasing molecular weight an unusual noncircular morphology is observed [see Fig. 1(c)]. In the early coarsening stages of the lower molecular weight system, some of the uniform droplets developed in the early stages of phase separation grow rapidly while the remainder stay roughly uniform in size. The smaller droplets then dissolve, with an inexplicable tendency for the smaller droplets farther from the larger droplets to evaporate faster than those closer to the larger droplets. Figure 4 shows d as a function of time for the several lower molecular weight systems. The high growth rate ($d \sim t^{1.2}$) present at early times coincides with the presence of the smaller satellite droplets; once the satellites disappear, the growth rate slows considerably ($d \sim t^{1/3}$), although at very long times the larger droplets cannot be measured accurately due to their size ($d > 100$ μm).

This accelerated early-time behavior can be attributed to added interconnectivity of the matrix phase caused by the apparent affinity the hydrophilic solvent (dispersed phase) has towards the polar substrates. Since the diameter of the satellites (~ 2 μm) is considerably smaller than the gap thickness (10 μm), a wetting layer of the matrix phase surrounds the satellites. A similar time dependence of d has been reported recently by Bodensohn and Goldburg [14] for small-molecule coarsening. They explained that the dispersed phase acted as a wetting layer surrounding the matrix phase and the droplets acted as "reservoirs." This analysis was supported by plotting F_A versus time; the high power law at early times coincided with a growth in F_A, supposedly caused by a shrinking wetting layer. However, since most of the particle diameters at these early times in their study were significantly smaller than the gap size, the observed particles may in fact have been spheres instead of disks; therefore, it is possible that the volume fraction of particles, F_V, would be a more appropriate quantity to characterize than F_A [19]. Figure 5 shows d, F_A, and F_V as a function of time for one of the critical 300×10^3 MW PS-DEO samples used in this study; F_V measurements were made assuming the satellites were spherical and the larger droplets were disks of width equal to the gap thickness (10 μm). The early-time growth in F_V suggests the presence of a shrinking wetting layer; this wetting layer either stabilizes or stops growing at approximately 10 min, coinciding with the d growth-rate deceleration. Two additional features of Fig. 5 are worth noting: The early-time growth in F_V is slightly faster than for F_A, and F_V differs slightly from 0.50, the value expected [20] from a shallow, critical quench involving small molecule–small molecule coarsening. The latter point may be explained by the slight

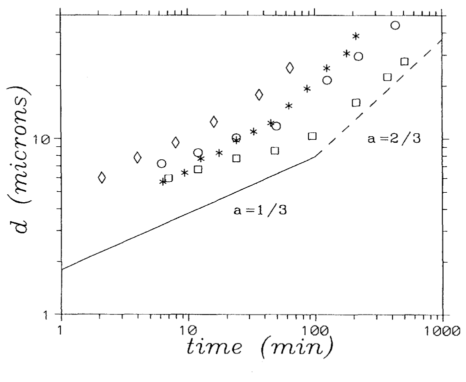

FIG. 3. Temporal dependence of minority phase d for near-critical PS-DEO solutions with glass substrate and a gap width of 10 μm. ○: 5 wt % 300×10^3 MW PS-DEO (wet [16]), $\Delta T = 2$ °C; ◇: 5 wt % 300×10^3 MW PS-DEO (wet), $\Delta T = 4$ °C; □: 1 wt % 2000×10^3 MW PS-DEO (wet), $\Delta T = 2$ °C; *: 5 wt % 300×10^3 MW PS-DEO (dry), $\Delta T = 2$ °C. The slopes are not fits, only guides.

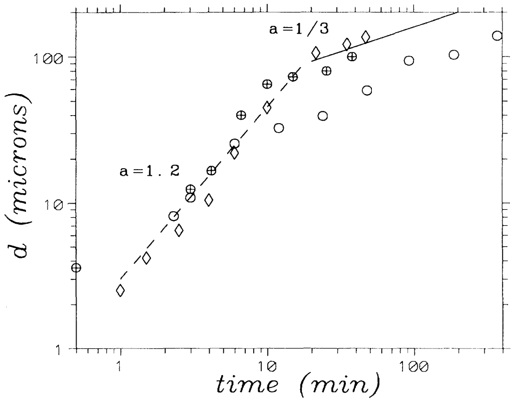

FIG. 4. Temporal dependence of minority phase d for 7.5 wt % 300×10^3 MW PS-DEO (wet [16]) solutions (critical) with quartz or glass substrates and a gap width of 10 μm. Glass: ○, $\Delta T = 0.5$ °C; ◇, $\Delta T = 3$ °C. Quartz: ⊕, $\Delta T = 0.5$ °C. The slopes are not fits, only guides.

