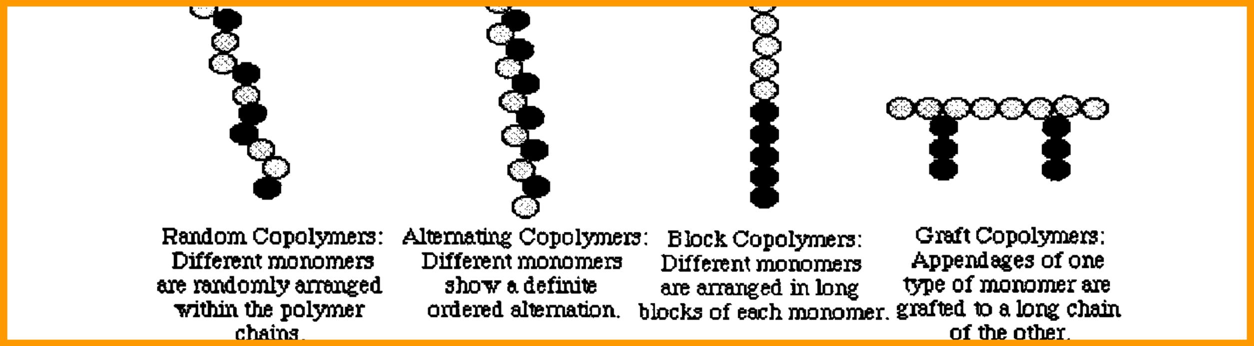
Copolymerisation



Random Copolymers: Different monomers are randomly arranged within the polymer chains.

Alternating Copolymers: Different monomers show a definite ordered alternation.

Block Copolymers: Different monomers are arranged in long blocks of each monomer.

Graft Copolymers: Appendages of one type of monomer are grafted to a long chain of the other.

Step copolymerisation

- Alternative copolymer

- HO2C-RCO2H + H2N-R-NH2 + H2N-R-NH2

- 2 **HO2C-R-CO2H + H2N-R-NH2** → **HO2C-R-CONH-RNHCO-R-CO2H**
-
- **HO2C-R-CONH-RNHCO-R-CO2H + H2N-R-NH2** → **HO(-CO-RCONH-R-NHCO-R-CONH-R-NH-)H**

Block copolymerisation

- $\text{HO2C-R-CO2H} + \text{H2N-R-NH2} \longrightarrow \text{H2N-R-NH-(CO-R-CONH-RNH-)}\ \text{nH}$
- $\text{HO2C-R-CO2H} + \text{H2N-R-NH2} \longrightarrow \text{HO2C-R-CO-(NH-RNHCO-R-CO-)nOH}$
-
- $\text{HO}\left\{\text{—CO-R-CO-}\left(\text{NH-R-NHCO-R-CO-}\right)_{n}\text{—NH—R-NH-}\left(\text{CO-R-CONH-R-NH-}\right)_{n}\text{-}\right\}\text{---H}$

CHAIN COPOLYMERISATION

$M_1 + M_2$

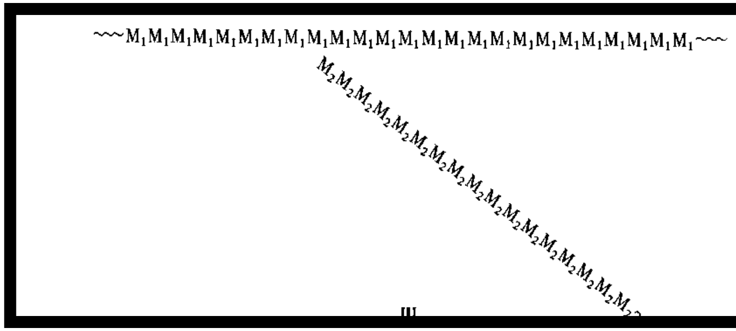
$\sim\sim\sim M_1M_2M_2M_1M_2M_2M_2M_1M_1M_2M_2M_1M_1M_2M_1M_1M_1M_2M_2M_1M_1\sim\sim\sim$

$\sim\sim\sim M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1\sim\sim\sim$

I

$\sim\sim\sim M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2\sim\sim\sim$

II



III

Copolymerisation Equation

$$M_1^* + M_1 \xrightarrow{k_{11}} M_1^* \qquad (6\text{-}2)$$

$$M_1^* + M_2 \xrightarrow{k_{12}} M_2^* \qquad (6\text{-}3)$$

$$M_2^* + M_1 \xrightarrow{k_{21}} M_1^* \qquad (6\text{-}4)$$

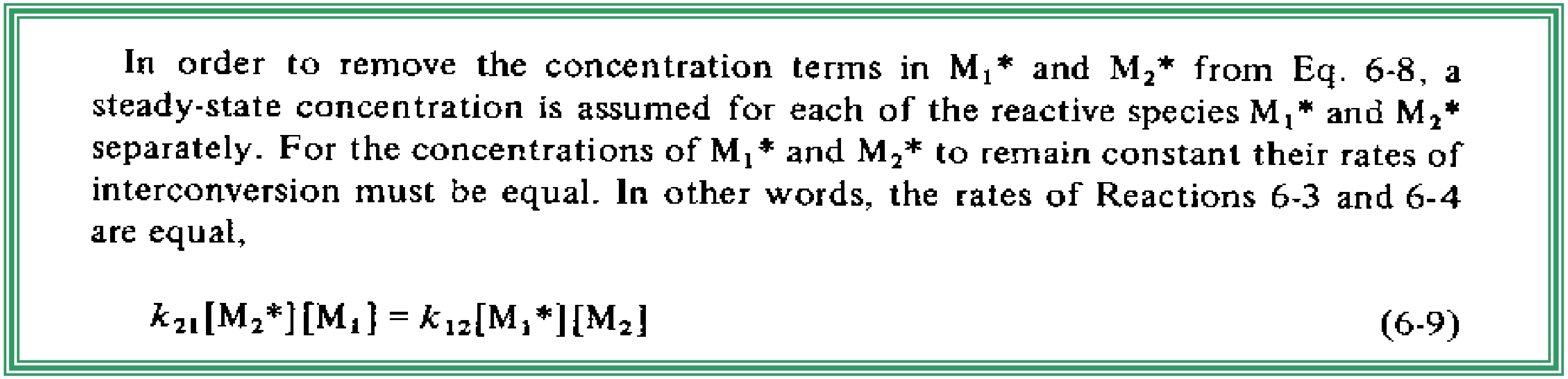
$$M_2^* + M_2 \xrightarrow{k_{22}} M_2^* \qquad (6\text{-}5)$$

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] \qquad (6\text{-}6)$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2] \qquad (6\text{-}7)$$

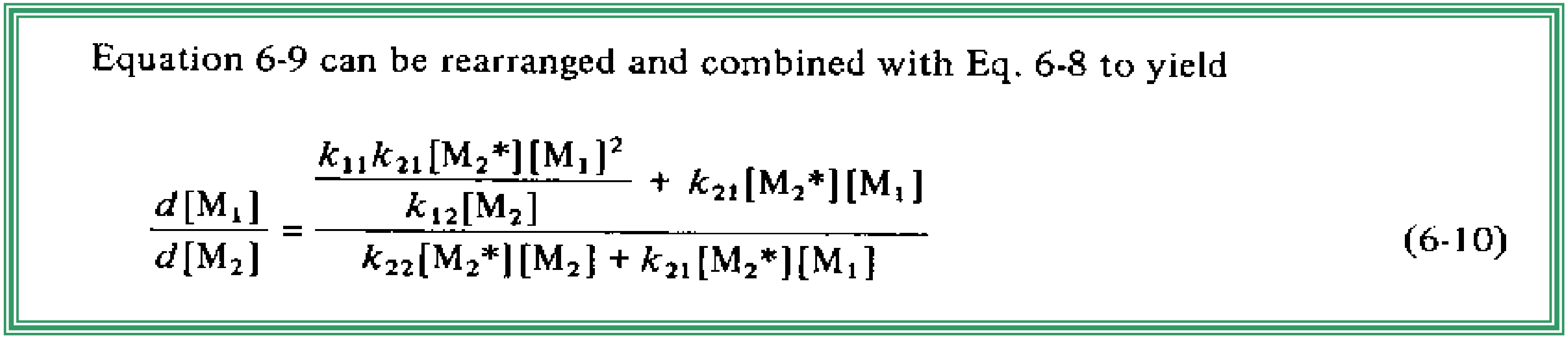
$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]} \qquad (6\text{-}8)$$

Copolymerisation Equation



In order to remove the concentration terms in M_1^* and M_2^* from Eq. 6-8, a steady-state concentration is assumed for each of the reactive species M_1^* and M_2^* separately. For the concentrations of M_1^* and M_2^* to remain constant their rates of interconversion must be equal. In other words, the rates of Reactions 6-3 and 6-4 are equal,

