

**PS #8**

**64. Solution:**

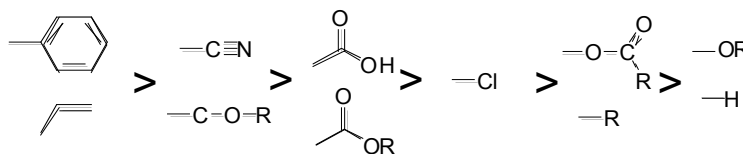
Based on styrene, the reactivity sequence of monomers is:

Methacrylonitrile > Acrylonitrile > 2-Vinyl pyridine > **Styrene** > Vinylidene chloride  
 > 1,2-bichloropropene-2 > Vinyl chloride > Allyl acetate

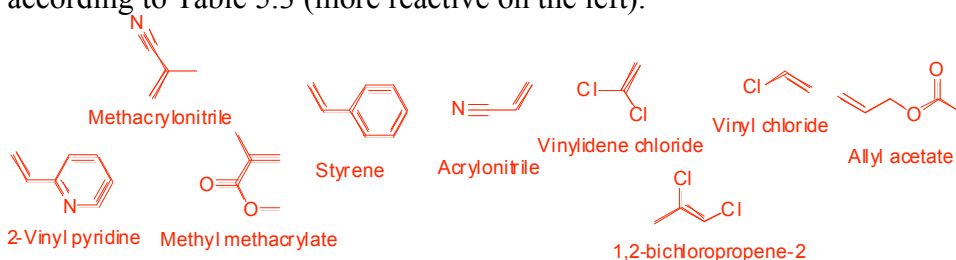
For methyl methacrylate:

2-Vinyl pyridine > Methacrylonitrile > **Methyl methacrylate** > Acrylonitrile > Vinylidene chloride  
 > 1,2-bichloropropene-2 > Vinyl chloride > Allyl acetate

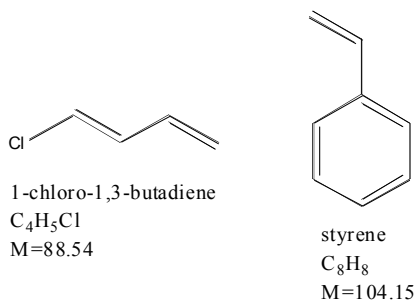
Table 5.3



For those monomers in this problem, generally we can arrange in the following way according to Table 5.3 (more reactive on the left).



**65. Solution:**



$M_1$  is styrene,  $M_2$  is 1-Chloro-1,3-butadiene.

Assume we have **1g** copolymer. Each  $M_2$  unit has one Cl atom, so the total mass of  $M_2$  in the copolymer is:  $m_2=1*(Cl\ wt\%)*(88.54/35.45)$

The total mass of  $M_1$  in the copolymer is  $(1-m_2)$ ;

$$F_1=(m_1/104.15)/\{(m_1/104.15)+m_2/88.54)\}$$

$f_1$	C wt% in polymer	Cl wt% in polymer	$m_2$	$m_1$	$F_1$
0.892	81.8	10.88	0.2717	0.7283	0.695
0.649	71.34	20.14	0.503	0.497	0.456
0.324	64.95	27.92	0.6973	0.3027	0.27
0.153	58.69	34.79	0.8689	0.1311	0.114

