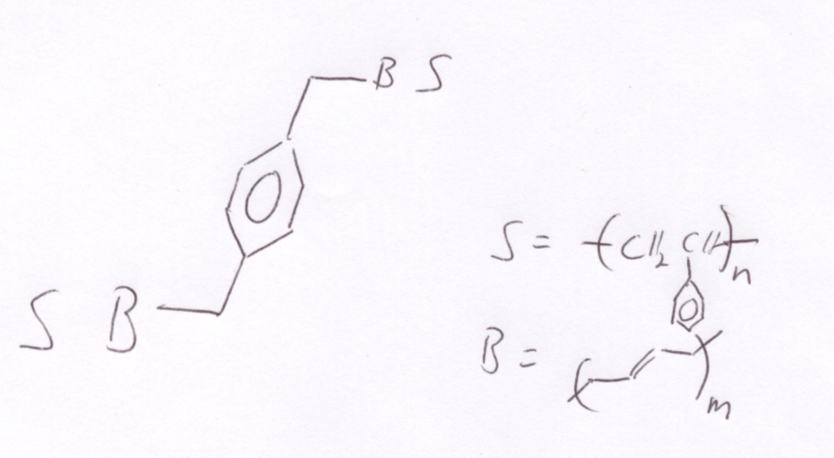
100603 Quiz 8 Introduction to Polymers

1) a) Why is there no real termination for ionic polymerizations (i.e. no coupling or disproportionation)?

b) Briefly outline how you would produce Kraton Rubber which is a block copolymer with the structure:



c) How would you make a 4-arm star polymer of polystyrene?

d) Name a typical initiator for anionic polymerization.

e) Why are the number of monomers that can possibly be polymerized by anionic and cationic polymerization extremely limited? Give examples of monomers that can be polymerized by these two mechanisms and show the propagating species.

2) a) Styrene is less reactive for free radical polymerization when compared with vinyl chloride. Explain two possible reasons that this might be the case and give an explanation using resonance structures to show that one of these two is more likely.

b) There are at least 4 types of copolymers. List these and sketch their structure.

c) Derive an expression for the copolymer composition ratio, M_1/M_2 in terms of the monomer concentrations $[M_1]$, $[M_2]$ and the reactivity ratios r_1 and r_2. (Define r_1 and r_2 in this derivation).

d) Describe 5 special cases for specific ranges of the reactivity ratios as discussed in class.

e) Which case does vinylidene chloride and vinyl chloride copolymers correspond to?

3) a) Give the Flory-Huggins equation for polymer blends and explain which part corresponds to entropy and which to enthalpy of interaction.

b) Sketch this function for χ below the critical point, at the critical point and above the critical point.

c) Show where the binodal and spinodal points are determined in the plot of b.

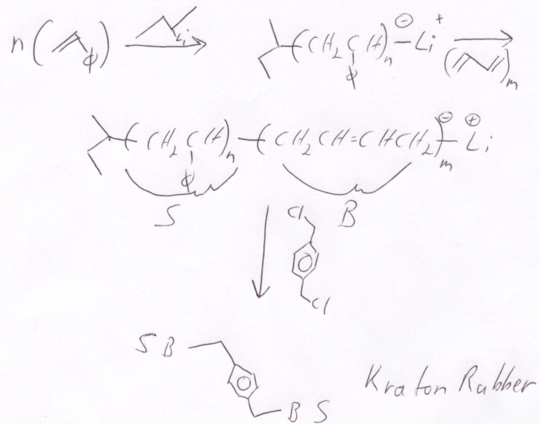
d) Show how the plot of part c can be used to construct a phase diagram.

e) Explain what an LCST and UCST phase diagram is and how they can be obtained from an interaction parameter of the form A + B/T. Why does PVME/water display an LCST phase diagram?