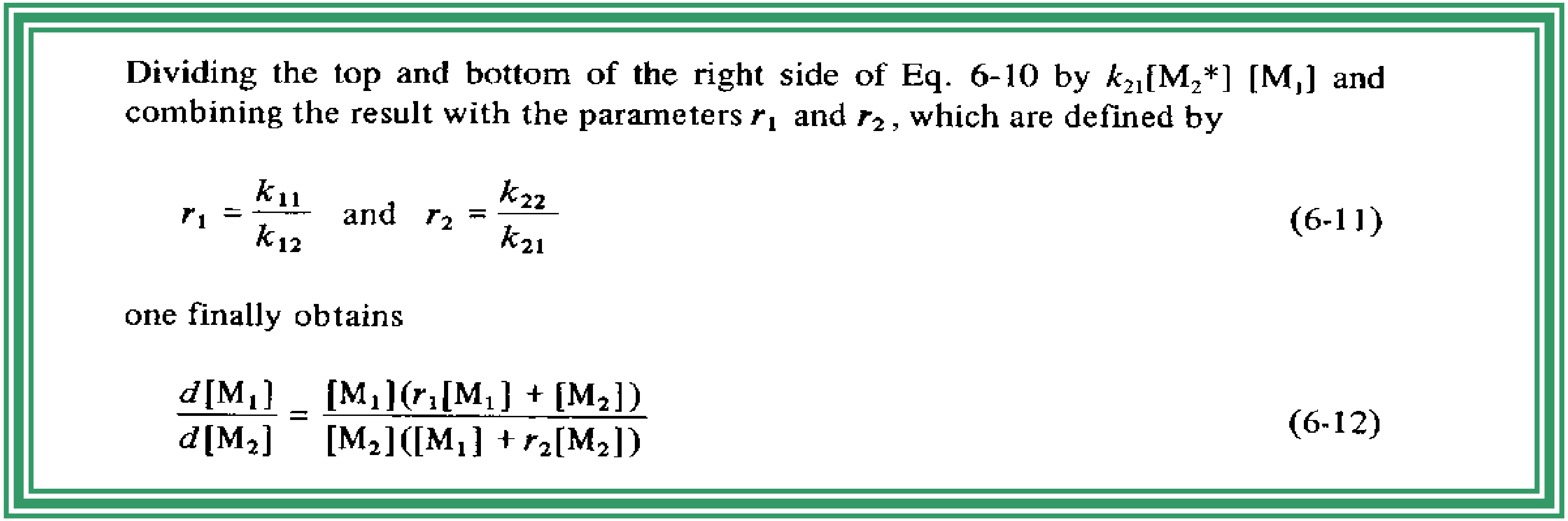
$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2] \tag{6-9}$$



Equation 6-9 can be rearranged and combined with Eq. 6-8 to yield

$$\frac{d[M_1]}{d[M_2]} = \frac{\dfrac{k_{11}k_{21}[M_2^*][M_1]^2}{k_{12}[M_2]} + k_{21}[M_2^*][M_1]}{k_{22}[M_2^*][M_2] + k_{21}[M_2^*][M_1]} \tag{6-10}$$

Copolymerisation Equation



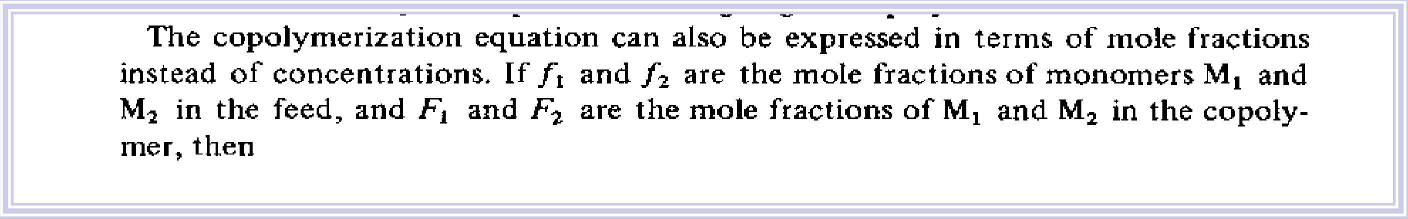
Dividing the top and bottom of the right side of Eq. 6-10 by $k_{21}[M_2^*]$ $[M_1]$ and combining the result with the parameters r_1 and r_2, which are defined by

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}} \tag{6-11}$$

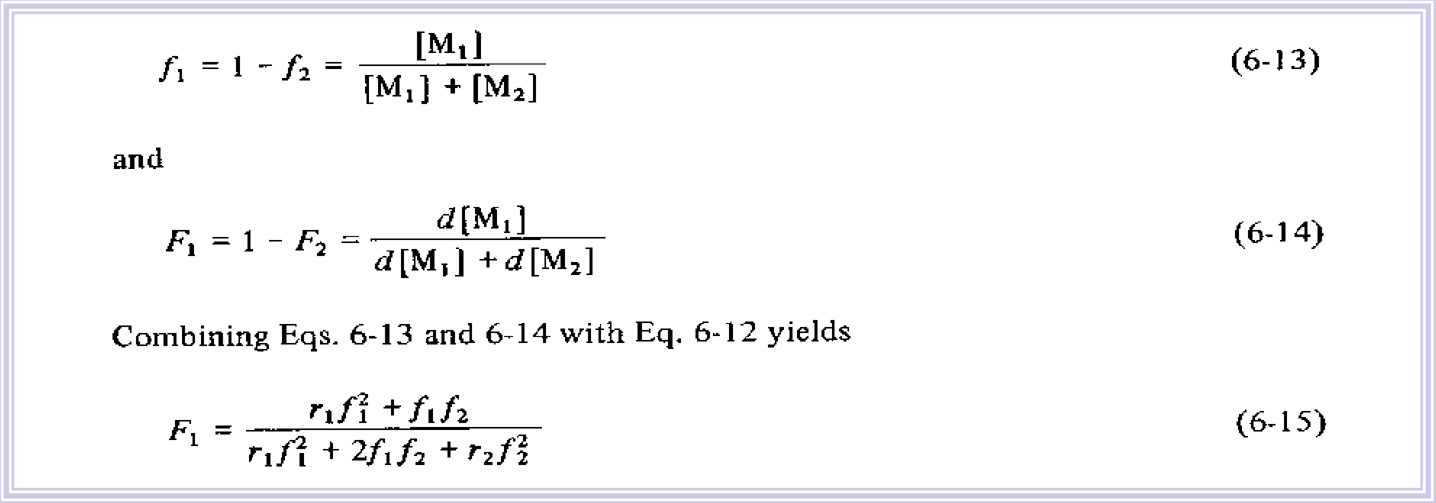
one finally obtains

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \tag{6-12}$$

Mole fractions Copolymerisation



The copolymerization equation can also be expressed in terms of mole fractions instead of concentrations. If f_1 and f_2 are the mole fractions of monomers M_1 and M_2 in the feed, and F_1 and F_2 are the mole fractions of M_1 and M_2 in the copolymer, then



