

## Spinodal Decomposition Lab

The phase diagram for a polymer-polymer blend is shown in figure 1. The miscible region is in the center. At higher temperatures phase separation is observed. Within the two-phase region, deep quenches or quenches near the critical point lead to spinodal decomposition with spontaneous phase separation in the absence of nucleating sites while shallow quenches away from the critical composition lead to nucleation and growth of phases in a metastable regime requiring nucleation sites. Nucleation and growth is characterized by spherical domains that form on dust particles. Spinodal decomposition is characterized by a web-like structure that forms on random concentration fluctuations. Since spinodal decomposition depends on the depth of quench and the rate of transport, the spacing of the domains display a preferred distance, the longest distance being limited by diffusion and the shortest distance by the miscibility following Kahn-Hilliard theory. Kahn-Hilliard theory was developed for metals but can only be clearly observed in systems with small diffusion coefficients, particularly polymeric systems. Polyvinylmethylether (PVME) blended with polystyrene (PS) is the main polymer blend which has been studied. PVME/PS displays LSCT phase separation.

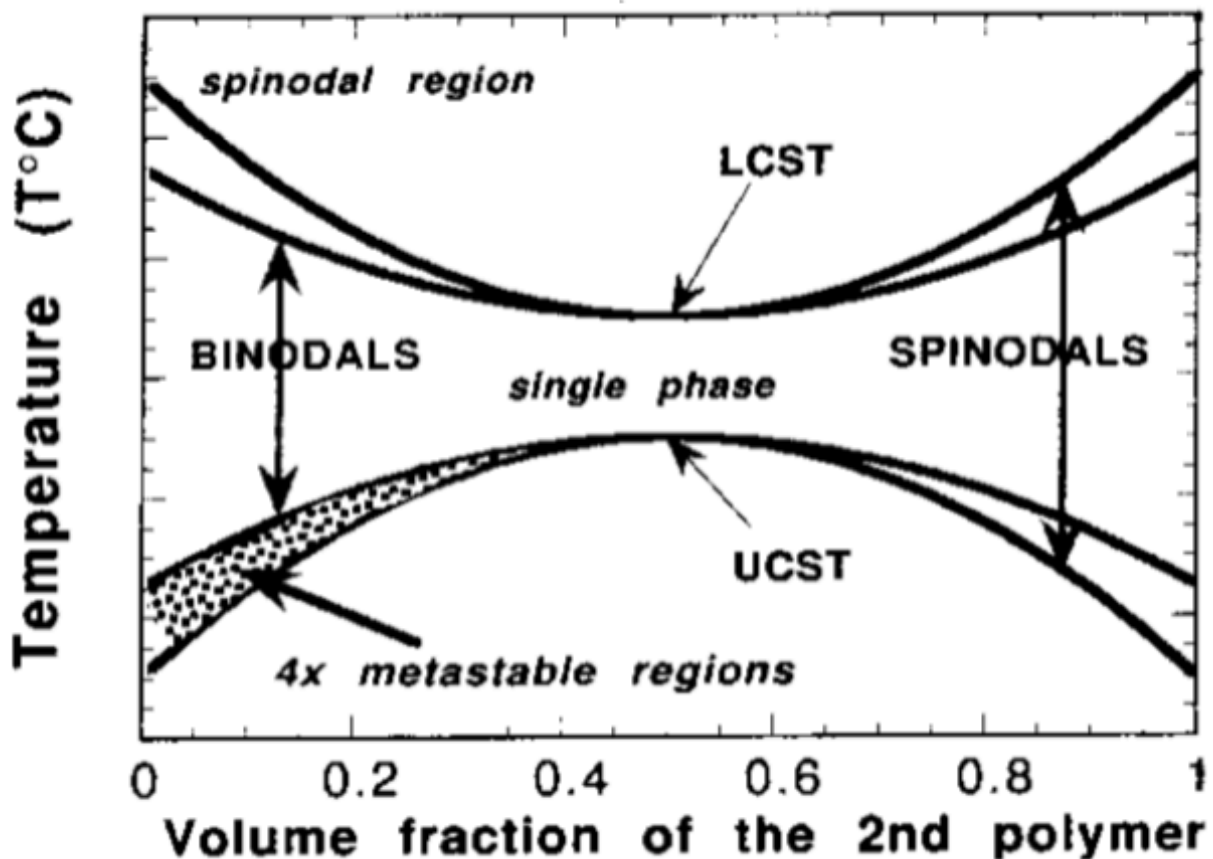


Figure 1. Schematic of a phase diagram for a polymer blend displaying LCST and UCST behavior with a miscibility gap. Generally, only an LSCT or a UCST are observed. For PVME/PS an LSCT is observed with phase separation on heating which is typical for a polymer blend with specific interactions.