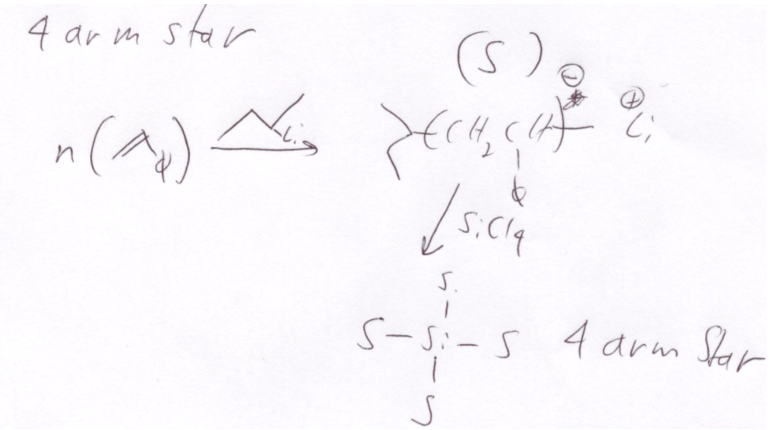
ANSWERS: 100603 Quiz 8 Introduction to Polymers

1) a) The propagating species is charged and two of these groups repel each other electrostatically.

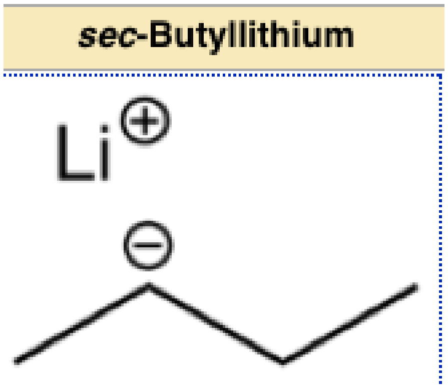
b) This is produced anionically in a living polymerization that is used on an industrial scale.

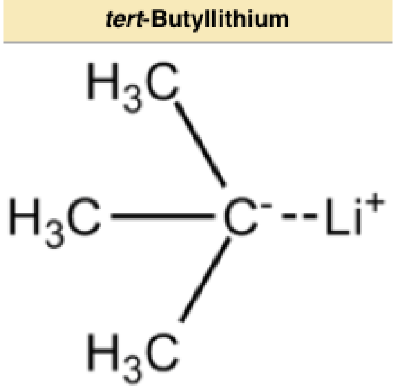


c)



d) sec-butyl lithium or tert-butyl lithium (t-butyl lithium).


sec-Butyllithium


tert-Butyllithium

2) a) Either the monomer is less reactive to attack by a free radical or the propagating free radical is more stable. In all cases it is the stability of the propagating free radical that is the dominant feature governing monomer reactivity. For styrene the propagating free radical has three resonance structures as shown in class.

b) Statistical (Random), Alternating, Block, Graft. These are described in the Tirrell/McCarthy notes.

c)

There are four possible combinations for a copolymer

$$\sim M_1\cdot + M_1 \xrightarrow{K_{11}} \sim M_1 M_1\cdot$$

$$\sim M_1\cdot + M_2 \xrightarrow{K_{12}} \sim M_1 M_2\cdot$$

$$\sim M_2\cdot + M_1 \xrightarrow{K_{21}} \sim M_2 M_1\cdot$$

$$\sim M_2\cdot + M_2 \xrightarrow{K_{22}} \sim M_2 M_2\cdot$$

We have,

$$-\frac{d[M_1]}{dt} = K_{11}[M_1\cdot][M_1] + K_{21}[M_1][M_2\cdot]$$

and
$$-\frac{d[M_2]}{dt} = K_{12}[M_2][M_1\cdot] + K_{22}[M_2\cdot][M_2]$$

The Copolymer Composition Ratio is given by
$$= \frac{\frac{d[M_1]}{dt}}{\frac{d[M_2]}{dt}} = \frac{K_{11}[M_1\cdot][M_1] + K_{21}[M_1][M_2\cdot]}{K_{12}[M_1\cdot][M_2] + K_{22}[M_2\cdot][M_2]}$$

$$= \frac{m_1}{m_2}$$ #moles m_1 & m_2 in the copolymer <u>At</u> <u>Low</u> <u>Conversions</u>