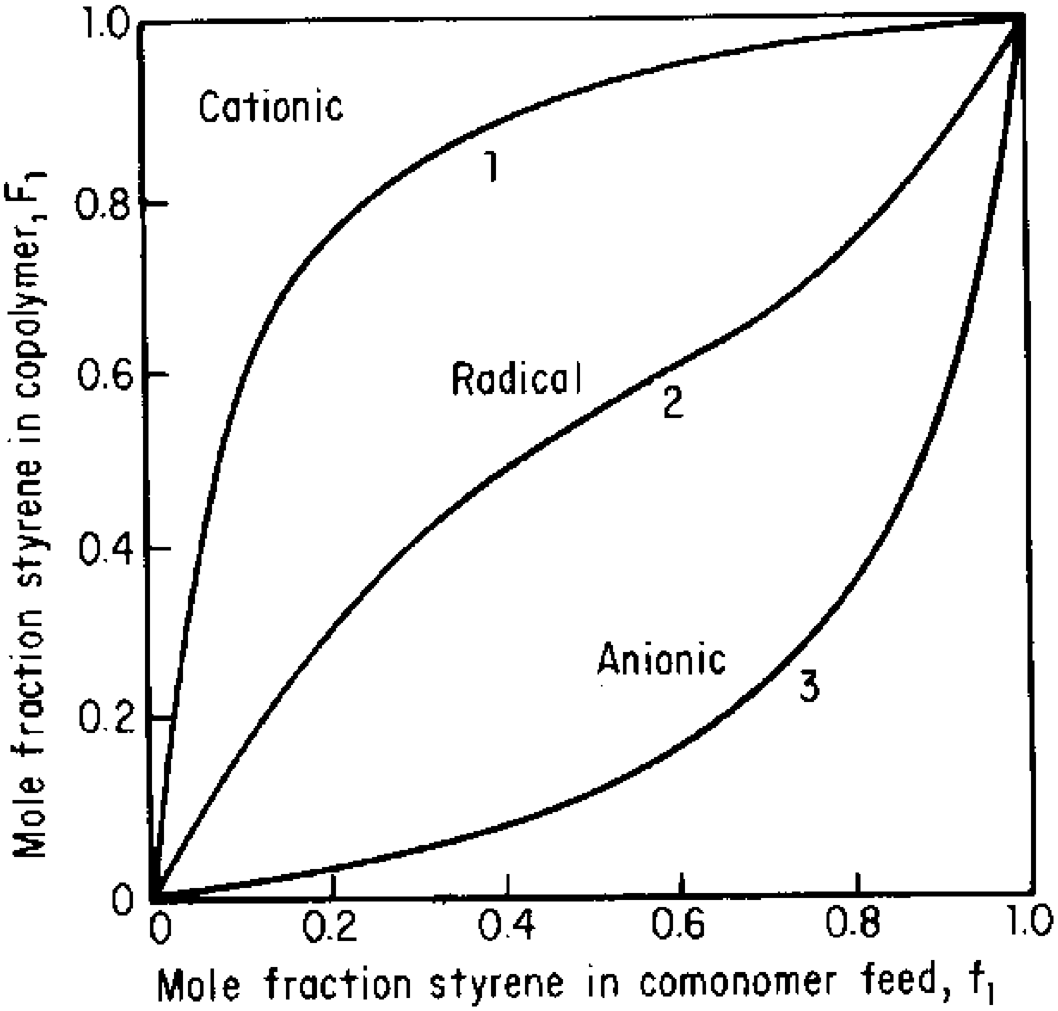
$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \tag{6-13}$$

and

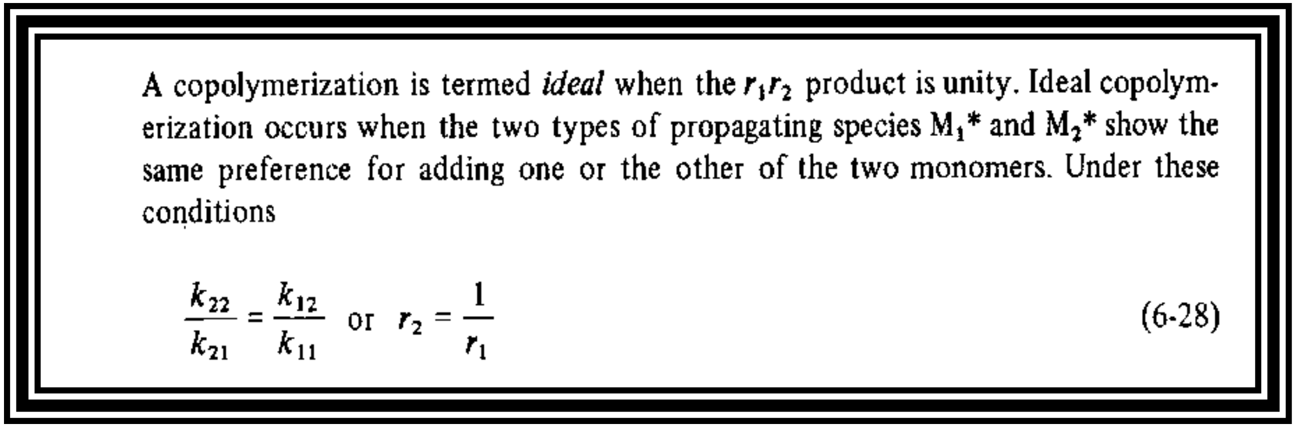
$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \tag{6-14}$$

Combining Eqs. 6-13 and 6-14 with Eq. 6-12 yields

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{6-15}$$

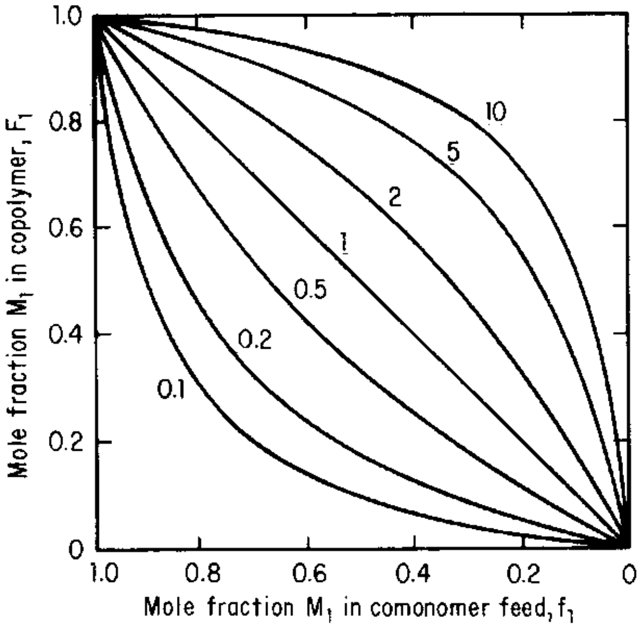

Cationic
1
Radical
2
Anionic
3
Mole fraction styrene in copolymer, F_1
Mole fraction styrene in comonomer feed, f_1
0
0.2
0.4
0.6
0.8
1.0

IDEAL COPOLYMERISATION



A copolymerization is termed *ideal* when the r_1r_2 product is unity. Ideal copolymerization occurs when the two types of propagating species M_1^* and M_2^* show the same preference for adding one or the other of the two monomers. Under these conditions

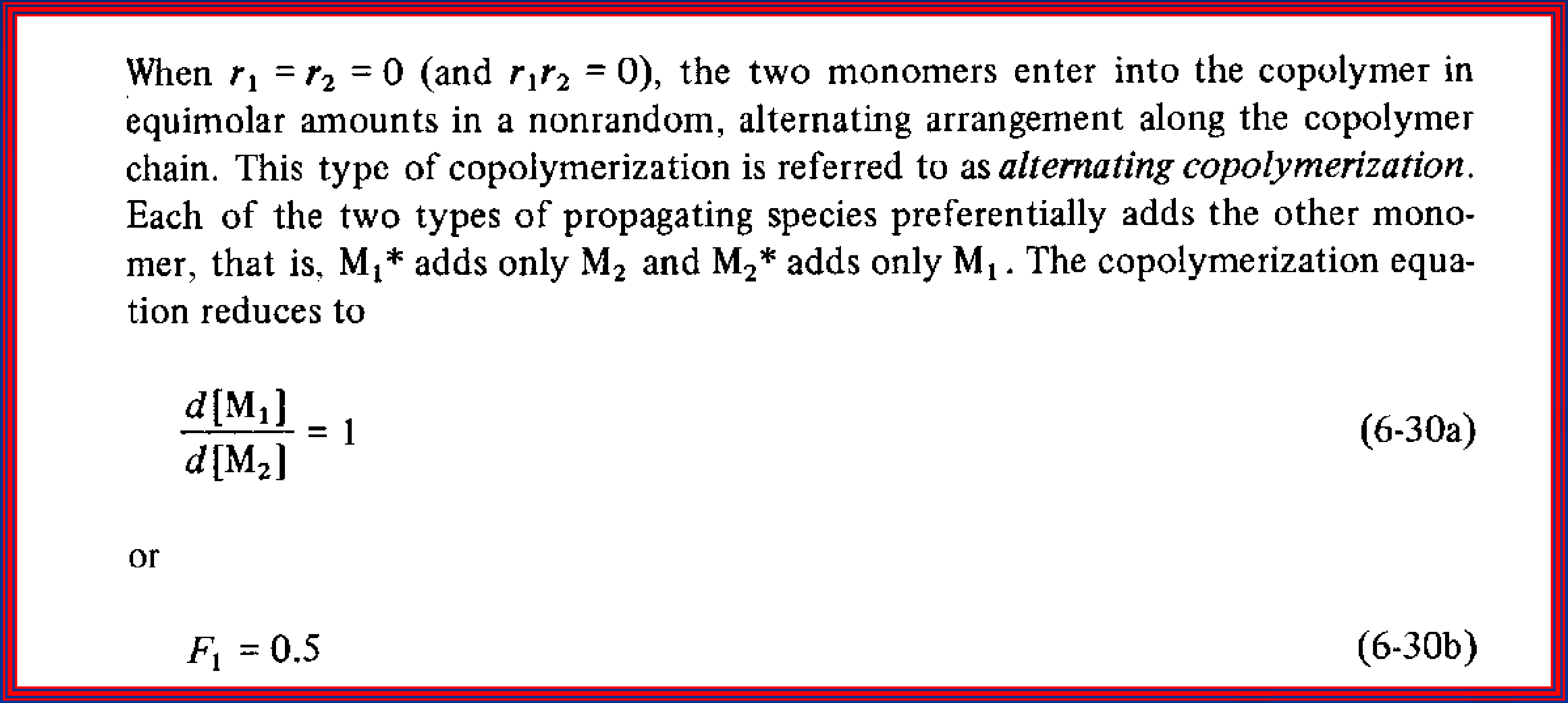
$$\frac{k_{22}}{k_{21}} = \frac{k_{12}}{k_{11}} \quad \text{or} \quad r_2 = \frac{1}{r_1} \tag{6-28}$$



