

CHEM514

COPOLYMERS AND POLYMER BLENDS

Multicomponent Polymeric Materials

- Copolymers
- Polymer Blends
- Interpenetrating Polymer Networks (IPN's)
- Polymer Composites

Copolymer: two or more polymers are combined to each other by chemical bonds.

Blends: two or more polymers form a physical mixture

Composite: mixture of a polymer(s) and a non polymer component(s).

In a multicomponent material interfaces exist. The nature and extent of bonding between these phases determine the properties of the material such as

- Mechanical strength
- Electrical conductivity
- Diffusion coefficients
- Biomedical compatibility
- Price; an important driving force

Classification

- Copolymers

- **Random** copolymers

- **Alternating** copolymers

- **Block copolymers**: diblock, triblock

- **Graft** Copolymers

Random and alternating copolymers: one phase

Block and Graft copolymers: two phase

Classification

- **Polymer Blends**: no chemical bonding physical interactions
 - Miscible
 - Semi-miscible
 - immiscible
- **Engineering Blends**; melt mixing, reactive blending, solution blending
- **Latex Blends**; two polymer latexes are mixed together (emulsion polymerization)
- **Mechanical Blends**; polymer 1 and monomer 2 are mixed under shear. Polymer degrades producing radicals, anions, cations which initiate polymn of the monomer.

Classification

- IPN's
 - **IPN**; a blend of two cross linked polymers. One cross linked polymer prepared then the other monomer polymerized and crosslinked in the presence of the first one
 - **Semi IPN's**; one cross linked and one uncross linked polymer
 - **Latex IPN's**; blends of two precross linked latexes
 - **Simultaneous IPN'S**; simultaneous polymn and crosslinking of the two monomers

Classification

- Polymer Composites

- **Filled porous systems**: continuous phase is nonpolymer

Ceramic, concrete or wood filled with polymer under pressure then polymerization carried out

- **Reinforced Polymers**: continuous phase is polymer

Inorganic materials are dispersed in the polymer

- **Macroscopic Composites**: both phases are large enough to be visible to naked eye e.g alternate layers of inorganic cloth and plastic

Applications of Copolymerization

- PS and High Impact PS
 - PS: brittle, low impact resistance, low solvents resistance
 - HIPS: PS copolymerized with AN
 - Improved impact resistance
 - Improved solvent resistance
- SAN or nitrile plastics

- SBR rubber
- Styrene copolymerized with 1,3-butadiene
- 25%S +75%BD
 - Automobile tires
 - Hoses
 - Molded goods
 - Shoe soles
 - Electrical insulation
- SBR 50-75% S + 50-25% BD latex paints

SBR blended with SAN

Or

S copolymerized with AN in the presence of PB
=ABS plastics

Used in

- Pipings
- Cars and other vehicles
- Sporting goods so on

Some commercial blends

- PVC/nitrile rubber : permanent plasticization of PVC
- PET/PMMA: electrical and electronic applications, lower cost than PMMA, lower warp and shrink than PET

Copolymer Composition

- Different monomers have different tendencies to undergo copolymerization

Reactivity during homopolymerization

May or may not be

The same in copolymerization

- Copolymer composition usually different than comonomer feed

- Propagation reactions
- Derivation of the Copolymer Composition equation (Copolymerization equation)
- Assumptions:
 - All propagation reactions are irreversible
 - Rate of disappearance of M_1 or M_2 =
Rate of entry of M_1 or M_2 in the copolymer
 - Steady state assumption for propagating species
 - Rate of appearance of M_1^* or M_2^* = Rate of
disappearance of M_1^* or M_2^*

Applicability of Copolymerization equation

- Applicable to radical, cationic or anionic polymerizations
 - Ionic polymerizations more selective than radical polymerization

S	MMA		
r_1	r_2	Mechanism	
0.52	0.46	radical	
10	0.1	cationic	
0.1	6.0	anionic	

Types of Copolymerization Behavior

- Ideal copolymerization

$$r_1 r_2 = 1$$

$$r_2 = 1/r_1$$

Both type of propagating species show the same preference for both monomers

Mostly encountered in ionic polymerizations

- Random (Bernoullian Copolymerization)
A variation of ideal copolymerization

$$r_1 = r_2 = 1$$

Two monomers show equal reactivities toward both monomers

Copolymer composition = comonomer feed

Random order of two monomers along the copolymer chain

- Random (Bernoullian Copolymerization)

