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APPENDIX

Copolymerization of the two monomers leads to two types of propagating species one with M_1 at the propagating end and the other with M_2. If it is assumed that the reactivity of the propagating species is dependent only on the monomer unit at the end of the chain. Four propagation reactions are possible.

$$M^*_1 + M_1 \longrightarrow M^*_1 \quad \text{-------------(1)}$$

$$M^*_1 + M_2 \longrightarrow M^*_2 \quad \text{-------------(2)}$$

$$M^*_2 + M_1 \longrightarrow M^*_1 \quad \text{-------------(3)}$$

$$M^*_2 + M_2 \longrightarrow M^*_2 \quad \text{-------------(4)}$$

Monomer M_1 disappears by reaction (1) and (3), while monomer M_2 disappear by reaction (2) and (4). The rate of disappearance of the two monomers, which are synonymous with their rates of entry into the copolymer, are given by

$$-d[M_1]/dt = k_{11}[M^*_1][M_1] + k_{21}[M^*_2][M_1] \quad \text{-------(5)}$$

$$-d[M_2]/dt = k_{12}[M^*_1][M_2] + k_{22}[M^*_2][M_2] \quad \text{-------(6)}$$

Dividing equation (5) and (6) yields the ratio of the rates at which the two monomers enter the copolymer,

$$d[M_1]/d[M_2] = \frac{k_{11}[M^*_1][M_1] + k_{21}[M^*_2][M_1]}{k_{12}[M^*_1][M_2] + k_{22}[M^*_2][M_2]} \quad \text{----(7)}$$

A steady state concentration is assumed for each of the reactive species M^*_1 and M^*_2

$$k_{21}[M^*_2][M_1] = k_{12}[M^*_1][M_2] \quad \text{-------------(8)}$$

equation (7) can be rearranged and combined with equation (8) to yeild

$$d[M_1]/d[M_2] = \frac{[M_1]\,(r_1[M_1] + [M_2])}{[M_2]\,([M_1] + r_2[M_2])} \quad \text{----------(9)}$$

which are defined by, $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$

Equation (9) is known as the copolymerization equation or the copolymer composition equation as being related to the parameters r_1 and r_2 which are termed the monomer reactivity ratios.

The equation (9) can also be expressed in term of mole fraction instead of concentrations, f_1 and f_2 are the mole fraction of monomer M_1 and M_2 in the feed, and F_1 and F_2 are the mole fraction of monomer M_1 and M_2 in the copolymer, then

$$f_1 = 1 - f_2 = [M_1]/([M_1] + [M_2]) \quad \text{-----------(10)}$$

and

$$F_2 = 1 - F_2 = d[M_1]/(d[M_1] + d[M_2]) \quad \text{---------(11)}$$

Combining equation (10) and (11) with equation (9) yields

$$F_1 = (r_1 f_1 + f_1 f_2)/(r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2) \quad \text{---(12)}$$

Equation (12) gives the copolymer composition as the mole fraction of monomer feeding and is often more convenient to use.

Most procedures for evaluating r_1 and r_2 involve the experimental determination of the copolymer compositions for several different comonomer feed compositions. The experimental data can be analysed in several ways. One very useful method involves equation (12) rearranged in the form

$$f_1(1-2F_1)/F_1(1-f_1) = r_2 + [f_1^2(F_1-1)/F_1(1-f_1)^2]r_1 \quad \text{--------}(13)$$

The left side of this equation is plotted against the coefficient of r_1 to yield a straight line with slope r_1 and intercept r_2.

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