Random copolymerization

- When $r_1=r_2$ the two monomers show equal reactivates toward both propagating species . such behavior is referred to random

Alternating copolymerisation



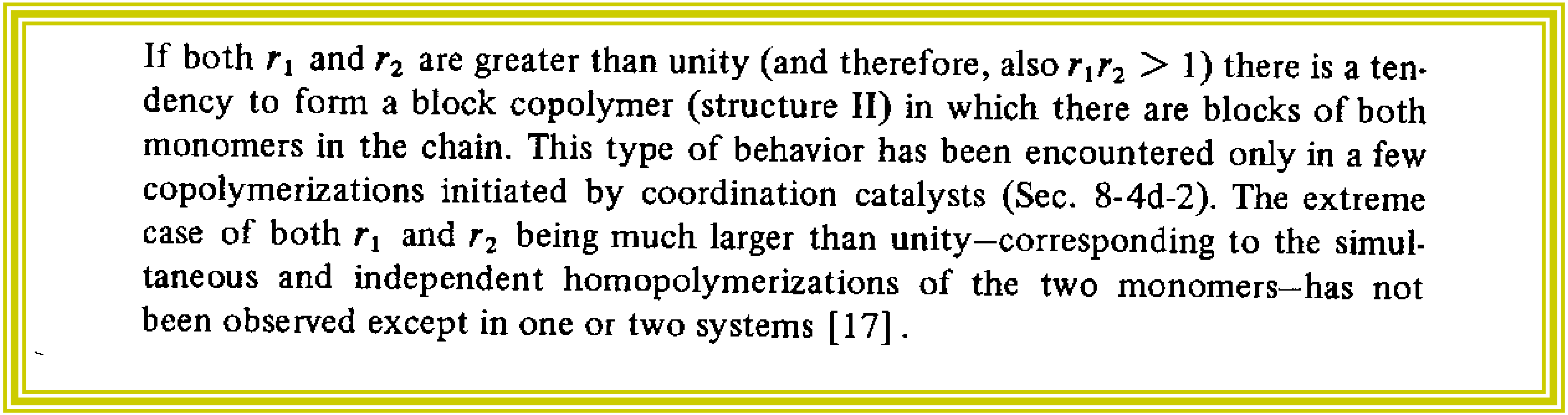
When $r_1 = r_2 = 0$ (and $r_1 r_2 = 0$), the two monomers enter into the copolymer in equimolar amounts in a nonrandom, alternating arrangement along the copolymer chain. This type of copolymerization is referred to as *alternating copolymerization*. Each of the two types of propagating species preferentially adds the other monomer, that is, $M_1{}^*$ adds only M_2 and $M_2{}^*$ adds only M_1. The copolymerization equation reduces to

$$\frac{d[M_1]}{d[M_2]} = 1 \tag{6-30a}$$

or

$$F_1 = 0.5 \tag{6-30b}$$

Bloock copolymerisation



If both r_1 and r_2 are greater than unity (and therefore, also $r_1r_2 > 1$) there is a tendency to form a block copolymer (structure II) in which there are blocks of both monomers in the chain. This type of behavior has been encountered only in a few copolymerizations initiated by coordination catalysts (Sec. 8-4d-2). The extreme case of both r_1 and r_2 being much larger than unity—corresponding to the simultaneous and independent homopolymerizations of the two monomers—has not been observed except in one or two systems [17].

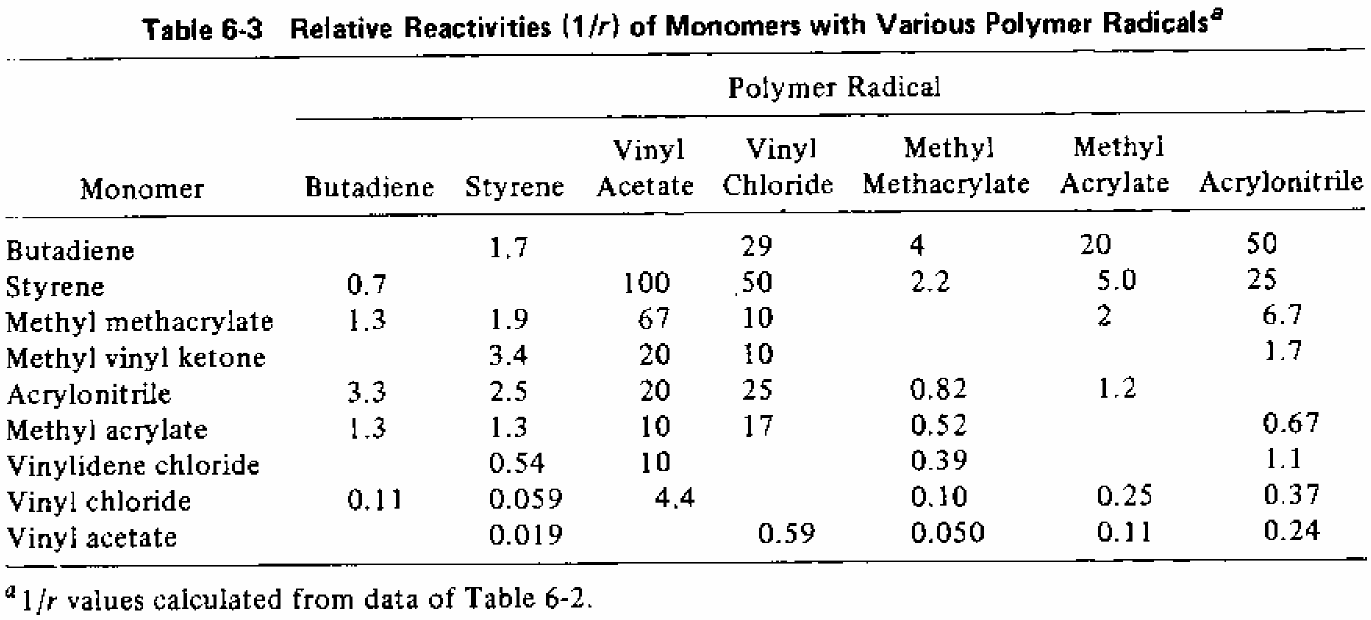


Table 6-3 Relative Reactivities (1/*r*) of Monomers with Various Polymer Radicals[a]

	Polymer Radical						
Monomer	Butadiene	Styrene	Vinyl Acetate	Vinyl Chloride	Methyl Methacrylate	Methyl Acrylate	Acrylonitrile
Butadiene		1.7		29	4	20	50
Styrene	0.7		100	50	2.2	5.0	25
Methyl methacrylate	1.3	1.9	67	10		2	6.7
Methyl vinyl ketone		3.4	20	10			1.7
Acrylonitrile	3.3	2.5	20	25	0.82	1.2	
Methyl acrylate	1.3	1.3	10	17	0.52		0.67
Vinylidene chloride		0.54	10		0.39		1.1
Vinyl chloride	0.11	0.059	4.4		0.10	0.25	0.37
Vinyl acetate		0.019		0.59	0.050	0.11	0.24

[a] 1/*r* values calculated from data of Table 6-2.