A variation of ideal copolymerization

$$r_1 > 1 \text{ and } r_2 < 1$$

$$r_1 < 1 \text{ and } r_2 > 1$$

Copolymer richer in the more reactive monomer

adding one or the other of the two monomers. Under these conditions

$$\frac{k_{22}}{k_{21}} = \frac{k_{12}}{k_{11}} \quad \text{or} \quad r_2 = \frac{1}{r_1} \quad (6-28)$$

and 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 species. For an ideal copolymerization Eq. 6-28 is combined with Eq. 6-12 or 6-15 to yield the copolymerization equation as

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1]}{[M_2]} \quad (6-29a)$$

or

$$F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2} \quad (6-29b)$$

Most ionic copolymerizations (both anionic and cationic) are characterized by the ideal type of behavior.

When $r_1 = r_2 = 1$, the two monomers show equal reactivities toward both propagating species. The copolymer composition is the same as the comonomer feed with a random placement of the two monomers along the copolymer chain. Such behavior is referred to as *random* or *Bernoullian*. For the case where the two monomer reactivity ratios are different, that is, $r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$, one of the monomers is more reactive than the other toward both propagating species. The copolymer will contain a larger proportion of the more reactive monomer in random placement.

Figure 6-1 shows the variation in the copolymer composition as a function of the comonomer feed composition for different values of r_1 {Mayo and Walling, 1950}. The term *ideal*

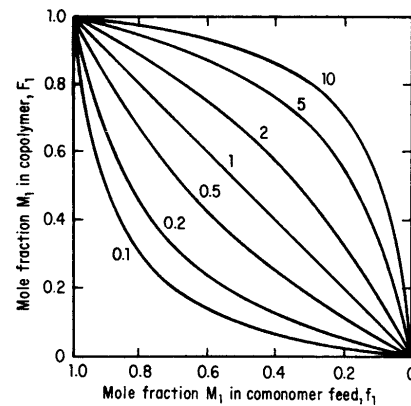


Fig. 6-1 Dependence of the instantaneous copolymer composition F_1 on the initial comonomer feed composition f_1 for the indicated values of r_1 , where $r_1 r_2 = 1$. After Walling [1957] (by permission of Wiley, New York) from plot in Mayo and Walling [1950] (by permission of American Chemical Society,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

- Alternating Copolymerization

$$r_1 = r_2 = 0$$

$$r_1 = 0 \text{ and } r_2 = 0$$

Each propagating species prefers to add the other monomer

$$F_1 = 0.5$$

Copolymerizations lie in between the ideal and the alternating extremes

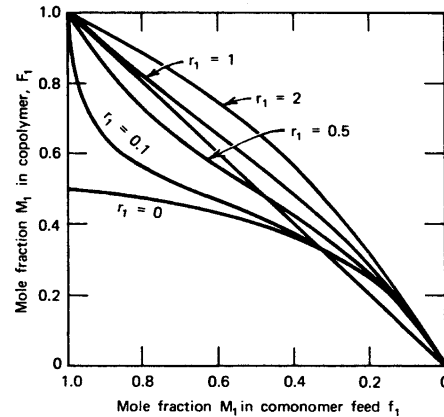


Fig. 6-2 Dependence of the instantaneous copolymer composition F_1 on the initial comonomer feed composition f_1 for the indicated values of r_1 , where r_2 is constant at 0.5. After Walling [1957] (by permission of Wiley, New York) from plot in Mayo and Walling [1950] (by permission of American Chemical Society, Washington, DC).

alternation tendency is measured by the tendency of the product $r_1 r_2$ to approach zero. Of great practical significance is the fact that a larger range of feed compositions will yield copolymers containing sizable amounts of both monomers. However, when $r_1 r_2$ is very small or zero the alternation tendency is too great and the range of copolymer compositions that can be obtained is again limited. In the extreme case where both r_1 and r_2 are zero, only the 1 : 1 alternating copolymer can be produced. This would show in Fig. 6-2 as a horizontal line at $F_1 = 0.5$ (but the line would not touch either the left or right ordinates).