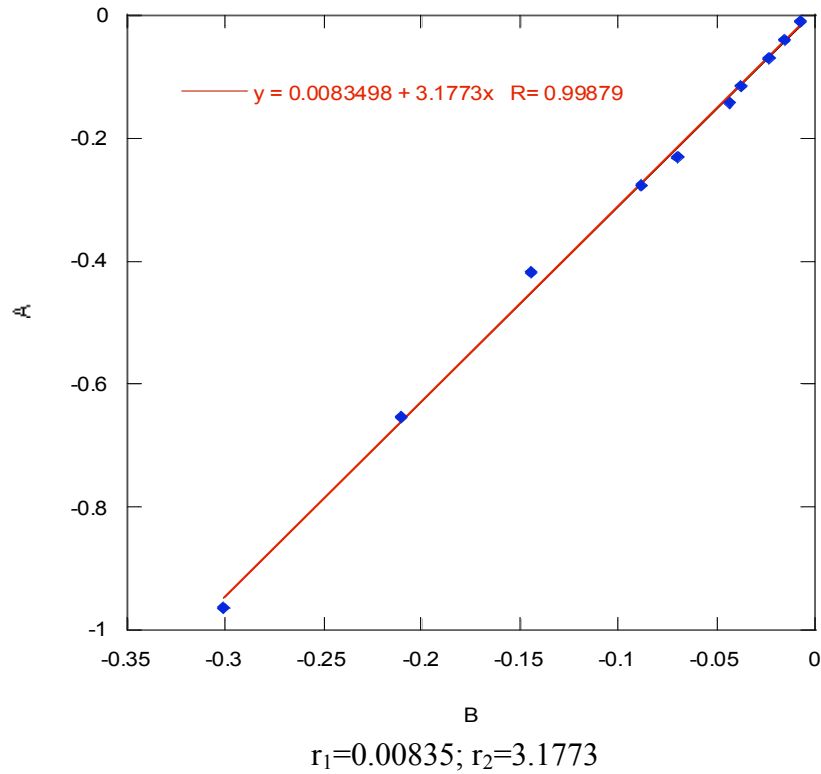
**66. Solution:**

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

$$\frac{f_1(1-2F_1)}{F_1(1-f_1)} = r_1 \left( \frac{f_1^2 (F_1 - 1)}{F_1 (1-f_1)^2} \right) + r_2$$

$$A=r_1 B+r_2$$

$f_1$	$F_1$	<b>A</b>	<b>B</b>
0.083	0.52	-0.00696	-0.00756
0.126	0.58	-0.03977	-0.01505
0.159	0.61	-0.06819	-0.02285
0.206	0.64	-0.11351	-0.03786
0.225	0.66	-0.14076	-0.04342
0.288	0.7	-0.23114	-0.07012
0.318	0.71	-0.27583	-0.0888
0.391	0.74	-0.41646	-0.14483
0.471	0.79	-0.65368	-0.21073
0.548	0.83	-0.96407	-0.30106



The data fit very well with the equation

**67. Solution:**

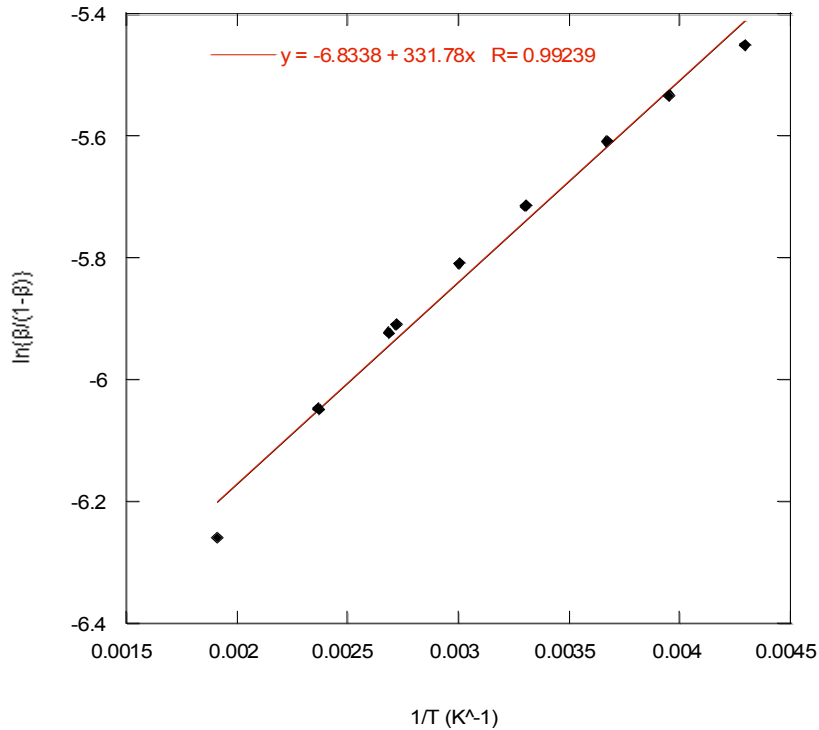
Eqn 5.7.4:

