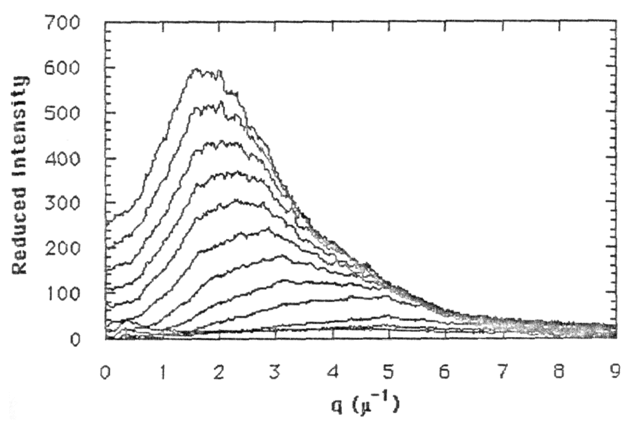
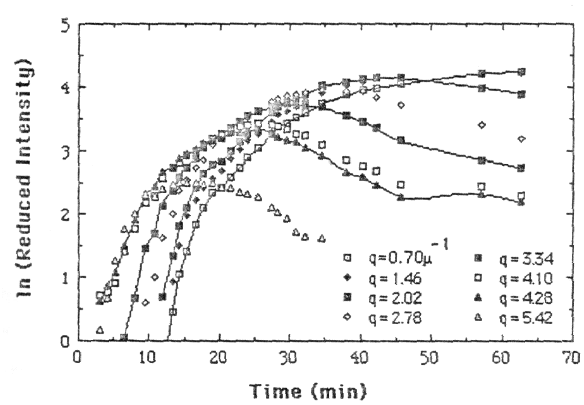
Take Home Quiz 8, 030523 Polymer Properties

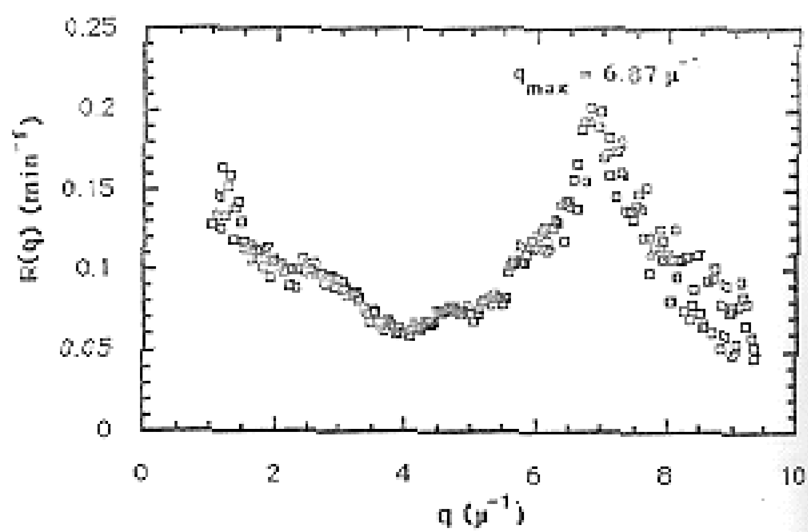
1) The following light scattering data was obtained for PVME/PS at 130°C (critical temperature 109°C) at 75% wt PVME which is the critical composition for this blend. The patterns to the right are separated by about 10 minutes. To the right is a ln-linear plot of intensity at various q-vectors as a function of time following an exponential growth law.





a) What part of these plots can be used to obtain the growth rate R(q) (be specific)? Calculate the growth rate for the growth curve (from right hand plot) given in the excel file.

b) R(q) has been determined from these plots and is plotted in the figure below:



Why does this plot take this shape?

c) If this figure is taken for a 16°C quench and the critical point occurs at 109°C calculate $(\chi_s - \chi)/\chi_s$ assuming $\chi = K/T$ (For an LCST sign is changed).

d) Determine R_0 and D_c from the data for this plot given in an excel file on the web (use the highest-q part of the data for this determination).

e) How does your R_0 from part d) compare with that calculated using an average molecular weight for the two components and an average statistical segment length of 8Å?

f) How does q_c from question d) compare with the q* peak value seen in the figure for part b)?

2) Wignall in Chapter 22 of the Physical Properties of Polymers Handbook, describes scattering from a polymer blend using,

$$I(q) = \frac{(a_H - a_D)^2}{V} S(q)$$

$$\frac{1}{S(q)} = \frac{1}{\varphi_A N_A D(q, R_{gA})} + \frac{1}{\varphi_B N_B D(q, R_{gB})} - 2\chi$$

where D(q) is the Debye function for a Gaussian Coil and a_i is is the scattering length for the monomer of type I, which is obtained by summing the scattering lengths, b, of the component atoms in the monomer (see Wignall's table 22.1 below). N is the polymerization index (number of monomers), φ is the volume fraction. V is the average monomer volume defined by the geometric mean, $V = \sqrt{v_A v_B} = \sqrt{\frac{M_A}{\rho_A}\frac{M_B}{\rho_B}}$ where M_A is the molecular weight of monomer A.

TABLE 22.1. *Bound atom scattering lengths and cross-sections for typical elements in synthetic and natural polymers.*

Atom	Nucleus	b_{coh} (10^{-12} cm)	$\sigma_{coh} = 4\pi b_{coh}^2$ (10^{-24} cm)	σ_{inc} (10^{-24} cm)	σ_{abs} (10^{-24} cm)	$f_{x\text{-}ray}$ (10^{-12} cm)
H	^1H	−0.374	1.76	79.7	0.33^b	0.28
D	^2H (D)	0.667	5.59	2.01	0	0.28
C	^{12}C	0.665	5.56	0	0	1.69
N	^{14}N	0.930	11.1	0	1.88^b	1.97
O	^{16}O	0.580	4.23	0	0	2.25
F	^{19}F	0.556	4.03	0	0	2.53
S	^{28}Si	0.415	2.16	0	0.17^b	3.94
C	Cl^a	0.958	11.53	5.9	33.6^b	4.74

[a] Values are for the naturally occurring element and are an average over the mixture of isotopoes; $f_{x\text{-}ray}$ is given for θ=0, though the angular dependence is small (<1%) for Q<0.1 Å^{-1}.
[b] Values of the absorption cross section (σ_{abs}) are a function of wavelength (λ) and are given at λ=1.8 Å. As $\sigma_{abs} \sim \lambda$, values at other wavelengths may be estimated by scaling via the ratio λ/1.8.

PVME has a chemical composition per mer unit of C_3H_6O and d-PS of C_8D_8.

a) Calculate all of the values needed to use the RPA equation for a 50/50 volume fraction blend of PVME, 121 kg/mole and d-PS of 85 kg/mole. Remember D weighs 2 g/mole. The statistical segment length for d-PS is about 10Å and for PVME is about 7Å.

b) Calculate and plot on a log/log scale the scattering curve if the interaction parameter has a value of -0.03.

c) Neutron scattering data from a 50/50 volume fraction blend is given for three temperatures below the LCST temperature, 70°C, 90°C and 110°C in the excel file for problem 2. Fit this data using the RPA equation and the constants you calculated in part a).

d) Plot the interaction parameter versus inverse temperature to obtain A and B from the equation $\chi = A + B/T$. (Remember to use absolute temperature for all thermodynamic calculations and plots.)

e) What is the temperature at the miscibility limit for this blend (actually the spinodal)?

f) Comment on the temperature dependence of the interaction parameter you observed. (Does it follow classical Flory-Huggins theory?)