As the conversion proceeds the seed is depleted. The [M·]'s are unknown. Thus the steady state approximation is used,

$$K_{12}\,[M_1\cdot]\,[M_2] = K_{21}\,[M_2\cdot]\,[M_1]$$

The number of $[M_1\cdot]$ terminated chains changing to $[M_2\cdot]$ terminated chain equals the number of $[M_2\cdot]$ terminated chains changing to $[M_1\cdot]$ terminated chains. ∴ the number of $[M_1\cdot]$ and $[M_2\cdot]$ terminated chains remains constant,

Thus,

$$\frac{m_1}{m_2} = \frac{\left[\dfrac{K_{11}\,[M_1\cdot][M_1]}{K_{12}[M_1\cdot]\,[M_2]} + 1\right]}{\left[\dfrac{K_{22}\,[M_2\cdot][M_2]}{K_{21}\,[M_2\cdot][M_1]} + 1\right]} = \frac{\left[\dfrac{K_{11}}{K_{12}}\dfrac{[M_1]}{[M_2]} + 1\right]}{\left[\dfrac{K_{22}}{K_{21}}\dfrac{[M_2]}{[M_1]} + 1\right]}$$

$$r_1 = \frac{K_{11}}{K_{12}} \qquad r_2 = \frac{K_{22}}{K_{21}}$$

$$\frac{m_1}{m_2} = \frac{\left[r_1\frac{[M_1]}{[M_2]} + 1\right]}{\left[r_2\frac{[M_2]}{[M_1]} + 1\right]} = \frac{r_1[M_1]^2 + [M_1][M_2]}{[M_2](r_2[M_2] + [M_1])}$$

$$\boxed{\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]}\;\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}} \qquad r_1 = \frac{K_{11}}{K_{12}} \qquad r_2 = \frac{K_{22}}{K_{21}}$$

d)

A number of special cases will be considered.

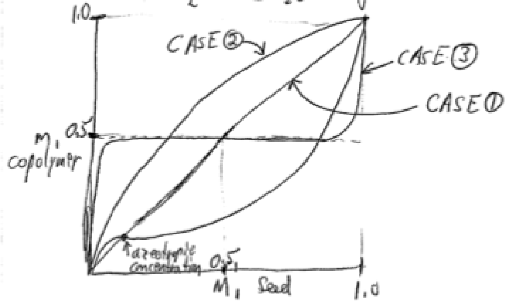
Case ①

Homopropagation rate = Copropagation Rate

$$r_1 = r_2 = 1$$

This is the Bernullian statistics case

$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]}$$ the copolymer composition is given by the feed composition



Case ②

$$r_1 = \frac{1}{r_2}$$

$M_1°$ adds M_2
at the same rate
as
$M_2°$ adds M_1

$$\frac{m_1}{m_2} = \frac{r_1 \frac{[M_1]}{[M_2]} + 1}{r_2 \frac{[M_2]}{[M_1]} + 1} = \frac{r_1 [M_1]}{[M_2]}$$

∴ the copolymer is richer in the more reactive monomer

Case ③

$$r_1 = r_2 \cong 0$$

neither chain end adds its own type of monomer

⇓

an alternating copolymer

$$\frac{m_1}{m_2} = 1$$

Case ④

$r_1 < 1$ As $r_1 r_2 \Rightarrow 0$

$r_2 < 1$ the tendency to alternate increases

In this case an azeotropic composition forms. For the azeotropic composition

$$\left(\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]}\right)_{\text{Azeotrope}}$$

or

$$r_1 [M_1] + [M_2] = [M_1] + r_2 [M_2]$$

$$\therefore \boxed{\frac{[M_1]}{[M_2]} = \frac{r_2 - 1}{r_1 - 1}}_{\text{Azeotrope}}$$