$$k_i/k_s = \text{iso dyads/syndio dyads} = A_i/A_e \cdot \exp\{-(E_i^* - E_s^*)/RT\}$$

$$\ln(k_i/k_s) = -(E_i^* - E_s^*)/RT + C$$

\* $\beta$  is the probability of an isotactic placement in the products, so  $(1-\beta)$  is the probability of a syndiotactic placement.

$$k_i/k_s = \text{iso dyads/syndio dyads} = \beta/(1-\beta)$$



$$-(E_i^* - E_s^*)/R = 331.78$$

$$(E_i^* - E_s^*) = -2.76 \text{ (kJ/mol)}$$

**68. Solution:**

(5.9.1)

$$N_{ni} = N_{ns}$$

$$\sum N_{ni} = \sum N_{ns}$$

$$p_h = \frac{v_h}{v_h + v_i + v_s} = \frac{\sum N_{ni} + \sum N_{ns}}{\sum N_{ni} + \sum N_{ns} + \sum N_{ni}(n_i - 1) + \sum N_{ns}(n_s - 1)}$$

$$= \frac{(\sum N_{ni} + \sum N_{ns})}{\{\sum N_{ni} + \sum N_{ns} + \sum N_{ni}(n_i - 1) + \sum N_{ns}(n_s - 1)\}} * \frac{1/\sum N_{ns}}{1/\sum N_{ns}}$$

$$p_h = \frac{2}{n_i + n_s}$$

From the expression,  $\bar{n}_s$  should be equally important as  $\bar{n}_i$ . The proposition is wrong. The sequence DL is an "r", it has a 50:50 chance to be rm (hetero) or rr (syndio). The DD is an

"m", half way to hetero mr or iso mm

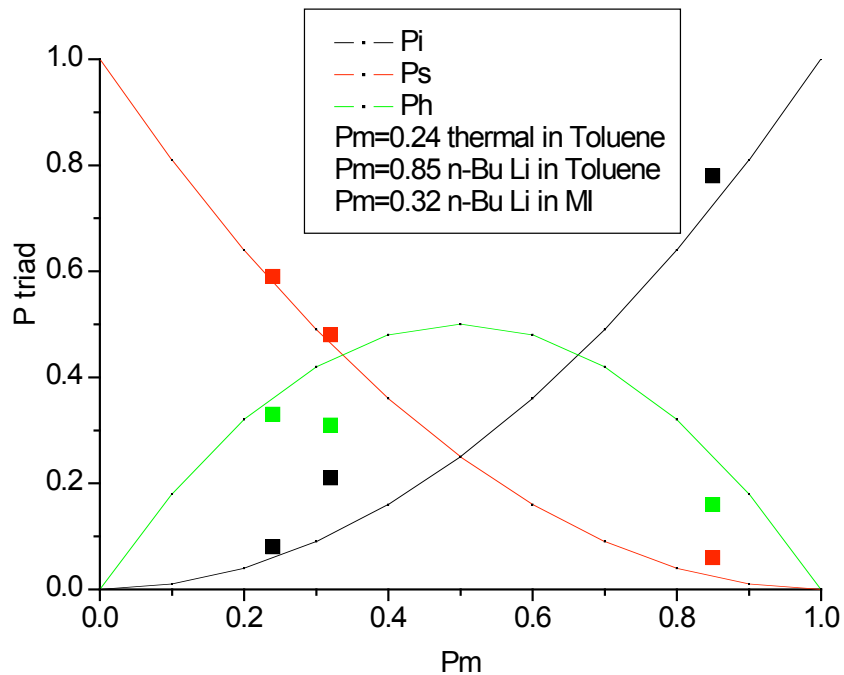
69.

