Nucleation and Growth in a Polymer Solution

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The first experimental investigation of nucleation, growth, and coalescence in a polymer solution near the critical point is reported. A large asymmetry is observed in the kinetics of phase separation although the coexistence curve itself is only slightly asymmetric near the critical point. The observed effects are explained by the strong composition dependence of viscosity, diffusion coefficient, and correlation length in polymer solutions.

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Recent experimental and theoretical efforts[1-5] devoted to the study of nucleation and growth in binary liquid mixtures near the critical point have revealed the interesting effects of critical slowing down on the phase-separation process. The observation of the simultaneous occurrence of nucleation of new droplets and growth of previously nucleated droplets has necessitated a coupling of Becker-Döring–type nucleation theory[6] with Lifshitz-Slyozov–type growth theory[7] for a proper description of the kinetics.

Here, we report the first experimental study of nucleation and growth in a polymer solution near the critical point. We observe a large asymmetry in the kinetics of phase separation even though the coexistence curve is only slightly asymmetric near the critical point.[8,9] We find that the nucleation and growth of polymer-rich droplets in a polymer-poor solution is characterized by high initial nucleation rate, high number density of droplets, small initial droplet radius, and a large number of coalesence events in the growth phase. In contrast, for the same relative supercooling in a polymer-rich solution, we observe low initial nucleation rate, low number density, larger initial droplet size, and very few coalesence events in the growth stage of the phase-separation process. These effects are in striking contrast with binary liquid mixtures, where the kinetics is essentially the same on the two sides of the coexistence curve near the critical point.[10]

The measurements were performed on solutions of polystyrene (Polysciences, $M_w = 299\,000$, $M_w/M_n = 1.06$) in cyclohexane (PS-CH), whose coexistence curve is shown schematically in Fig. 1. The solid line is the coexistence curve $T_{cx}(C)$, where C is the weight fraction of polystyrene, and $\Delta T_{cx} = T_{cx}(C) - T_c$. Here the critical temperature T_c for PS-CH is 28 °C.[9] If a sample is quickly cooled through the interval $dT = T_m(C) - T_{cx}(C)$, homogeneous nucleation should occur. The parameters ΔT_{cx} and dT are the only quantities required to characterize the degree of supercooling of the initial state.

In these experiments the sample was supercooled through the temperature dT from above the coexistence curve. Phase separation was observed photographically by use of a 35-mm camera attached to a microscope with the magnification set at 70. The PS-CH sample was mixed and sealed under atmospheric pressure in a quartz cell of reentrant shape so that observations could be made on that portion of the mixture contained in a disk-shaped region 2 cm in diameter and 0.1 mm thick.[2] The photographs exposed a portion of the sample of dimensions $1.4 \times 1.0 \times 0.1$ mm^3. The estimates of the droplet size were made by a comparison with a cross hair, which also appeared in the photographs.

The experiments were carried out in a temperature-controlled water bath (stability 1 mK over the period of 10 h). The sample prepared at an off-critical composition ($\Delta T_{cx} = 100 \pm 5$ mK) was

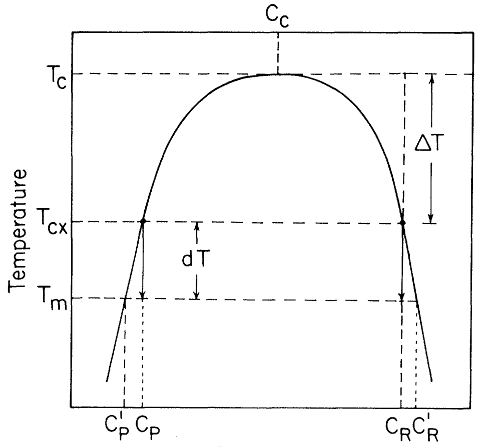

FIG. 1. The coexistence curve for a polymer solution such as polystyrene in cyclohexane with an upper consolute point. The relevant quantities shown in the figure are defined in the text.

equilibrated at a temperature a few millikelvin above T_{cx} and then supercooled by adding a premeasured amount of ice water into the well stirred bath. The quench was attained in about 10 s. Microphotographs obtained at various times after the quench provided detailed information regarding the time dependence of the droplet size distribution and the droplet density.

We studied two samples of PS-CH on opposite sides of the coexistence curve of compositions C_P and C_R (shown schematically in Fig. 1 with $\Delta T_{cx} = 100$ mK). The subscripts P or R here denote that the solution is poorer or richer than the critical solution in polystryene content. In this section we compare the results of the experiments for samples supercooled through the same quench depth ($dT = 10 \pm 1$ mK) into the two-phase region.

