Chain Copolymerization

Tailoring polymer properties

Polystyrene	Brittle, low impact strength, low solvent resistance
Copolymer of styrene and acrylonitrile	Increased impact strength and solvent resistance • SAN: typically 10-40 % acrylonitrile
Copolymer of styrene and butadiene	Elastomeric properties • Low styrene contents (~ 25 %): SBR rubber (Buna) • High styrene contents (50 -75 %): latex paints
Copolymer of styrene, acrylonitrile and butadiene	Elastomeric properties, increased impact strength and solvent resistance • ABS polymers

Is this trivial? Things to think about:

Step copolymerization

- Polymerization is usually carried out to 100 % conversion

  Copolymer composition = composition of the monomer feed

- Most step polymerizations are equilibrium reactions, i.e. the initially obtained copolymer composition is rapidly changed by equilibration („chain scrambling")

  „random" copolymer, i.e. purely statistical comonomer sequence

The situation, however, can be different for **chain copolymerization**

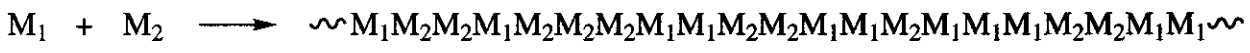
- Copolymer composition and comonomer sequence depend on the relative concentrations of both monomers and their relative reactivities

Copolymer composition, Comonomer sequence } → { Relative monomer concentrations, Relative reactivities

This implies that analysis of copolymer composition can provide information about monomer reactivity

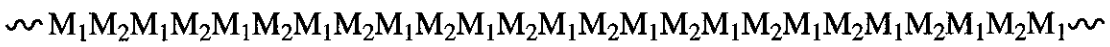
Types of Copolymers

Statistical copolymers

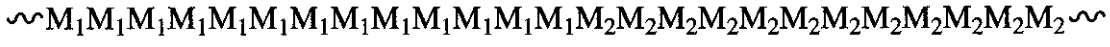


Random copolymers are statistical copolymers formed via Bernoullian (zero-order Markov) processes

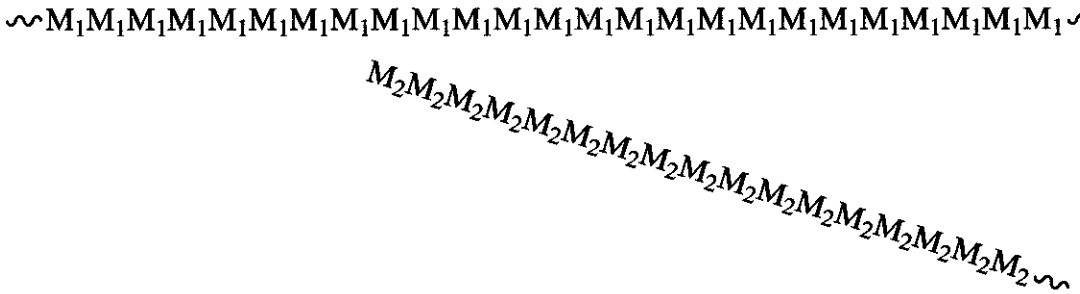
Alternating copolymers



Block copolymers



Graft copolymers



Copolymer Composition

The instantaneous copolymer composition, i.e. the composition of the copolymer formed at very low conversions (< 5%) is usually different from the composition of the comonomer feed from which the copolymer is produced, because different monomers have different tendencies to undergo copolymerization

First-order Markov / terminal model:

- The reactivity of the propagating chain (radical, cation, anion) is dependent only on the identity of the monomer unit at the growing end

Four possible propagation reactions:

$$M_1^* + M_1 \xrightarrow{k_{11}} M_1^*$$ Homopropagation/self-propagation

$$M_1^* + M_2 \xrightarrow{k_{12}} M_2^*$$ Cross-propagation/crossover reaction

$$M_2^* + M_1 \xrightarrow{k_{21}} M_1^*$$ * = radical, cation, anion

$$M_2^* + M_2 \xrightarrow{k_{22}} M_2^*$$

- The rates of disappearance of the 2 monomers = their rates of entry into the copolymer:

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]$$

- $d[M_1]/d[M_2]$ is the ratio of the rates at which the monomers enter the copolymer, that is the copolymer composition:

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]}$$

- Steady-state assumption: the concentrations of M_1^* and M_2^* remain constant throughout the polymerization. This implies that their rates of interconversion are equal:

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2]$$

as a result:

$$\frac{d[M_1]}{d[M_2]} = \frac{\frac{k_{11}k_{21}[M_2^*][M_1]^2}{k_{12}[M_2]} + k_{21}[M_2^*][M_1]}{k_{22}[M_2^*][M_2] + k_{21}[M_2^*][M_1]}$$

Defining monomer reactivity ratios: $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, this can be rearranged to:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])}$$

the copolymerization equation / the copolymer composition equation

$r_1 > 1$; homopolymerization is favored
$0 < r_1 < 1$; copolymerization is preferred

- The copolymerization equation can also be expressed in mole fractions:

f_1 and f_2 are the mole fractions of M_1 and M_2 in the feed
F_1 and F_2 are the mole fractions of M_1 and M_2 in the polymer

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]}$$

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]}$$

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

$$\frac{F_1}{F_2} = \frac{f_1(r_1 f_1 + f_2)}{f_2(r_2 f_2 + f_1)}$$

Applicability of the Copolymerization Equation

- The copolymerization equation is equally applicable to radical, cationic and anionic chain copolymerization, although the r_1 and r_2 values for any particular comonomer pair can be different depending on the mode of initiation
- Monomer reactivity ratios are independent of differences in rates of initiation and termination and the presence or absence of inhibitors or chain transfer agents
- The particular initiation system used in radical polymerization has no effect on copolymer composition

- Solvent effects can be found in radical copolymerizations and are usually significant in ionic copolymerizations. Ionic copolymerizations are also sensitive to the nature of the counterion
- The monomer reactivity ratios and copolymer compositions in living polymerizations are generally the same as those in the corresponding non-living systems. Exception: living systems which involve a recycling equilibrium (activation and deactivation) between active and dormant species (e.g. ATRP, NMP, RAFT as well as ionic systems with an activation deactivation equilibrium). In these systems, there are 2 separate activation-deactivation equilibria for each of the two propagating species (M_1^* and M_2^*). Deviations from the copolymer composition occur if:
  - (i) The propagating species have different activation and/or deactivation rate constants
  - (ii) The homopropagation rate constant for each propagating species is different from its cross-propagation rate constant (i.e. $r_1 \neq r_2 \neq 1$)

    One monomer is consumed faster than the other and copolymer composition changes with conversion differently from the nonliving system

What's next ?

- Types of copolymerization behaviour
- Variation of copolymer composition with conversion
- Evaluation of monomer reactivity ratios

Types of Copolymerization Behavior

Ideal copolymerization: $r_1 r_2 = 1$

Ideal copolymerization occurs when the two types of propagating species M_1^* and M_2^* exhibit the same relative reactivities for monomers M_1 and M_2. The relative rates of incorporation of the two monomers into the copolymer are independent of the identity of the unit at the end of the propagating chain.

$$\frac{k_{22}}{k_{21}} = \frac{k_{12}}{k_{11}} \quad \text{or} \quad r_2 = \frac{1}{r_1}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \Longrightarrow \frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1]}{[M_2]}$$

$$\frac{F_1}{F_2} = \frac{f_1(r_1 f_1 + f_2)}{f_2(r_2 f_2 + f_1)} \Longrightarrow F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2}$$

Most ionic polymerizations (both anionic and cationic) are ideal copolymerizations

- When $r_1 = r_2 = 1$, the 2 monomers show equal reactivity toward both propagating species. The copolymer composition is the same as the comonomer feed with a random placement of the two monomers; random or Bernoullian behavior
- For $r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$, one of the monomers will be more reactive than the other towards propagation and the copolymer will contain a larger proportion of the more reactive monomer in random placement