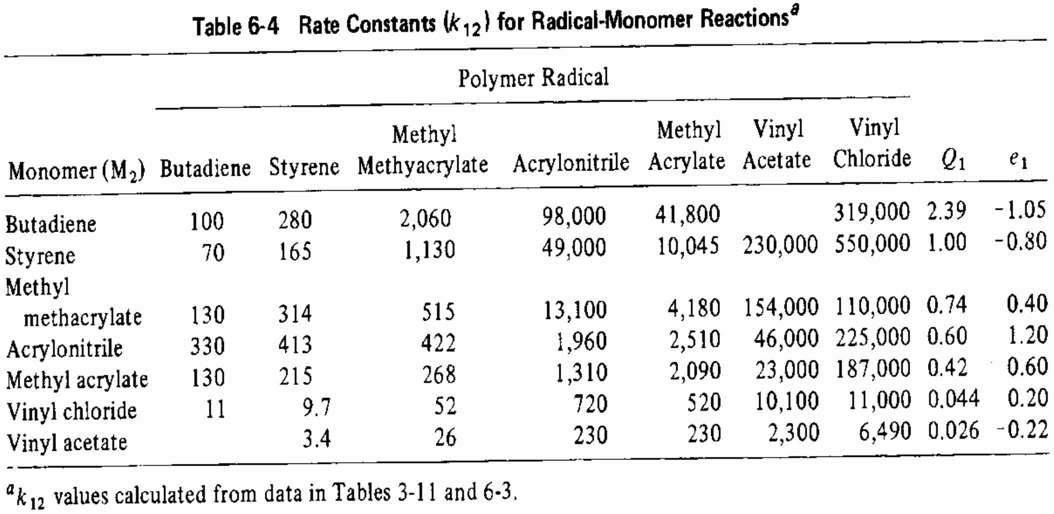
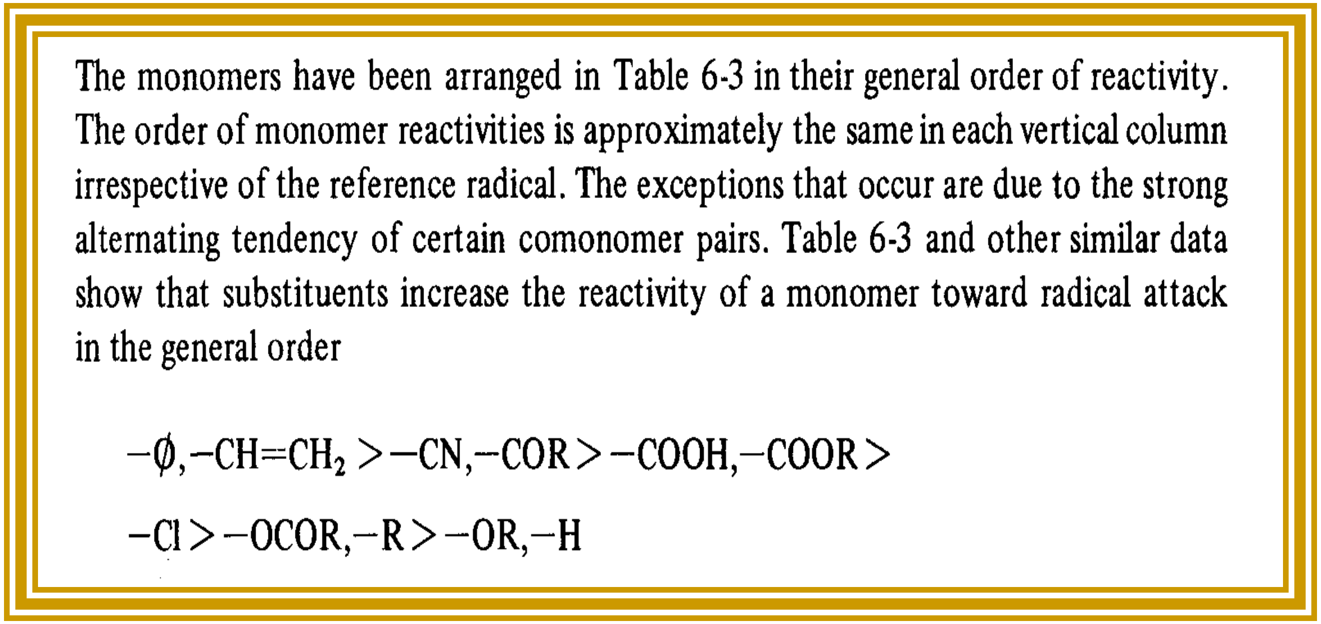


Table 6-4 Rate Constants (k_{12}) for Radical-Monomer Reactions[a]

	Polymer Radical								
Monomer (M_2)	Butadiene	Styrene	Methyl Methyacrylate	Acrylonitrile	Methyl Acrylate	Vinyl Acetate	Vinyl Chloride	Q_1	e_1
Butadiene	100	280	2,060	98,000	41,800		319,000	2.39	-1.05
Styrene	70	165	1,130	49,000	10,045	230,000	550,000	1.00	-0.80
Methyl methacrylate	130	314	515	13,100	4,180	154,000	110,000	0.74	0.40
Acrylonitrile	330	413	422	1,960	2,510	46,000	225,000	0.60	1.20
Methyl acrylate	130	215	268	1,310	2,090	23,000	187,000	0.42	0.60
Vinyl chloride	11	9.7	52	720	520	10,100	11,000	0.044	0.20
Vinyl acetate		3.4	26	230	230	2,300	6,490	0.026	-0.22

[a] k_{12} values calculated from data in Tables 3-11 and 6-3.

RESONANCE EFFECTS

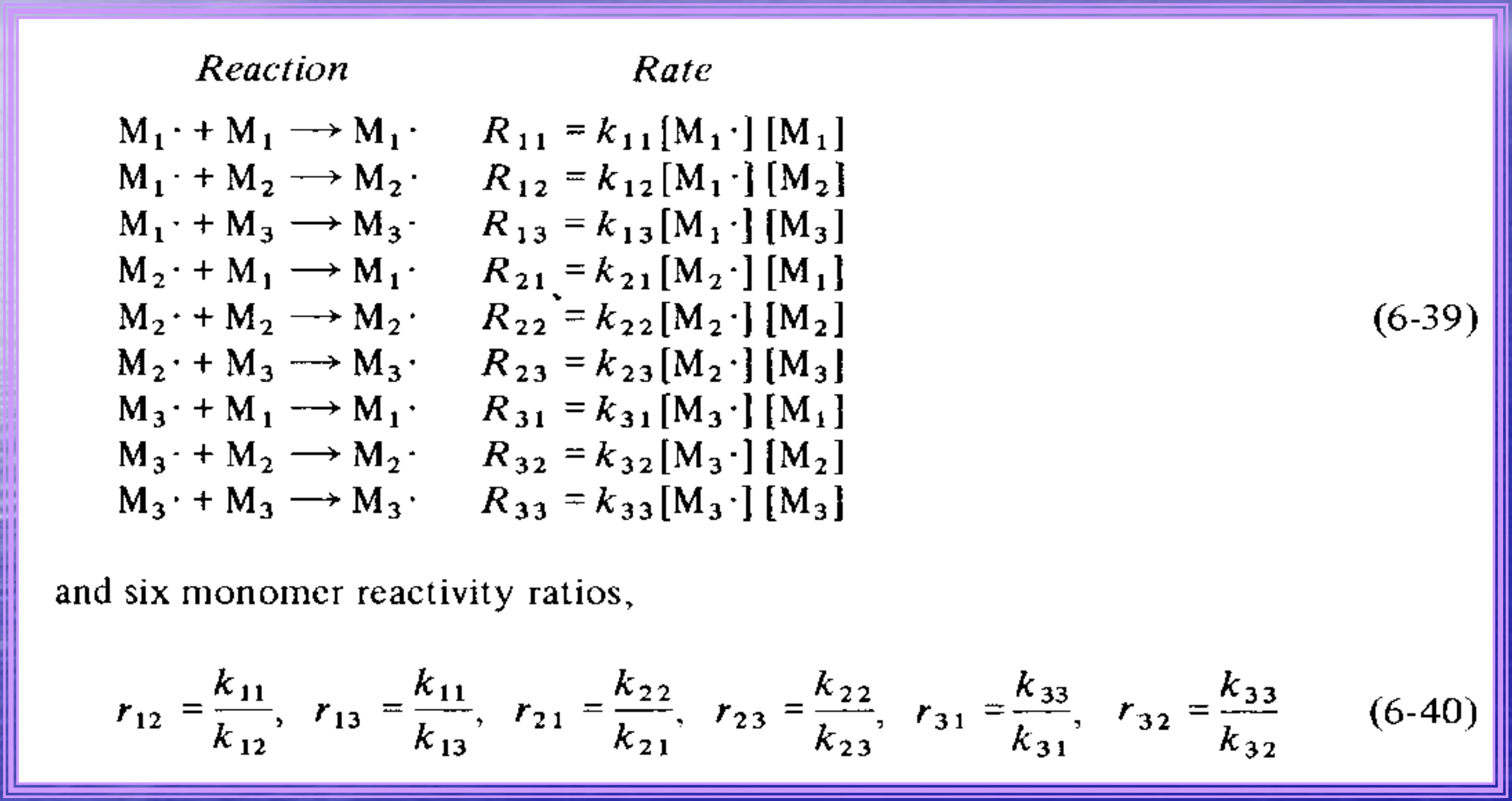


The monomers have been arranged in Table 6-3 in their general order of reactivity. The order of monomer reactivities is approximately the same in each vertical column irrespective of the reference radical. The exceptions that occur are due to the strong alternating tendency of certain comonomer pairs. Table 6-3 and other similar data show that substituents increase the reactivity of a monomer toward radical attack in the general order

