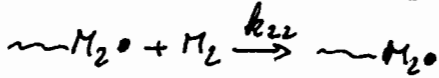
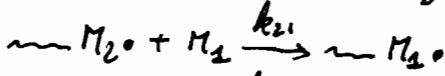
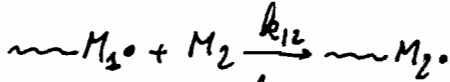
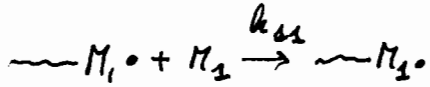


4:55 → 5:25 (30 min)

①

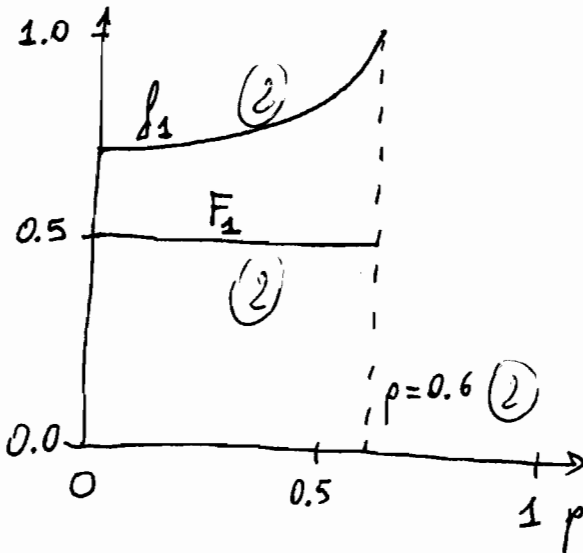
Q#1:

1.1.  $r_1 = \frac{k_{11}}{k_{12}}$  and  $r_2 = \frac{k_{22}}{k_{21}}$  (3)



1.2.  $r_1 = r_2 = 0.1 \Rightarrow r_1 \times r_2 = 0.01 \neq 0$  (2)

$(f_1)_{t=0} = 0.7 \Rightarrow (f_1)_{t=0} = 0.3$



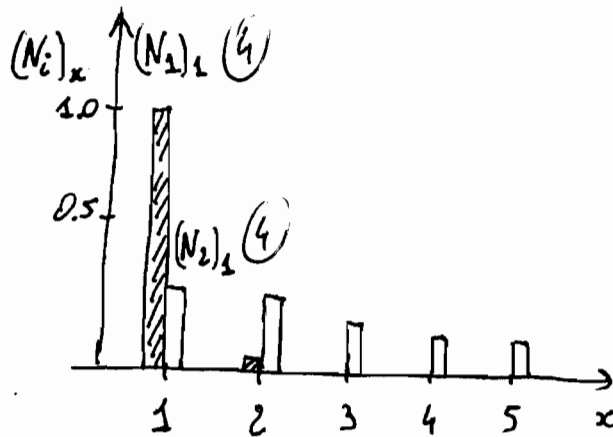
The copolymerization is alternating. (2)

Since there is less  $M_2$  than  $M_1$ , and since there is a 1:1 ratio of monomers  $M_1$  and  $M_2$  in the copolymer,  $M_2$  disappears more quickly so that  $f_1$  increases up to 1.0 when all  $M_2$  is consumed. All  $M_1$  will be consumed for  $p = 0.6$

Since this is an alternating copolymerization,  $F_2 = 0.5$  for the copolymer composition.

1.3.  $f_1 = f_2 = 0.5$      $r_1 = \frac{k_{11}}{k_{12}} = 0.2$      $r_2 = \frac{k_{22}}{k_{21}} = 5.0$     (2)

Since  $r_2 > 1$  and  $r_1 < 1$ , the monomer  $M_2$  is incorporated more preferentially. It implies that the chance of having a monomer  $M_2$  followed by a second monomer  $M_2$  in the copolymer is very slim  $\Rightarrow (N_2)_1 \approx 1.0$  and  $(N_2)_x = 0$  for  $x > 1$ .  
 Longer stretches of monomers  $M_1$  will be generated which can be interrupted by a monomer  $M_2$ .



1.4. The Q-e scheme quantifies the effects that stabilization of a monomer or radical by resonance or the polarity of a monomer have on the copolymerization. (4)

$$k_{12} = P_1 Q_2 \exp(-e_1 e_2) \quad (1)$$

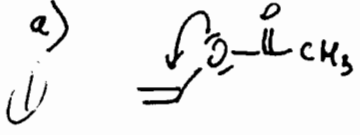
$P_1$  accounts for the stabilization of the radical  $M_1\cdot$  by resonance.