Figure 2 shows the mean radius of droplets as a function of time for the two samples. Note that the droplets nucleating out of the supercooled PS-poor sample (composition C_P) would be polymer rich (composition C_R'), whereas droplets nucleating out of the supercooled PS-rich sample (composition C_R) would be polymer poor (composition C_P'). The polymer-rich droplets in a polymer-poor solution appear within a minute after the quench, and the polymer-poor droplets in a polymer-rich solution appear 5 min after the quench. However, the droplet size could not be reliably estimated in this very early stage. As is evident from Fig. 2, the growth rate for polymer-rich droplets is apparently much higher than that for the polymer-poor droplets over the period of observation.

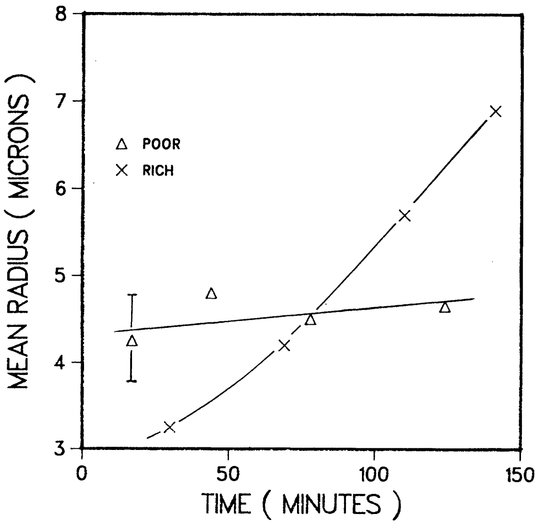

FIG. 2. Mean radius $(\bar{R}^3)^{1/3}$ as a function of time for polymer-poor droplets (composition C_P') in a polymer-rich solution (triangles) and for polymer-rich droplets (composition C_R') in a polymer-poor solution (crosses).

In Fig. 3 we show the number of droplets in the volume of observation as a function of time for both experiments. Whereas the number density is unchanged for the polymer-poor droplets, there is an appreciable decrease in the number density of polymer-rich droplets over the same time period after the quench. This decrease in droplet density could be attributed to coalescence of polymer-rich droplets.

As a first qualitative step to understanding the experimental observations, we invoke the theory proposed by Langer and Schwartz[5] for nucleation and growth from a supercooled binary solution. The quantities relevant to our discussion are the initial critical droplet size R^*, the nucleation rate J, and the activation energy ΔE^*.

The initial critical droplet radius R^*, the minimum size for a droplet to be stable and grow, is given by

$$R^* = 2\xi/x, \tag{1}$$

where ξ is the correlation length in the majority phase, and

$$x = (1/\beta)[1 - 1/(1 + dT/\Delta T_{cx})^{\beta}]$$

is the initial relative supercooling, with β the critical exponent associated with the shape of the coexistence curve. Here $x = 0.095 \pm 0.015$. In the absence of correlation-length measurements for the samples used in this study, we use as estimates the data of Kuwahara *et al.*[11] on PS-CH (molecular weight of polystyrene, 1.1×10^5). The measured correlation length along the coexistence

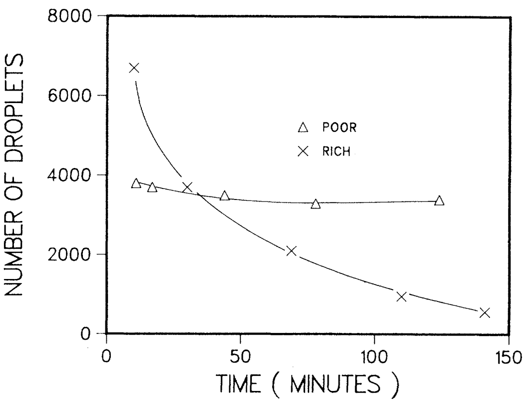

FIG. 3. Number of droplets in a volume $1.4 \times 1.0 \times 0.1$ mm^3 as a function of time for the two experiments of Fig. 2.

curve for the polymer-rich phase is $\xi=\xi_0\epsilon^{-\nu}$, where $\epsilon=(T_c-T_{cx})/T_c$ with $\xi_0=2.40$ Å and $\nu=0.65$. For $\Delta T=110$ mK, this gives $\xi=410$ Å, and the critical radius $R^*=0.8$ μm. This would be our estimate for the initial critical droplet size after supercooling the polymer-rich phase.

However, on the polymer-poor side of the coexistence curve, for $\Delta T=110$ mK the correlation length is $\xi=160$ Å, giving a critical radius $R^*=0.32$ μm.[12] The observation of a smaller mean size for the polymer-rich droplets can thus be attributed to this difference in the correlation length and hence in the critical radius. It should be emphasized that the critical-size droplets were not directly observable in our experiment, since the smallest size we could measure under our microscope was 3 to 4 μm.