$$-\phi, -CH{=}CH_2 > -CN, -COR > -COOH, -COOR >$$

$$-Cl > -OCOR, -R > -OR, -H$$

Multicomponent copolymerisation

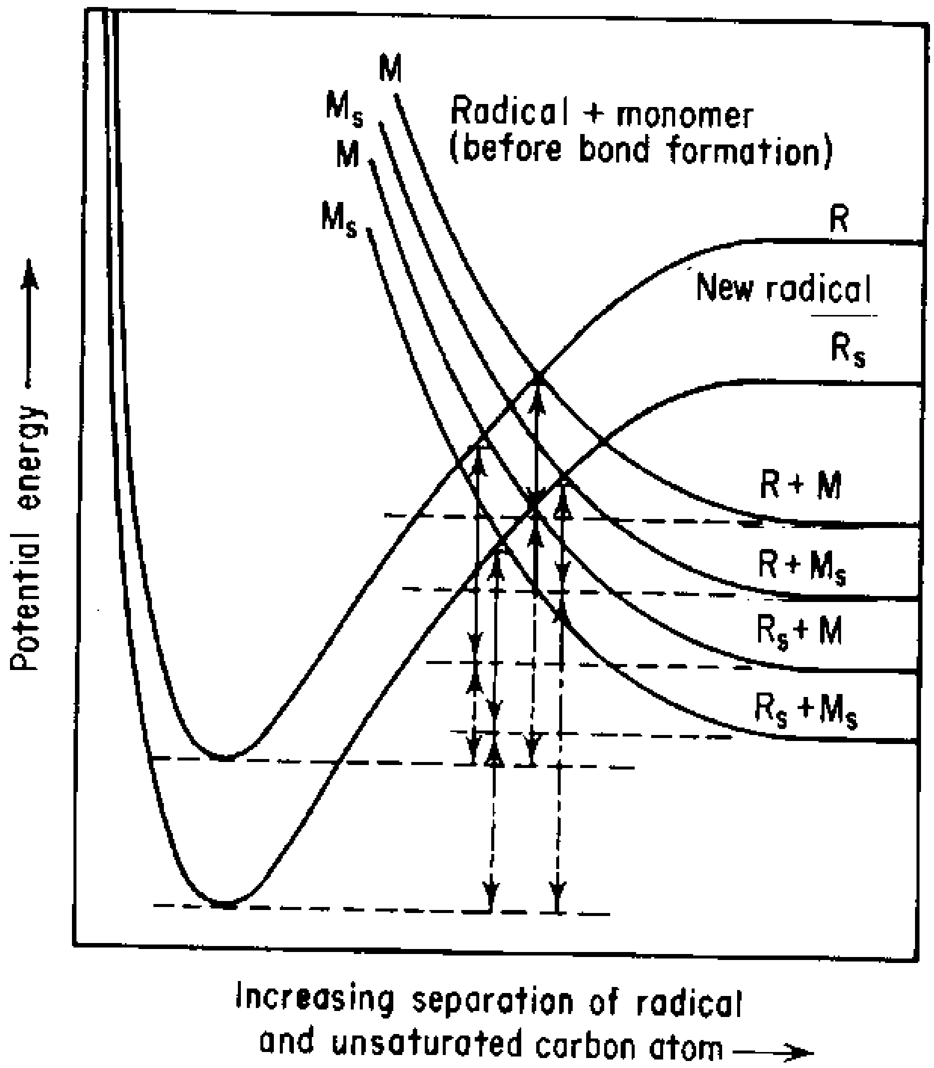


$$\begin{array}{ll}
\textit{Reaction} & \textit{Rate} \\
M_1\cdot + M_1 \longrightarrow M_1\cdot & R_{11} = k_{11}[M_1\cdot][M_1] \\
M_1\cdot + M_2 \longrightarrow M_2\cdot & R_{12} = k_{12}[M_1\cdot][M_2] \\
M_1\cdot + M_3 \longrightarrow M_3\cdot & R_{13} = k_{13}[M_1\cdot][M_3] \\
M_2\cdot + M_1 \longrightarrow M_1\cdot & R_{21} = k_{21}[M_2\cdot][M_1] \\
M_2\cdot + M_2 \longrightarrow M_2\cdot & R_{22} = k_{22}[M_2\cdot][M_2] \\
M_2\cdot + M_3 \longrightarrow M_3\cdot & R_{23} = k_{23}[M_2\cdot][M_3] \\
M_3\cdot + M_1 \longrightarrow M_1\cdot & R_{31} = k_{31}[M_3\cdot][M_1] \\
M_3\cdot + M_2 \longrightarrow M_2\cdot & R_{32} = k_{32}[M_3\cdot][M_2] \\
M_3\cdot + M_3 \longrightarrow M_3\cdot & R_{33} = k_{33}[M_3\cdot][M_3]
\end{array} \tag{6-39}$$

and six monomer reactivity ratios,

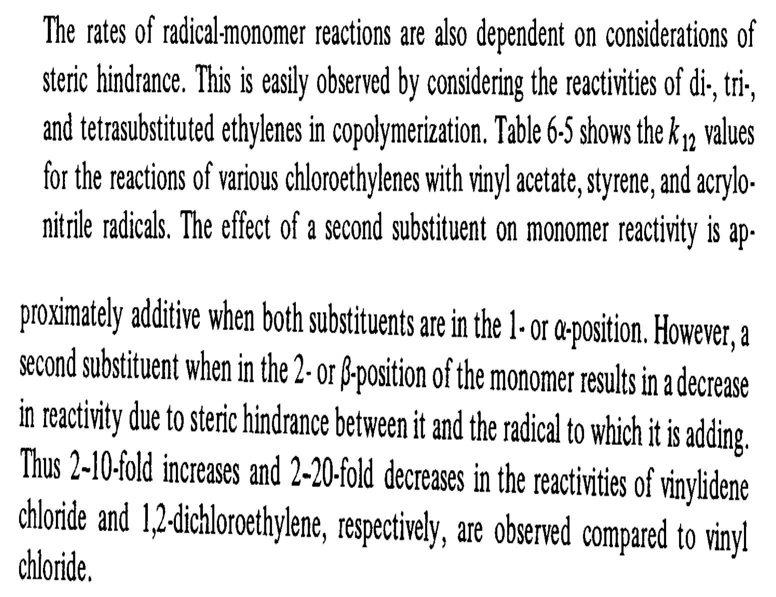
$$r_{12} = \frac{k_{11}}{k_{12}}, \quad r_{13} = \frac{k_{11}}{k_{13}}, \quad r_{21} = \frac{k_{22}}{k_{21}}, \quad r_{23} = \frac{k_{22}}{k_{23}}, \quad r_{31} = \frac{k_{33}}{k_{31}}, \quad r_{32} = \frac{k_{33}}{k_{32}} \tag{6-40}$$

Potential energy curves



$$R_s\cdot + M < R_s\cdot + M_s < R\cdot + M < R\cdot + M_s$$

Steric effects



The rates of radical-monomer reactions are also dependent on considerations of steric hindrance. This is easily observed by considering the reactivities of di-, tri-, and tetrasubstituted ethylenes in copolymerization. Table 6-5 shows the k_{12} values for the reactions of various chloroethylenes with vinyl acetate, styrene, and acrylonitrile radicals. The effect of a second substituent on monomer reactivity is approximately additive when both substituents are in the 1- or α-position. However, a second substituent when in the 2- or β-position of the monomer results in a decrease in reactivity due to steric hindrance between it and the radical to which it is adding. Thus 2-10-fold increases and 2-20-fold decreases in the reactivities of vinylidene chloride and 1,2-dichloroethylene, respectively, are observed compared to vinyl chloride.