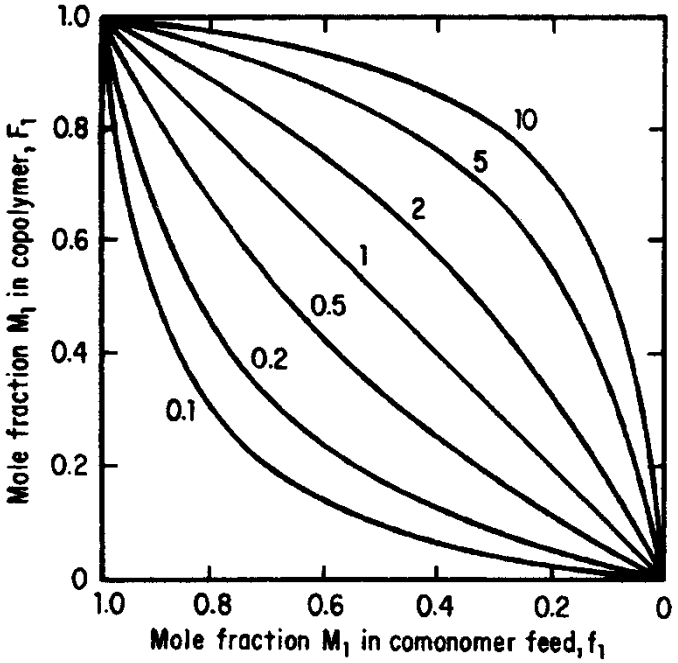


Fig. 6-1 Dependence of the instantaneous copolymer composition F_1 on the initial comonomer feed composition f_1 for the indicated values of r_1, where $r_1 r_2 = 1$. After Walling [1957] (by permission of Wiley, New York) from plot in Mayo and Walling [1950] (by permission of American Chemical Society, Washington, DC).

Extreme ideal behavior; large difference in r_1 and r_2 (e.g.: 10 and 1)
Moderate ideal behavior; r_1 and r_2 are not too different (e.g.: 0.5 and 2)

Alternating copolymerization: $r_1 r_2 = 0$ ($r_1, r_2 < 1$)

- Extreme alternating behavior: r_1 and r_2 are zero and $\frac{d[M_1]}{d[M_2]} = 1$

$$F_1 = 0.5$$

The copolymer has a perfect alternating structure irrespective of the comonomer feed composition

- Moderate alternating behavior occurs when:
  - (i) both r_1 and r_2 are small ($r_1 r_2$ very small, close to 0)
  - (ii) one r value is small and the other is zero ($r_1 r_2 = 0$)

The copolymer tends towards alternation but is not perfectly alternating

The behavior of most comonomer systems lies between the two extremes of ideal and alternating copolymerization

Block copolymerization: $r_1 > 1$, $r_2 > 1$

Variation of Copolymer Composition with Conversion

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])}$$

$$\frac{F_1}{F_2} = \frac{f_1(r_1 f_1 + f_2)}{f_2(r_2 f_2 + f_1)}$$

Instantaneous copolymer composition: the composition of the copolymer formed at a particular feed composition at very low conversion (< 5%) such that the composition of the comonomer feed is relatively unchanged from its initial value

In reality, however, the feed composition will change with conversion, which also leads to a change in the copolymer composition

Consider a system consisting of M moles M_1 and M_2, which produces a copolymer richer in M_1 than M_2, i.e. $F_1 > f_1$:

- When dM moles of monomer has polymerized,
  - the polymer will contain $F_1 dM$ moles M_1, and
  - the feed will contain $(M - dM)(f_1 - df_1)$ moles M_1

- Materials balance for M_1: $Mf_1 - (M - dM)(f_1 - df_1) = F_1 dM$, which can be rearranged to:

$$\int_{M_0}^{M} \frac{dM}{M} = \ln\frac{M}{M_0} = \int_{(f_1)_0}^{f_1} \frac{df_1}{(F_1 - f_1)}$$

Integration yields:

$$1 - \frac{M}{M_0} = 1 - \left[\frac{f_1}{(f_1)_0}\right]^{\alpha}\left[\frac{f_2}{(f_2)_0}\right]^{\beta}\left[\frac{(f_1)_0 - \delta}{f_1 - \delta}\right]^{\gamma}$$

$$\alpha = \frac{r_2}{(1 - r_2)} \qquad \beta = \frac{r_1}{(1 - r_1)}$$

$$\gamma = \frac{(1 - r_1 r_2)}{(1 - r_1)(1 - r_2)} \qquad \delta = \frac{(1 - r_2)}{(2 - r_1 - r_2)}$$