The plots in Fig. 6-2 illustrate an interesting characteristic of copolymerizations with a tendency toward alternation. For values of r_1 and r_2 both less than unity, the F_1/f_1 plots cross the line representing $F_1 = f_1$. At these intersections or *crossover points* the copolymer and feed compositions are the same and copolymerization occurs without a change in the feed composition. Such copolymerizations are termed *azeotropic copolymerizations*. The condition under which azeotropic copolymerization occurs, obtained by combination of Eq. 6-12 with $d[M_1]/d[M_2] = [M_1]/[M_2]$, is

$$\frac{[M_1]}{[M_2]} = \frac{(r_2 - 1)}{(r_1 - 1)} \quad (6-31a)$$

or

$$f_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)} \quad (6-31b)$$

- Consecutive homopolymerization

$$r_1 \gg r_2$$

$$r_1 \gg 1 \text{ and } r_2 \ll 1$$

- Block copolymerization

$$r_1 > 1 \text{ and } r_2 > 1$$

$$r_1 r_2 > 1$$

- Consecutive homopolymerization

$$r_1 \gg 1 \text{ and } r_2 \gg 1$$

Variation of copolymer composition with conversion

- Copolymerization equation valid up to around 5% conversion
- Low conversions
- Comonomer feed drifts from the initial feed with conversion
- Becomes richer in the less reactive monomer and poorer in the more reactive monomer

Integrated Copolymerization Equation

variations in the feed and copolymer compositions with the degree of conversion (defined as $1 - M/M_0$).

Equation 6-33 has been integrated to the useful closed form

$$1 - \frac{M}{M_0} = 1 - \left[\frac{f_1}{(f_1)_0} \right]^\alpha \left[\frac{f_2}{(f_2)_0} \right]^\beta \left[\frac{(f_1)_0 - \delta}{f_1 - \delta} \right]^\gamma \quad (6-34)$$

which relates the degree of conversion to changes in the comonomer feed composition [Dionisio and O'Driscoll, 1979; Meyer and Chan, 1968; Meyer and Lowry, 1965]. The zero subscripts indicate initial quantities and the other symbols are given by

$$\begin{aligned} \alpha &= \frac{r_2}{(1-r_2)} & \beta &= \frac{r_1}{(1-r_1)} \\ \gamma &= \frac{(1-r_1r_2)}{(1-r_1)(1-r_2)} & \delta &= \frac{(1-r_2)}{(2-r_1-r_2)} \end{aligned} \quad (6-35)$$

Equation 6-34 or its equivalent has been used to correlate the drift in the feed and copolymer compositions with conversion for a number of different copolymerization systems [Capek et al., 1983; O'Driscoll et al., 1984; Stejskal et al., 1986; Teramachi et al., 1985]. The larger the difference in the r_1 and r_2 values of a comonomer pair, the greater is the variation in copolymer composition with conversion [Dadmun, 2001].

A few examples will illustrate the utility of Eqs. 6-33 and 6-34. Figure 6-3 shows the behavior observed in the radical copolymerization of styrene and methyl methacrylate. F_1 and F_2 are the instantaneous copolymer compositions for the instantaneous feed

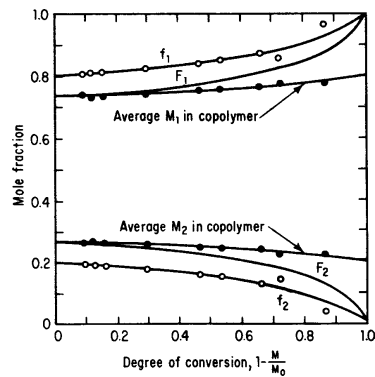


Fig. 6-3 Variations in feed and copolymer compositions with conversion for styrene (M_1)-methyl methacrylate (M_2) with $(f_1)_0 = 0.80$, $(f_2)_0 = 0.20$ and $r_1 = 0.53$, $r_2 = 0.56$. After Dionisio and O'Driscoll [1979] (by permission of Wiley, New York).