For binary systems the Flory-Huggins equation can be expressed in the following form<sup>[62, 63]</sup>:

$$\Delta G_m = RT \left[ \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi \phi_1 \phi_2 \right] \quad (4.8)$$

where  $\chi$  is the so called Flory-Huggins binary interaction parameter. R is the universal gas constant, and T is the absolute temperature. The first two terms of the right hand side in Equation 4.8 are related to the entropy of mixing and the third term is originally assigned to the enthalpy of mixing.

$r_i$  is the degree of polymerization of the polymer component “i”,  $\phi_i$  is the volume fraction of component “i”.

The first derivative of equation 4.8 with respect to composition is 0 at the binodal or cloud point curve in Figure 1. The second derivative of equation 4.8 is 0 at the spinodal curve. The third derivative is equal to 0 at the critical point where the binodal and spinodal curves meet. Measurement of the cloud point (binodal) and knowledge of the composition, temperature, and degree of polymerizations allow a calculation of the interaction parameter. Once the interaction parameter is determined at one cloud point, the cloud point, spinodal curves at any composition and temperature can be determined using equation 4.8 and  $\chi = z\Delta\epsilon/(kT)$ .

The following approach will be used in this lab:

### Cahn-Hilliard Theory

The linear Cahn-Hilliard theory<sup>2,3</sup> for the early stages of phase separation has been used to analyze light scattering data<sup>6,7</sup> from phase-separating polymer blends. During the initial stages of phase separation the intensity of light scattered at all angles is expected to increase exponentially,

$$I(q,t) = I(q,t=0) \exp(2R(q)t) \quad (2)$$

where  $q = (4\pi/\lambda) \sin(\theta/2)$ ,  $t$  is the time of phase separation, and  $R(q)$  is the amplification factor for phase separation or the growth rate for a size scale describe by  $2\pi/q$ . Cahn-Hilliard theory defines  $R(q)$  for an incompressible blend as

$$R(q) = D_c q^2 \left( - \left( \frac{\delta^2 f}{\delta \phi_2^2} \right) - 2\kappa q^2 \right) \quad (3)$$

where  $D_c$  is the translational diffusion constant,  $f$  is the free energy density of the system at composition  $\phi_2$ , and  $\kappa$  is the coefficient of the composition gradient.

**Table I**  
Flory-Huggins-Staverman Analysis Parameters from Fits to the Cloud-Point Curves (Values Determined in the First Paper of This Series<sup>1</sup>)

	$a$ ( $\times 10^3$ )	$b_0$ ( $\times 10^2$ )	$b_1$	$c$
hetero	-1.43	1.36	-4.69	0.36 <sup>a</sup>
iso	-0.57	1.77	-4.08	0.425
$\Delta$ value	0.86	0.20	0.14	0.17
avg value				

<sup>a</sup> From Bondi.<sup>10</sup>

For binary blends of linear polymers under the mean-field approximation, eq 3 has been given by (see refs 6 and 8)

$$R(q) = D_c q^2 \left( \frac{(\chi - \chi_s)}{\chi_s} - \frac{R_0^2 q^2}{36} \right) \quad (4)$$

where  $\chi$  is the Flory-Huggins interaction parameter,  $\chi_s$  is the interaction parameter at the spinodal temperature, and  $R_0$  is the unperturbed chain dimension. Equation 4 suggests plots of  $R(q)/q^2$  versus  $q^2$  in order to determine the apparent diffusion constant,  $D_{app}$ ,

$$D_{app} = D_c(T) \left( \frac{\chi - \chi_s}{\chi_s} \right) \quad (5)$$

and  $(D_c R_0^2 / 36)$ . As is indicated by eq 5,  $D_{app}$  is equal to zero at the spinodal temperature. The value of  $q$  for which  $R(q) = 0$  is termed the critical  $q$  ( $q_c$ ). Composition fluctuations with wavenumbers larger than this  $q_c$  value will not decompose into phase-separated structures. Equation 4 also predicts a balance between transport and thermodynamic effects which leads to a maximum in  $R(q)$  at “ $q_m$ ”. “ $q_m$ ” is related to “ $q_c$ ” by

$$q_m^2 = q_c^2 / 2 \quad (6)$$

“ $q_m$ ” is the  $q$  value at the initial stages for the scattering “halo” from spinodal decomposition of blends discussed in a previous paper.<sup>9</sup>

For blends displaying a composition-dependent interaction parameter,  $g(\phi)$ , eq 4 can be approximated by

$$R(q) = D_c q^2 \left( \frac{(g - g_s)}{g_s} - \frac{R_0^2 q^2}{36} \right) \quad (7)$$

and eq 5 by

$$D_{app} = D_c(T) \left( \frac{g - g_s}{g_s} \right) \quad (8)$$

as discussed in the appendix.