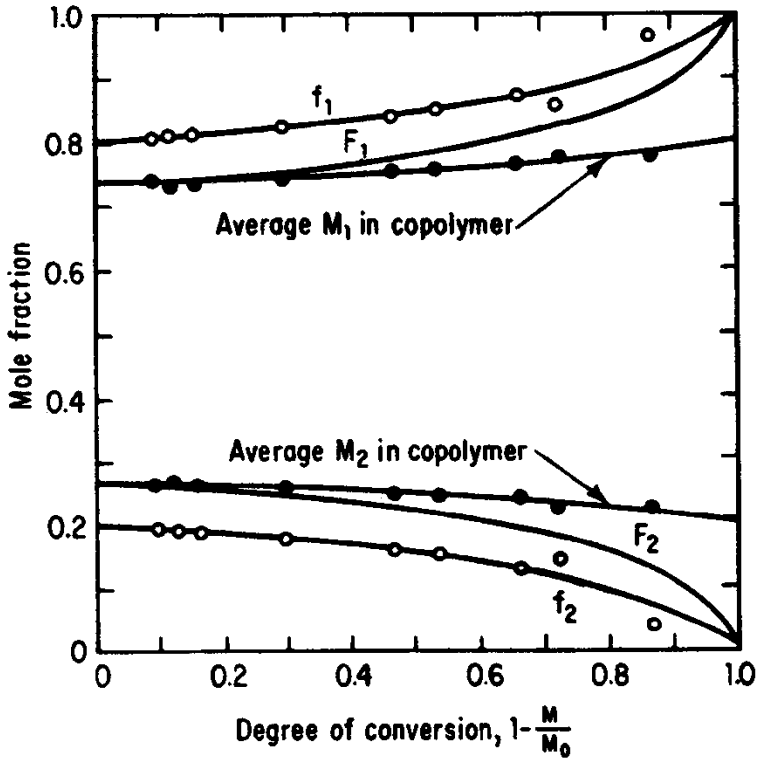


Fig. 6-3 Variations in feed and copolymer compositions with conversion for styrene (M_1)-methyl methacrylate (M_2) with $(f_1)_0 = 0.80$, $(f_2)_0 = 0.20$ and $r_1 = 0.53$, $r_2 = 0.56$. After Dionisio and O'Driscoll [1979] (by permission of Wiley, New York).

Evaluation of Monomer Reactivitiy Ratios

- Experimental determination of the copolymer composition for several different comonomer feed compositions
- Copolymerizations are carried out to low degrees of polymerization (< 5%)

Mayo-Lewis plot

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])}$$ can be rearranged to: $$r_2 = \frac{[M_1]}{[M_2]}\left[\frac{d[M_2]}{d[M_1]}\left\{1 + \frac{r_1[M_1]}{[M_2]}\right\} - 1\right]$$

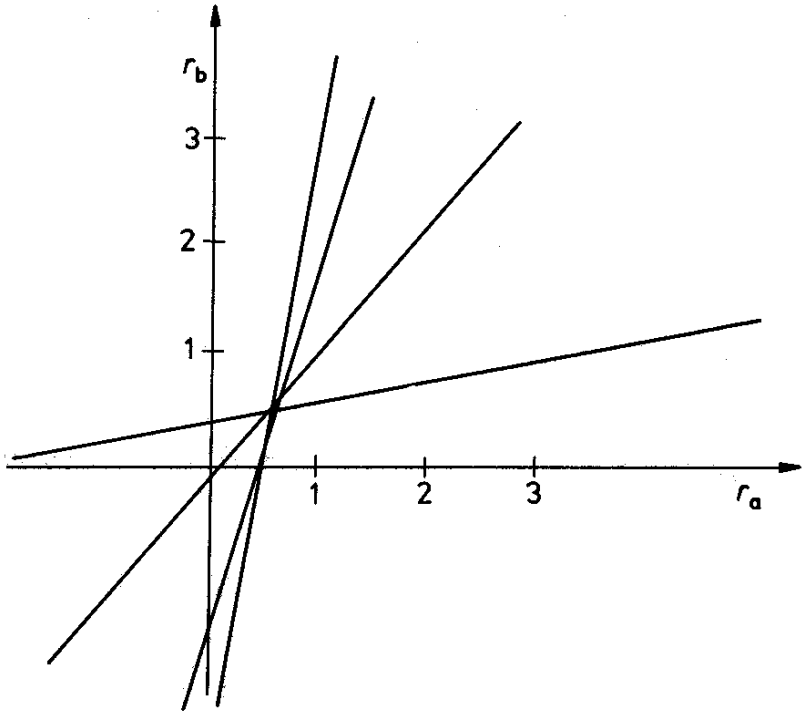


Fig. 4.8. Mayo-Lewis plot for the system styrene-MMA; (styrene: $r_a = 0.52$; methyl methacrylate: $r_b = 0.48$)

