

Copolymer composition drift

One monomer is consumed preferentially, causing f_A to change as the overall monomer conversion increases

The change in f_A gives rise to a variation in F_A with conversion

Copolymer composition drift leads to copolymers with significantly different compositions

$r_A > 1, r_B < 1$ monomer A \downarrow f_A (F_A) \downarrow eventually homopolymer B

$r_A < 1, r_B < 1$ ($k_{AA} < k_{AB}, k_{BB} < k_{BA}$)

$f_A \rightarrow 0$ or 1 , eventually homopolymer formation

$r_A > 1, r_B > 1$ ($k_{AA} > k_{AB}, k_{BB} > k_{BA}$)

$f_A \rightarrow (f_A)_{\text{azeo}} = (F_A)_{\text{azeo}}$

To avoid copolymer composition drift

- Terminate copolymerization reaction at low monomer conversion ($\leq 5\%$)
- Add the preferentially-consumed monomer to maintain f_A constant

Evaluation of monomer reactivity ratios

$$\frac{f_A(1-2F_A)}{F_A(1-f_A)} = r_B + r_A \frac{f_A^2(F_A-1)}{F_A(1-f_A)^2}$$

For each experimental f_A , F_A pair, the left-hand side of the equation is plotted against the coefficient of r_A

The slope of the straight line gives r_A and the intercept r_B

Free-Radical Copolymerization and the Q-e Scheme

Two main categories

- (1) $r_A > 1$, $r_B < 1$ (or $r_A < 1$, $r_B > 1$) copolymerization
 - (2) $r_A < 1$, $r_B < 1$ azeotropic copolymerization
- The greater is the stability of the polymer radical, the more readily it is formed by reaction of the monomer
 - Reactive monomers have substituent groups which stabilize the polymeric radical by delocalization of the unpaired electron
 - A monomer of high reactivity yields a polymeric radical of low reactivity

TABLE 2.10 Some typical values of reactivity ratios for free-radical copolymerization at 60°C

Monomer A	Monomer B	r_A	r_B	$r_A r_B$
Styrene	Butadiene	0.78	1.39	1.08
Styrene	Methyl methacrylate	0.52	0.46	0.24
Styrene	Methyl acrylate	0.75	0.18	0.14
Styrene	Acrylonitrile	0.40	0.04	0.02
Styrene	Maleic anhydride	0.02	0	0
Styrene	Vinyl chloride	17	0.02	0.34
Vinyl acetate	Vinyl chloride	0.23	1.68	0.39
Vinyl acetate	Acrylonitrile	0.06	4.05	0.24
Vinyl acetate	Styrene	0.01	55	0.55
Methyl methacrylate	Methyl acrylate	1.69	0.34	0.57
Methyl methacrylate	n-Butyl acrylate	1.8	0.37	0.67
Methyl methacrylate	Acrylonitrile	1.20	0.15	0.18
Methyl methacrylate	Vinyl acetate	20	0.015	0.30
<i>trans</i> -Stilbene	Maleic anhydride	0.03	0.03	0.001

- Resonance stabilization of common substituent group
 $-\text{C}_6\text{H}_5 > -\text{CH}=\text{CH}_2 > -\text{CO}-\text{R} > -\text{C}\equiv\text{N} >$
 $-\text{COOR} > -\text{Cl} > -\text{R} > -\text{OCO}-\text{R} > -\text{OR}$

- Vinyl monomers ($\text{CH}_2=\text{CHX}$) tend to be of lower reactivity than the corresponding 1,1-disubstituted monomers ($\text{CH}_2=\text{CXY}$)
 - Additional resonance effects
 - Steric shielding effects
 } in $\sim\sim\text{CH}_2-\text{C}^\bullet\text{XY}$
- 1,2-disubstituted monomers ($\text{CHX}=\text{CHY}$) are of low reactivity due to steric hindrance of the propagation reaction by the 2-substituent in the monomer
 - Difficult to be homopolymerized but can be copolymerized (reduced steric hindrance in the cross-propagation reaction)

In $r_A > 1, r_B < 1$ (or $r_A < 1, r_B > 1$) copolymerization

- Difference between the reactivities of the monomers \uparrow
 r_A/r_B (or r_B/r_A) \uparrow
 Cf., copolymerization of VAc with VC, AN, and St
- Difference between the electron densities of $\text{C}=\text{C}$ (polarities) \uparrow
 alternating tendency \uparrow (i.e., $r_A r_B \downarrow$)
 Cf., copolymerization of St with MMA, AN, and MAn

Q-e Scheme

Rate constant k_{pm} for reaction of a polymeric radical (p) with a monomer (m)

$$k_{pm} = P_p Q_m \exp(-e_p e_m)$$

where

P_p and Q_m : measures of reactivities of polymeric radical and monomer, respectively.

e_p and Q_m : measures of “electrostatic charge” associated with polymeric radical and monomer, respectively.

Assuming $e_A = e_{pA} = e_{mA}$ and $e_B = e_{pB} = e_{mB}$,

$$r_A = \frac{p_{pA} Q_A \exp(-e_A e_A)}{p_{pA} Q_B \exp(-e_B e_A)} = \frac{Q_A}{Q_B} \exp(-e_A (e_A - e_B))$$

$$r_B = \frac{Q_B}{Q_A} \exp(-e_B (e_B - e_A))$$

Alternating tendency

$$r_A r_B = \exp [-(e_A - e_B)^2]$$

$$e_A - e_B \uparrow \quad r_A r_B \downarrow$$

$$e_A = e_B \Rightarrow r_A r_B = 1 \text{ (ideal copolymerization)}$$

TABLE 1 Values of Q and e for some important monomers

Monomer	Q	e
Isoprene	3.33	-1.22
Butadiene	2.39	-1.05
Styrene	1.00	-0.80
Methyl methacrylate	0.74	0.40
Acrylonitrile	0.60	1.20
Ethyl acrylate	0.52	0.22
Maleic anhydride	0.23	2.25
Vinyl chloride	0.044	0.20
Vinyl acetate	0.026	-0.22

Reference styrene: $Q = 1.00$, $e = -0.80$

Q , e values for other monomers

Copolymerization experiments with styrene or from the equations discussed above

Monomer reactivity \uparrow $Q \uparrow$

Electron deficiency of $C = C \uparrow$ $e \uparrow$

(Negative value of e indicates that $C = C$ bond is electron rich)