**Solution:**

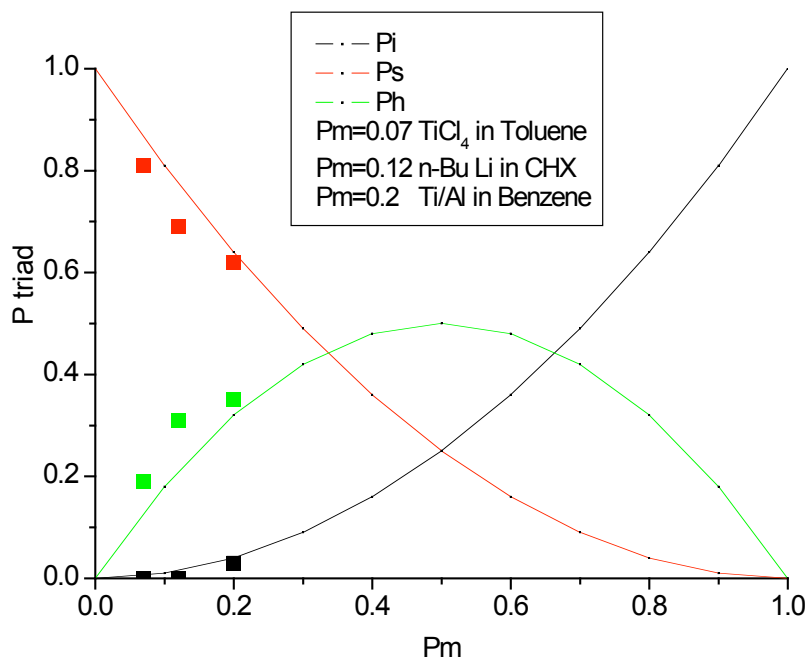
Catalyst	Solvent	T, °C	Fraction of polymer		
			Iso	Hetero	Syndio
Methyl methacrylate					
Thermal	Toluene	60	8	33	59
n-Butyl lithium	Toluene	-78	78	16	6
n-Butyl lithium	Methyl isobutyrate	-78	21	31	48
$\alpha$ -Methyl styrene					
TiCl <sub>4</sub>	Toluene	-78	-	19	81
Et <sub>3</sub> Al/TiCl <sub>4</sub>	Benzene	25	3	35	62
n-Butyl lithium	Cyclohexane	4	-	31	69

\*Calculate  $P_{ms}$  separately based on three components in each reaction, and then use the averaged  $P_m$  for each reaction condition to plot point in the following figures.

**For methyl methacrylate:**



For  $\alpha$ -methyl styrene:



From above figures, zero-order Markov statistics apply to all free radical, cationic polymerizations, and also apply to Ziegler-Natta catalyzed systems. However, for anionic reactions, there are bigger deviations, so higher-order Markov statistics may be needed.

70. **Solution:**

Under *chain-end control*, the addition of a monomer is influenced most by the configuration of the previous repeat unit. Under *site control* the ligand set may be chosen to provide a chiral confining environment, which determines the stereochemistry of addition.

Basically, if you have site control, a stereodeflect is immediately "corrected". i.e. DDDDDLDDDDD. In other words, the catalyst knows D from L. This gives mmmrrrrmmm, i.e. r's always occur in pairs. For chain end control, isospecific means "keep adding the same way". It does not prefer D to L. A defect looks like this: DDDDDDLLLLLLL, or mmmmmmmrrmmm, i.e. r's occur singly. This can be seen in the triads.