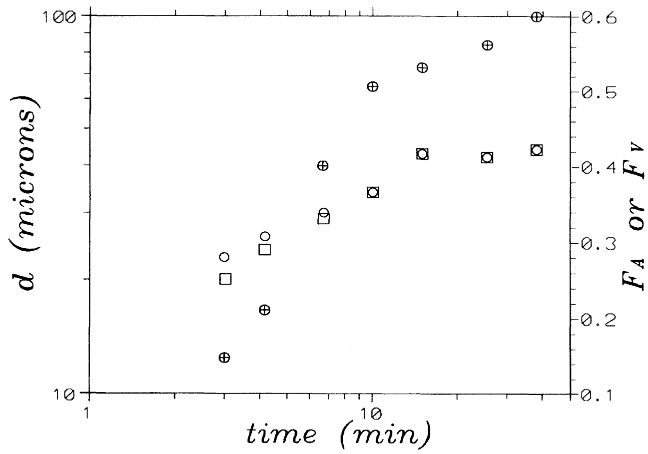

FIG. 5. Temporal dependence of d (⊕), area fraction F_A (○), and volume fraction F_V (□) of minority phase for 7.5 wt% 300×10^3 MW PS-DEO (wet [16]) solution (critical), $\Delta T = 0.5$ °C, with a quartz substrate and a gap width of 10 μm.

PS polydispersity, the possibly inexact determination of Φ_c, or, most likely, the combination of the inherent asymmetry of polymer-solvent phase-separation curves and the finite quench depth employed in these studies.

In conclusion, this is the first experimental 2D coarsening study demonstrating that domain-size growth rates are dependent on distance from criticality and that a crossover in growth rates is possible. For off-critical systems, the domains of the dispersed phase scale as approximately $t^{1/3}$ over several decades in time, in agreement with most theoretical and numerical studies [5–8]. The domains for phase-separated near-critical systems scale as approximately $t^{1/3}$ at early coarsening times and feature a crossover to approximately $t^{2/3}$ at longer times, in agreement with numerical studies [7,8]. Critical systems are often dominated by critical wetting, causing a high growth rate at early times. In addition, by increasing polymer molecular weight, fast-growing networklike structures can be formed. As increasing the polymer molecular weight lowers σ, this networklike morphology is not wholly unexpected (σ is the driving force for maintaining circular domains and their lower surface area) and merits further study.

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[16] DEO is a hygroscopic solvent, and much of the presented data were obtained using wet DEO (~0.3 wt% water absorbed from the atmosphere). The shapes of the phase-separation curves were similar in wet and dry solvents, i.e., only T_c varied.

[17] Only approximate Φ_c values were determined. These systems are defined here as "critical" based on the behavior of these approximately critical systems.

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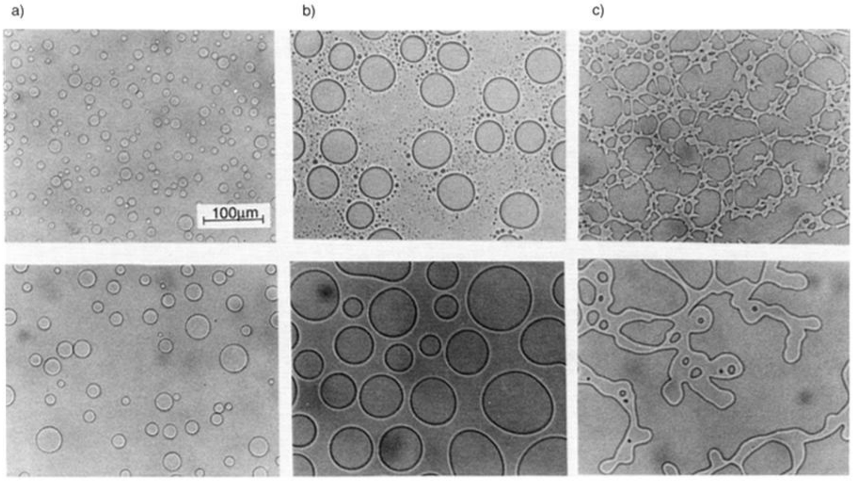
[19] It should also be noted that Bodensohn and Goldburg's (Ref. [14]) assumption that $F_A = Nd^2$, where N is the total number of droplets in a micrograph, may be invalid for a non-Gaussian distribution such as that observed in Fig. 1(b).

[20] F_A values that are smaller than expected for phase-separated polymer systems have also been reported by B. Crist and A. Nesarikar, Macromolecules **28**, 890 (1995), and Q. Pan and R. J. Composto, Bull. Am. Phys. Soc. **40**, 701 (1995). They suggested that this behavior is due to phase diagram differences between thin films and bulk; however, since 10 μm is not particularly thin, this explanation is unlikely to hold for the present study.



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