Fineman-Ross plot

$$r_2 = \frac{[M_1]}{[M_2]}\left[\frac{d[M_2]}{d[M_1]}\left\{1 + \frac{r_1[M_1]}{[M_2]}\right\} - 1\right]$$ can be rearranged to: $$G = r_1 F - r_2$$

With: $G = [X(Y-1)]Y$

$F = X^2/Y$

$X = [M_1]/[M_2]$

$Y = d[M_1]d[M_2]$

G versus F yields a straight line with slope r_1 and intercept r_2

Fineman-Ross plot

$$\frac{F_1}{F_2} = \frac{f_1(r_1 f_1 + f_2)}{f_2(r_2 f_2 + f_1)}$$

rearrange

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

Table 5.5 Values of F_1 as a Function for f_1 for the Methyl Acrylate (M_1)–Vinyl Chloride (M_2) System

f_1	F_1	f_1	F_1
0.075	0.441	0.421	0.864
0.154	0.699	0.521	0.900
0.237	0.753	0.744	0.968
0.326	0.828	0.867	0.983

Note: These data are also plotted in Figure 5.4.

Source: Data from Chapin, E.L., Ham, G., and Fordyce, R., *J. Am. Chem. Soc.*, 70, 538, 1948.

$f_1(1-2F_1)/F_1(1-f_1)$	0.0217	−0.1036	−0.2087	−0.3832	−0.6127	−0.9668	−2.8102	−6.4061
$f_1^2(F_1-1)/F_1(1-f_1)^2$	−0.0083	−0.0143	−0.0316	−0.0486	−0.0832	−0.1315	−0.2792	−0.7349

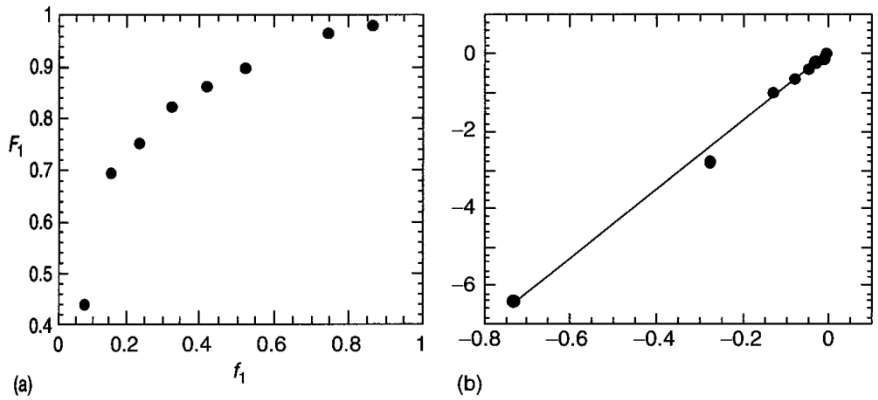


Figure 5.4 (a) Mole fraction of methyl acrylate in copolymers with vinyl chloride as a function of feedstock composition, and (b) Finemann–Ross plot to extract reactivity ratios, as described in Example 5.4.

Summary: Ionic Versus Radical Copolymerization

- Ionic copolymerizations are much more selective:
  - Cationic copolymerization is limited to monomers with electron donating substituents
  - Anionic copolymerization is limited to monomers with electron withdrawing substituents
- For comonomer pairs that undergo ionic copolymerization, the general tendency is towards the ideal type of behaviour (i.e. $r_1 r_2 \approx 1$)
- There is a lack of any tendency towards alternation
- Quite a few ionic copolymerizations proceed with values for $r_1 r_2$ greater than unity
- The monomer reactivity ratios in ionic copolymerizations are sensitive to changes in the initiator, reaction medium or temperature
- Monomer reactivity ratios in radical copolymerizations are far less sensitive to reaction conditions