$$r_1 \frac{m_1}{m_2} + 1 = \frac{m_1}{m_2} + r_2$$

$$-1 + r_2 = \frac{m_1}{m_2}(-1 + r_1)$$

Case ⑤ $r_1 > 1$

$r_2 > 1$

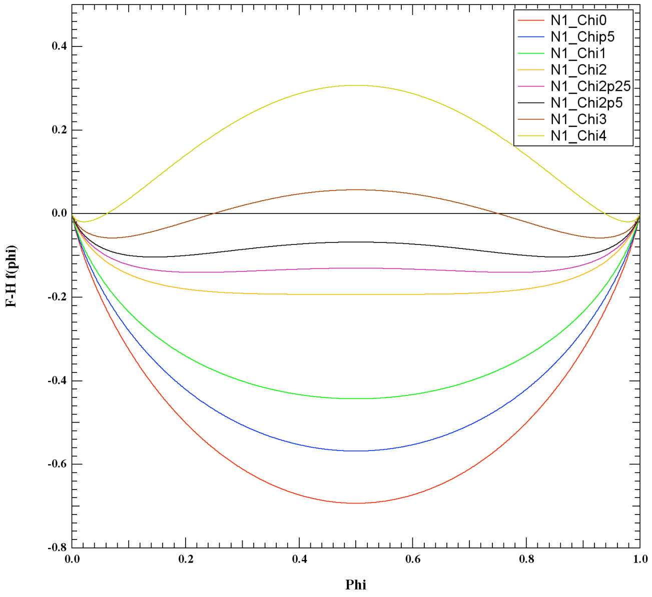
This case leads to a mixture of homopolymers or a "blocky" copolymer

e) Vinilidene chloride has a very low reactivity since it is a double substituted vinyl and the second chloride interferes sterically with propagation according to the Tirrell/McCarthy notes. Vinyl chloride has a high reactivity since chlorine is an electron withdrawing group that serves to destabilize the free radical and make it more reactive. You should draw the structure of these two in your answer showing the partial charge on the vinyl chloride chlorine group in the propagating free radical group. This would correspond to case 2 in answer d.

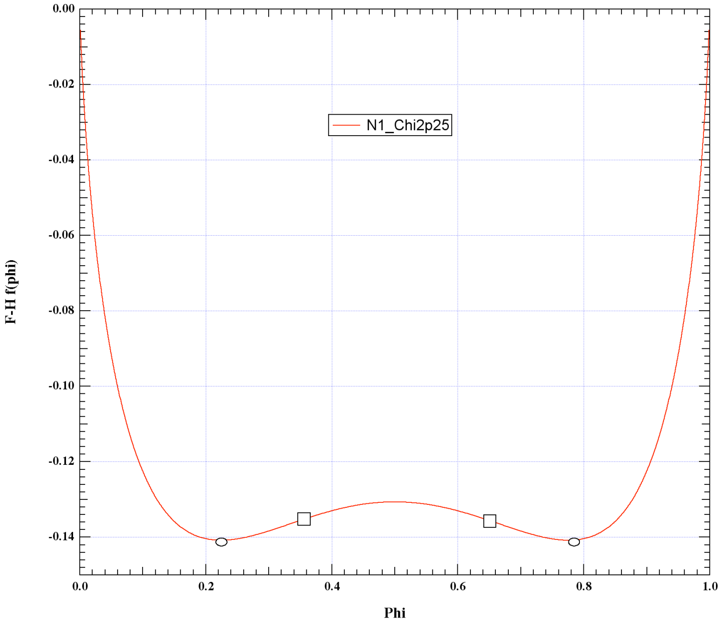
2) a) $\dfrac{\Delta G}{RT} = \dfrac{\phi_A}{x_A}\ln\phi_A + \dfrac{\phi_B}{x_B}\ln\phi_B + \phi_A\phi_B\chi_{AB}$

x_i is the degree of polymerization of component i.

b) Critical point is chi = 2



c) Binodal is where the first derivative is equal for two points (circles), this is the miscibility limit. Spinodal is where the second derivative is zero (squares). This defines the metastable region between binodal and spinodal. The critical point is where the third derivative is zero (central maximum).



d) The points of part c are plotted on a temperature versus composition plot as shown in the notes and in class. You should sketch out how to do this in your answer to this question.

e) Gone over in class.