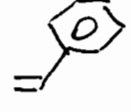
$Q_2$  ————— Monomer  $M_2$  —————.


$e_1$  accounts for the polarity of the radical  $M_1\cdot$ . (same as  $M_2$ )

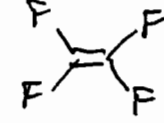
$e_2$  ————— Monomer  $M_2$  (same as  $M_2\cdot$ )

1.5. An efficient copolymerization occurs if both monomers are stabilized by resonance (large  $\rho$  values) or both monomers are not stabilized by resonance (small  $\rho$  values). (3)

a)  not stabilized by resonance:  $\rho$  is small  
~~poor~~ <sup>good</sup> candidate for copolymerization:  $e$  is negative.

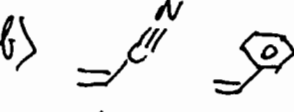
①  styrene is stabilized by resonance:  $\rho$  is large (not good)

①  maleic anhydride is stabilized by resonance:  $\rho$  is large (not good)

①  vinyl tetrafluoride is not stabilized by resonance:  $\rho$  is small  
 $\Rightarrow$  good candidate for copolymerization

The double bond of vinyl tetrafluoride is electron poor:  $e$  is positive

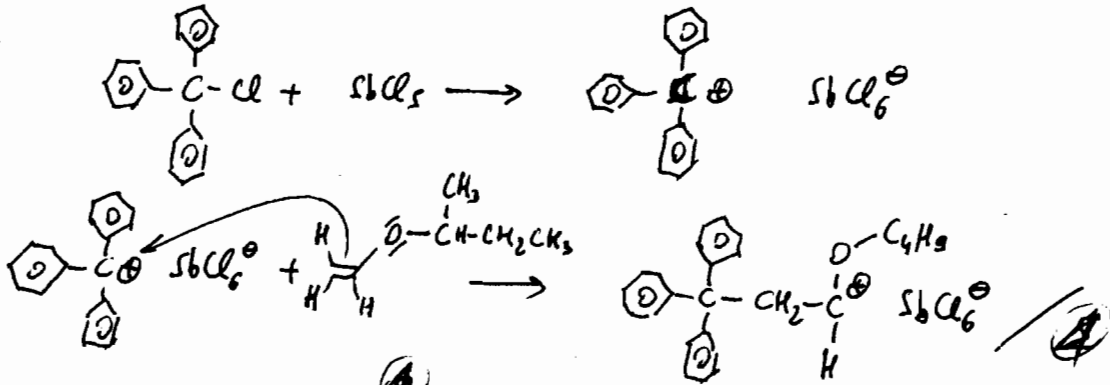
Certainly the copolymerization of vinyl acetate and vinyl tetrafluoride is efficient (small  $\rho$  values) and alternating ( $e$ -values of opposite signs). (1)

b)  Both acrylonitrile and styrene are stabilized by resonance  
 $\Rightarrow$  efficient copolymerization.

The double bond of acrylonitrile is electron poor (positive  $e$  value). The double bond of styrene is electron rich (negative  $e$ -value)  $\Rightarrow$  The polymerization is alternating. (1)

Q#2:

2.1.



The polymerization is cationic. The trityl cation is very stable but less so than the iBVE propagating cation. Furthermore the double bond of iBVE is electron rich, more so than the double bond of styrene. As a result, the initiation of styrene by the trityl cation is much less likely than for iBVE. (1)

2.2.

$$X_n = \frac{k_p^+ [M^+] [M]}{(k_t + k_{tr}) [M^+] + k_{tr} [M] [M]} = \frac{k_p^+ [M]}{(k_t + k_{tr}) + k_{tr} [M]}$$

[M]	X <sub>n</sub>
0.5M	37
2.0M	37

(2)

2.3 Initiation with naphthalene and sodium produces a monodisperse polystyrene with a number average degree of polymerization:  $X_n = \frac{2 \times [M]}{[I]} = 2 \times \frac{10^{-1} M}{10^{-5} M} = 20,000$   
 Since  $M_{sty} = 104 \text{ g/mol}$ ,  $M_n = 20,000 \times 104 = 2,080,000 = 2,080 \text{ kg/mol}$ .

$$M_n = 2080 \text{ kg/mol}$$

(5)