Next, we make an estimate for the nucleation rates using the Langer-Schwartz theory. The decay of the metastable state is governed by an activation energy ΔE^* required to form a critical-size nucleus,

$$\Delta E^*/k_BT=4\pi\sigma R^{*2}/3k_BT, \tag{2}$$

where σ is the interfacial tension, k_B the Boltzmann constant, and T the temperature in kelvins. Substituting for R^* from Eq. (1) and defining $x_0=\pi\sigma\xi^2/18k_BT\beta^2$ we can express Eq. (2) as

$$\Delta E^*/k_BT=(x_0/x)^2. \tag{3}$$

x_0 is of the order unity for fluids and binary mixtures.[5] With the activation energy ΔE^* defined by (3) the nucleation rate J, expressed as number of droplets per cubic centimeter per second, is given by

$$J=P\left(x_0,\frac{x}{x_0}\right)\frac{D}{\xi^5}\exp\left[-\left(\frac{x_0}{x}\right)^2\right], \tag{4}$$

where P is a function of x_0 and x/x_0 only, and D is the diffusion constant in the majority phase.

Following Binder[13] and the notation therein, the quantity x_0 could be reexpressed as $x_0^2=(16\pi/3\beta^2)\hat{F}_s^3C_-^2/B^4$, where $\hat{F}_s$, C_-, and B are the critical amplitudes for the interfacial tension, for the isothermal compressibility along the coexistence curve, and for the diameter of the coexistence curve, respectively. In calculating x_0^2 for the problem of nucleation from either phase, we note that the values to be used for $\hat{F}_s$ and B will be unchanged. However, because of the asymmetry in the susceptibility amplitude C_- (the ratio $C_{-R}/C_{-P}=2.6$),[11] x_0^2 should differ in the two phases. We estimate $(x_0^2)_R/(x_0^2)_P=6.8$. This implies that for the same quench depth x, the nucleation rate will be several orders of magnitude larger in the polymer-poor solution in comparison to that in the polymer-rich solution. Further, for a given supercooling x (0.1 here) the nucleation rate (proportional to D/ξ^6) is determined to be 10^4 times larger for nucleation from a polymer-poor solution as compared to that from a polymer-rich solution. However, this large difference is masked by the strong sensitivity of the nucleation rate to the experimental uncertainty in the factor $(x_0/x)^2$ appearing as the exponent. Thus the nucleation rates remain uncontrolled in our experiment as in the previous studies in liquid mixtures.[2] Further, in the absence of experimental data for the critical amplitude of the interfacial tension for our system, an exact calculation of x_0^2 and hence the nucleation rates is not possible now.

The growth rate differs in the two polymer solutions because of the difference in the diffusion coefficient and in the incidence of coalescence events. The droplets in the polymer-poor solution have a greater mobility than in the polymer-rich solution. This is due to the lower viscosity of the polymer-poor solution. From the known coexistence curve for PS-CH systems, the composition of the solutions used in this investigation should have nominal values of $C_P=4\%$ and $C_R=10\%$. The critical composition $C_c=7\%$ weight fraction of polystyrene. The composition dependence of macroscopic viscosity of a polymer solution in a poor solvent for the composition range of interest here may be expressed as $\eta\sim C^{\chi_\eta}$ with $\chi_\eta\approx4.5$.[14,15] With this relationship, the viscosity of the polymer-rich solution is estimated to be larger than that of the polymer-poor solution by a factor of 50 to 60. The larger initial number density of droplets, coupled with the higher mobility, leads to the high incidence of coalescence events in the polymer-poor solution. This also causes a wider size distribution of droplets. Using the Stokes-Einstein relationship, we see that the larger droplets move faster under gravity and sweep the slowly moving smaller droplets along their path. This effect of enhanced coalescence due to gravity may account for the deviation of the observed growth rate from that predicted by Lifshitz and Slyozov[7] ($t^{1/3}$ law).

The effect of viscosity on mobility is further enhanced as a result of the presence of a depletion region around the droplets. The region immediately surrounding the polymer-poor droplet immersed in the polymer-rich solution will have a composition $C>C_R$ and hence the depletion region will have a higher viscosity than the region far from the droplet. This further impedes the movement of droplets in a polymer-rich solution. The opposite description holds for polymer-rich droplets immersed in a polymer-poor solution. In that case the composition of the depletion region is less than C_P. Hence the region in the vicinity of the droplet is less viscous than the region far from it, leading to a greater mobility of the droplets.

In summary, we have observed a large asymmetry in the kinetics of nucleation, growth, and coalescence in a polymer solution near the critical point. We attribute the observed effects to the strong composition dependence of correlation length, diffusion coefficient, and viscosity in polymer solutions.

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