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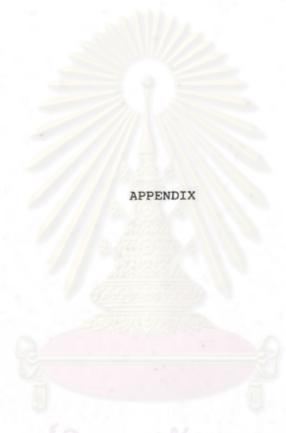
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์ ศูนย์วิทยทรัพยากร จุฬาลงกรณ์มหาวิทยาลัย

Copolymerization of the two monomers leads to two types of propagating species one with M at the propagating end and the other with M. 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.

Monomer M disappears by reaction (1) and (3), while monomer

M 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

$$- d[M]/dt = k [M*][M] + k [M*][M] -----(5)$$

$$- d[M]/dt = k [M*][M] + k [M*][M] -----(6)$$

$$2 12 1 2 22 2 2$$

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

$$\frac{d[M]/d[M]}{1} = k [M*][M] + k [M*][M] ----(7)$$

$$\frac{11}{k} [M*][M] + k [M*][M]$$

$$12 1 2 22 2 2$$

A steady state concentration is assumed for each of the reactive species M\* and M\*

$$k [M*][M] = k [M*][M] -----(8)$$
21 2 1 12 1 2

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

$$d[M]/d[M] = [M](r[M] + [M]) -----(9) .$$

$$1 2 [M]([M] + r[M])$$

$$2 1 2 2$$

which are defined by, r = k / k, r = k / k1 11 12 2 22 21

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

The equation (9) can also be expressed in term of mole fraction instead of concentrations, f and f are the mole fraction of monomer M and M in the feed, and F and F are the mole 1 2 1 2 1 2 1 2 1 2

$$f = 1 - f = [M]/([M] + [M]) -----(10)$$
1 2 1 1 2

and

$$F = 1 - F = d[M]/(d[M] + d[M]) -----(11)$$
2 2 1 1 2

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

$$F = (rf + ff)/(rf^{2} + 2ff + rf^{2}) ---(12)$$

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 and r involve the  $1 \ 2$  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

$$f(1-2F)/F(1-f) = r + [f^{2}(F-1)/F(1-f)^{2}]r$$
 -----(13)

> ศูนย์วิทยทรัพยากร าลงกรณ์มหาวิทยาลัย

VITA

Miss Pakamas Tongjaroensirikul May 3, 1963 Bangkok. She recieved her B.Sc. in Chemistry from Chulalongkorn University in 1984 and since then she has been a graduate student in Department of Chemistry, Chulalongkorn University. During the study towards the Master's Degree of Science, she was awarded a research grant for her Master Degree's Thesis from the Price of Dr.Buarech Khamthong.



ศูนยวิทยทรพยากร