### Predictions Concerning Kinetics of Phase Separation from F-H-S Analysis of Cloud-Point Curves

Using the values for  $a$ ,  $b_0$ ,  $b_1$ , and  $c$  (Table I) determined from cloud-point curves in the first paper of this series,<sup>1</sup> it is possible to predict  $g$  (composition-dependent  $\chi$ -parameter) over a range of temperatures. One use for such predicted  $g$  values is in the estimation of the growth rate for phases in the immiscible regime using eqs 7 and 8. Since the behavior of  $g$  is predicted from data at the miscibility limit (for the case of cloud-point data), a successful prediction into the immiscible regime could be considered a test of the formalisms used in deriving the  $g$  function.

As discussed above, the thermodynamic driving force for phase separation in the immiscible regime can be

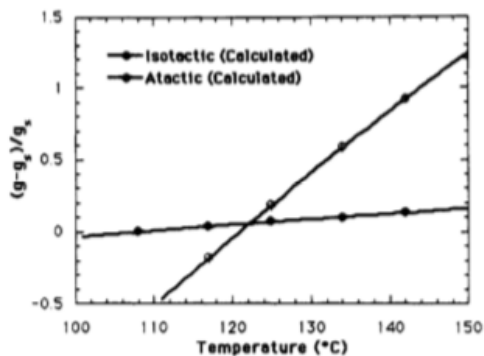


Figure 1. Predicted behavior for  $(g - g_s)/g_s$  from the F-H-S analysis. This is the thermodynamic driving force for phase separation above the coexistence curve. Isotactic PVME shows lower miscibility and much slower kinetics above the miscibility limit  $(g - g_s)/g_s = 0$ .

approximated as (appendix)<sup>6,8</sup>

$$\frac{D_{app}}{D_c(T)} = \frac{(g - g_s)}{g_s}$$

We consider blends of critical composition ( $\approx 75\%$  PVME by weight) so as to avoid the metastable binodal region) and predict the thermodynamic driving force for phase separation for the isotactic and atactic blends (Figure 1).

In this analysis  $g_s$  was calculated using the F-H-S parameters of Table I in eq 1 and the cloud-point temperature for a 75% PVME blend under the assumption that this is the critical composition and the critical temperature ( $T_{cp,iso} \approx 109^\circ\text{C}$ ,  $T_{cp,atactic} \approx 121^\circ\text{C}$ ).  $(g - g_s)/g_s$  values calculated in this way are much smaller for the isotactic blend for similar quenches above the critical temperature. The rate of phase separation for the i-PVME blend is predicted to be drastically slower than the rate for the a-PVME/PS blend ( $D_c(T)$  is expected to have very similar values for the different tacticities since they have essentially identical glass transition temperatures and similar molecular weights). The spinodal interaction parameter can also be calculated from the second derivative of the free energy which yields a comparable value for  $g_s$ . The experimentally measured critical point was used since it was felt that this was a more direct value.

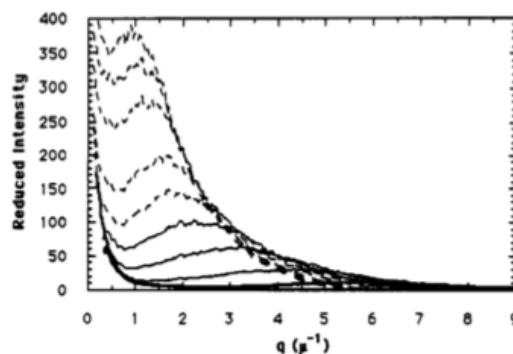


Figure 3. Series of light scattering measurements for atactic PVME blended with PS (75% PVME) at  $123^\circ\text{C}$ . (The critical temperature is  $121^\circ\text{C}$ .) The patterns are separated by about 1 min and monotonically increase in intensity with time.

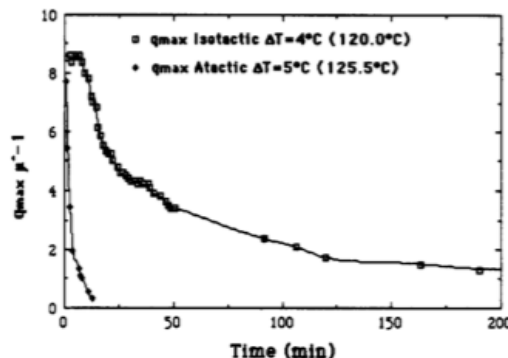


Figure 4.  $q_{max}$  versus time for isotactic and atactic PVME/PS blends of about  $4^\circ\text{C}$  quench.