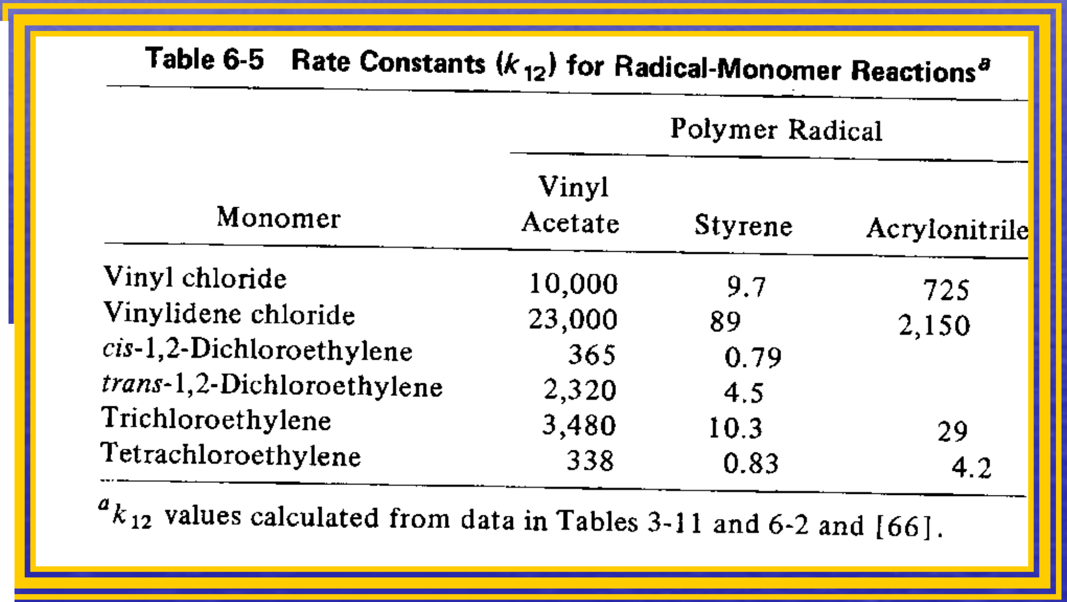
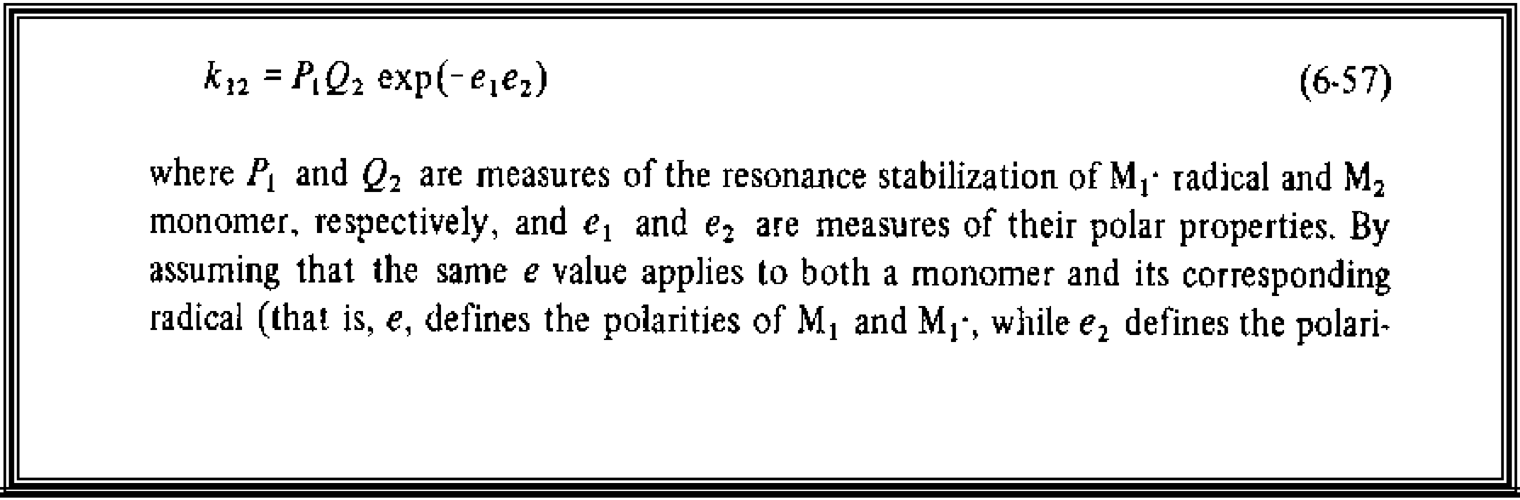


Table 6-5 Rate Constants (k_{12}) for Radical-Monomer Reactions[a]

	Polymer Radical		
Monomer	Vinyl Acetate	Styrene	Acrylonitrile
Vinyl chloride	10,000	9.7	725
Vinylidene chloride	23,000	89	2,150
cis-1,2-Dichloroethylene	365	0.79	
trans-1,2-Dichloroethylene	2,320	4.5	
Trichloroethylene	3,480	10.3	29
Tetrachloroethylene	338	0.83	4.2

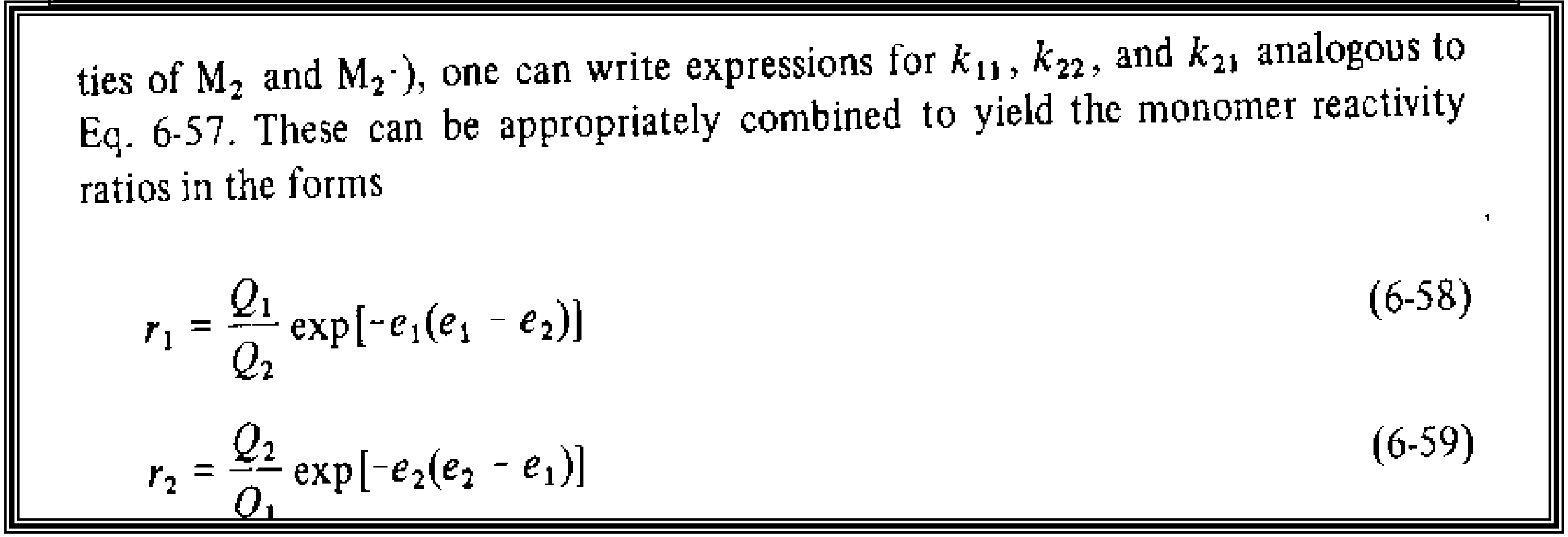
[a] k_{12} values calculated from data in Tables 3-11 and 6-2 and [66].

Q-E SCHEME



$$k_{12} = P_1 Q_2 \exp(-e_1 e_2) \qquad (6\text{-}57)$$

where P_1 and Q_2 are measures of the resonance stabilization of $M_1\cdot$ radical and M_2 monomer, respectively, and e_1 and e_2 are measures of their polar properties. By assuming that the same e value applies to both a monomer and its corresponding radical (that is, e_1 defines the polarities of M_1 and $M_1\cdot$, while e_2 defines the polari-



ties of M_2 and $M_2\cdot$), one can write expressions for k_{11}, k_{22}, and k_{21} analogous to Eq. 6-57. These can be appropriately combined to yield the monomer reactivity ratios in the forms

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)] \qquad (6\text{-}58)$$

$$r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)] \qquad (6\text{-}59)$$

