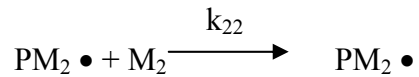
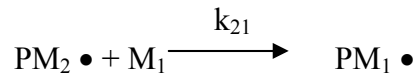
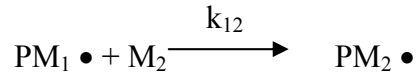
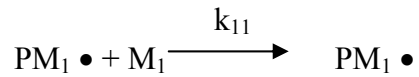


1. Consider the following copolymerization system:



$r_1 = 2.5$ ,  $r_2 = 0.5$  (from literature),  $\text{M}_1 = \text{IB}$ ,  $[\text{IB}]_0 = 27 \text{ wt}\%$ ,  $\text{M}_2 = \text{IP}$ ,  $[\text{IP}]_0 = 3 \text{ wt}\%$ ,  $d = 1 \text{ g/cm}^3$ , Conversion: IB = 80%; IP = 65%.

- What will be the copolymer composition in a batch reactor?
- What will be the copolymer composition in a continuous stirred tank reactor?

2. Consider the same copolymerization system. Four experiments were run to low conversion; Table 1 lists the results.

Table 1.

Run	$[\text{IB}]_0$ mol/L	$[\text{IP}]_0$ mol/L	IP mol % in feed	$[\text{IB}]_t$ mol/L	$[\text{IP}]_t$ mol/L	[IP] mol% in product
1	1.80	0.20	10.00	1.46	0.16	
2	1.75	0.45	20.25	1.58	0.40	
3	1.45	0.55	27.50	1.30	0.49	
4	0.97	0.96	49.80	0.92	0.90	

Calculate  $r_1$  and  $r_2$  using the following methods:

- Mayo-Lewis
- Fineman-Ross
- Kelen-Tüdös

Compare the values with those calculated using:

- The Q-e scheme
- Mayr's linear free energy correlation

## Solution

1. Hint: write the rate equations and simplify

2. Data evaluation

### *Method a: M-L (Mayo-Lewis)*

$$r_2 = \frac{[M_1]}{[M_2]} \left[ \frac{d[M_2]}{d[M_1]} \left\{ 1 + \frac{r_1[M_1]_t}{[M_2]_t} \right\} - 1 \right]$$

$$X = \frac{[M_1]_t}{[M_2]_t}; Y = \frac{d[M_1]_t}{d[M_2]_t}$$

$$r_2 = X/[1/Y\{1+r_1X\}-1]$$

Run	X	Y
1		
2		
3		
4		

### *Method b: F-R (Fineman-Ross)*

$$X = \frac{[M_1]_t}{[M_2]_t}; Y = \frac{d[M_1]_t}{d[M_2]_t}; G = \frac{X(Y-1)}{Y}; F = \frac{X^2}{Y}$$

$$G = r_1F - r_2$$

$$G/F = -r_2(1/F) + r_1$$

Run	G	F	G/F	1/F

**Method c: K-T (Kelen-Tüdös)**

$$\eta = \left[ r_1 + \frac{r_2}{\alpha} \right] \xi - \frac{r_2}{\alpha}$$

$$\eta = \frac{G}{\alpha + F}; \xi = \frac{F}{\alpha + F}; \alpha = \sqrt{(F_{\min} * F_{\max})}$$

Run	$\eta$	$\xi$

**d. Q – e scheme**

$$k_{ij} = P_i Q_j \exp(-e_i e_j)$$

$$r_1 = (Q_1/Q_2) \exp(-e_1 (e_1 - e_2))$$

$$r_2 = (Q_2/Q_1) \exp(-e_2 (e_2 - e_1))$$

Monomer	Q	e
IB	1.70	-0.50 (?? Odian??)
IP	1.99	-0.55

**e. Mayr's linear free energy correlation**

$$\log k = s(N+E)$$

	Isobutyl Cation (IB <sup>+</sup> )	Isoprenyl Cation (IP <sup>+</sup> )
E	7.5	8.1
	IB (Monomer 1)	IP (Monomer 2)
N	1.07	1.12
s	1.02	1.00

Rate Constants, L mol<sup>-1</sup> s<sup>-1</sup>

$k_{11}$

$k_{12}$

$k_{22}$

$k_{21}$

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Reactivity Ratios

$r_1 (=k_{11}/k_{12})$

$r_2 (=k_{22}/k_{21})$

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