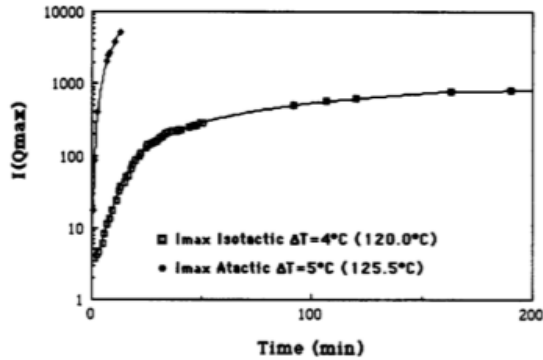


Figure 5. Dependence of the maximum in scattering intensity on time for isotactic and atactic PVME/PS blends.

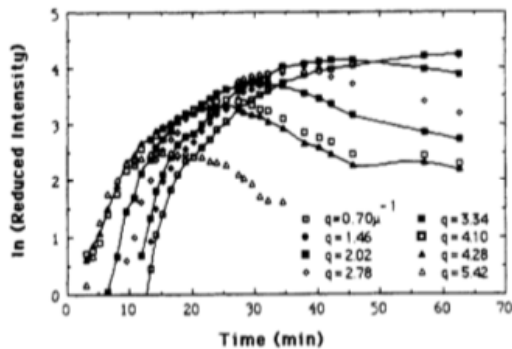


Figure 6.  $\ln I$  versus time for a 16 °C quench of the isotactic blend as suggested by eq 1.

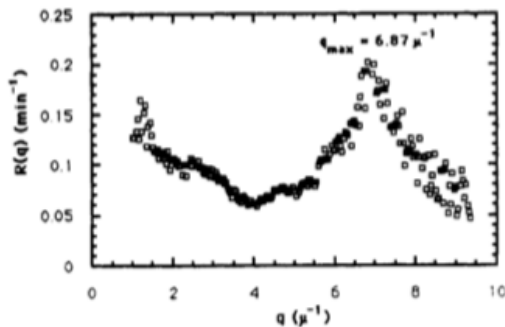


Figure 7.  $R(q)$  vs  $q$  for the isotactic blend of Figure 5.

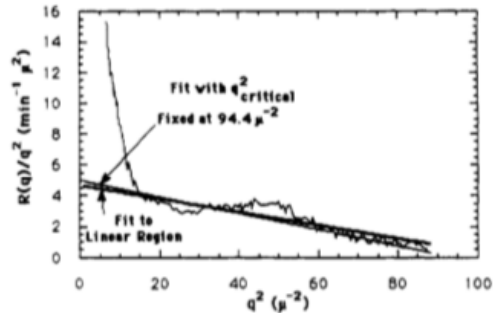


Figure 8.  $R(q)/q^2$  versus  $q^2$  for the isotactic blends of Figures 5 and 6.

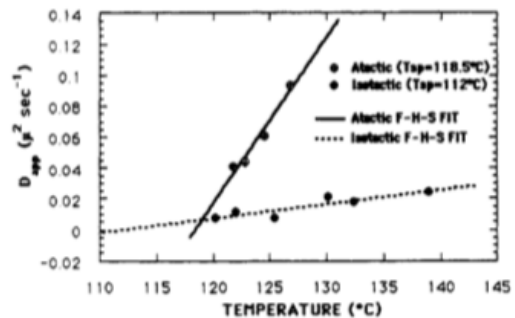


Figure 9.  $D_{app}$  versus quench temperature for 75 wt % isotactic and heterotactic PVME/PS blends for extrapolation to the spinodal point at  $D_{app} = 0$ . Lines are F-H-S fits using  $(-K_c T)(g - g_s)/g_s$  (with  $K_c$  as the only fit parameter) for the isotactic and atactic blends.

This can also be found in the Richard Jones notes from Sheffield on the web notes.

The lab will involve:

- 1) Determination of one cloud point for a PVME/PS blend.
- 2) Measurement of light scattering patterns as a function of time for a blend of PVME/PS in the spinodal regime.
- 3) Duplication of plots from figures 3 to 8 above.
- 4) Calculation of  $R_0$  in equation 4 and use of this value to determine the translational diffusion coefficient,  $D_c$ , and the quench depth ( $\chi$  ratio).
- 5) Make an optical micrograph of the spinodally decomposed sample to show the network structure.

**Questions:**

- 1) Why is it difficult to observe spinodal decomposition in metals, why is it easy to observe in polymers?
- 2) Explain in words the difference between phase growth in the nucleation and growth regime and in the spinodal regime.
- 3) Explain in words and with a cartoon what a concentration fluctuation is. How do concentration fluctuations relate to the spinodal structure?
- 4) Include answers to the quiz questions in the report.