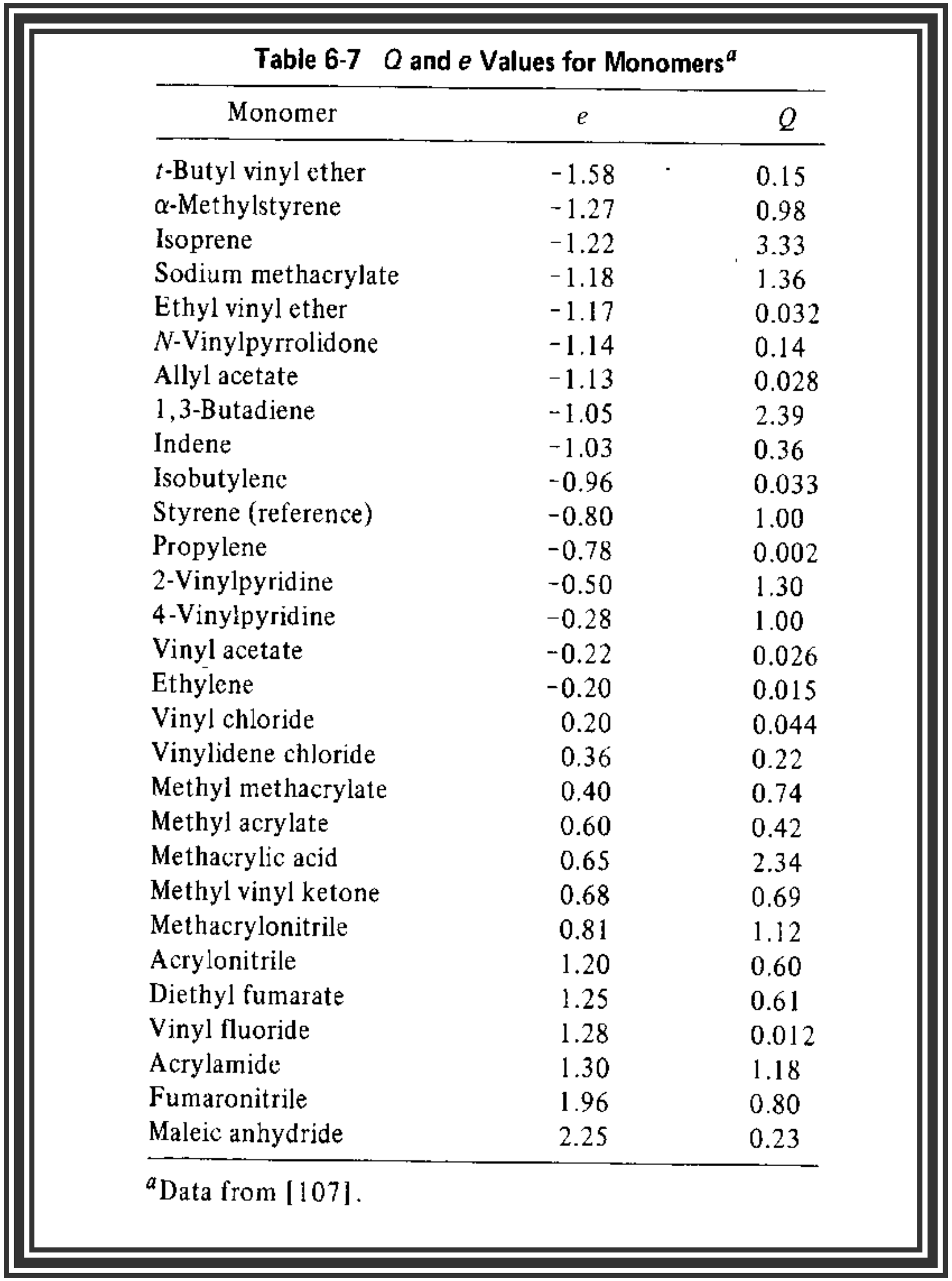


Table 6-7 Q and e Values for Monomers[a]

Monomer	e	Q
t-Butyl vinyl ether	-1.58	0.15
α-Methylstyrene	-1.27	0.98
Isoprene	-1.22	3.33
Sodium methacrylate	-1.18	1.36
Ethyl vinyl ether	-1.17	0.032
N-Vinylpyrrolidone	-1.14	0.14
Allyl acetate	-1.13	0.028
1,3-Butadiene	-1.05	2.39
Indene	-1.03	0.36
Isobutylene	-0.96	0.033
Styrene (reference)	-0.80	1.00
Propylene	-0.78	0.002
2-Vinylpyridine	-0.50	1.30
4-Vinylpyridine	-0.28	1.00
Vinyl acetate	-0.22	0.026
Ethylene	-0.20	0.015
Vinyl chloride	0.20	0.044
Vinylidene chloride	0.36	0.22
Methyl methacrylate	0.40	0.74
Methyl acrylate	0.60	0.42
Methacrylic acid	0.65	2.34
Methyl vinyl ketone	0.68	0.69
Methacrylonitrile	0.81	1.12
Acrylonitrile	1.20	0.60
Diethyl fumarate	1.25	0.61
Vinyl fluoride	1.28	0.012
Acrylamide	1.30	1.18
Fumaronitrile	1.96	0.80
Maleic anhydride	2.25	0.23

[a] Data from [107].

Cationic copolymerisation

- Monomer reactivity

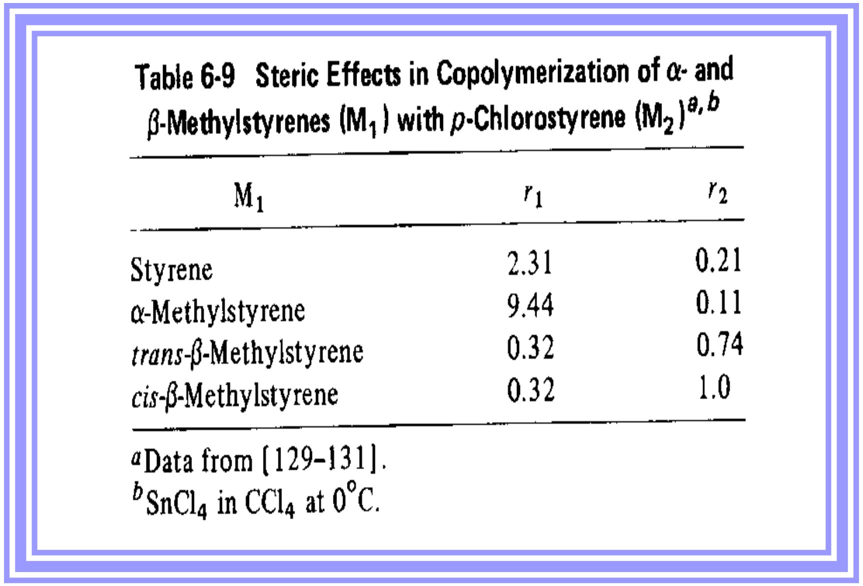
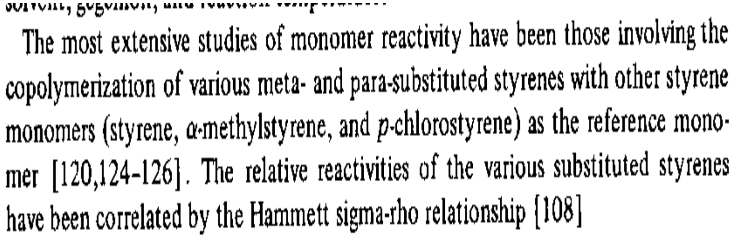


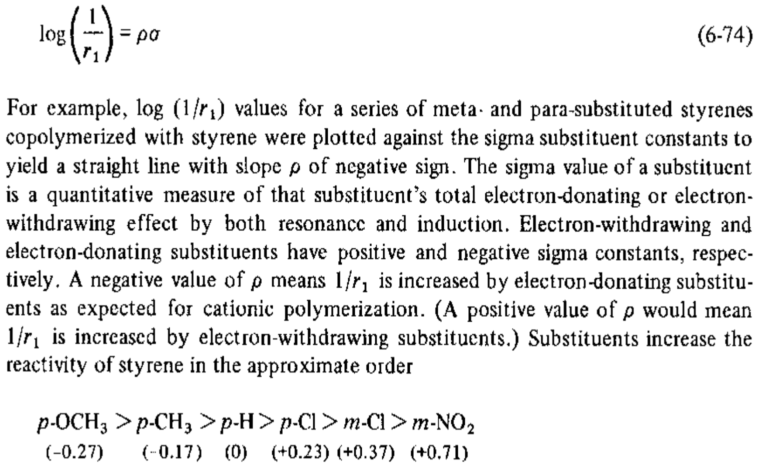
Table 6-9 Steric Effects in Copolymerization of α- and β-Methylstyrenes (M_1) with *p*-Chlorostyrene (M_2)[a,b]

M_1	r_1	r_2
Styrene	2.31	0.21
α-Methylstyrene	9.44	0.11
trans-β-Methylstyrene	0.32	0.74
cis-β-Methylstyrene	0.32	1.0

[a] Data from [129–131].
[b] $SnCl_4$ in CCl_4 at 0°C.



The most extensive studies of monomer reactivity have been those involving the copolymerization of various meta- and para-substituted styrenes with other styrene monomers (styrene, α-methylstyrene, and *p*-chlorostyrene) as the reference monomer [120,124-126]. The relative reactivities of the various substituted styrenes have been correlated by the Hammett sigma-rho relationship [108]



$$\log\left(\frac{1}{r_1}\right) = \rho\sigma \qquad (6\text{-}74)$$

For example, log $(1/r_1)$ values for a series of meta- and para-substituted styrenes copolymerized with styrene were plotted against the sigma substituent constants to yield a straight line with slope ρ of negative sign. The sigma value of a substituent is a quantitative measure of that substituent's total electron-donating or electron-withdrawing effect by both resonance and induction. Electron-withdrawing and electron-donating substituents have positive and negative sigma constants, respectively. A negative value of ρ means $1/r_1$ is increased by electron-donating substituents as expected for cationic polymerization. (A positive value of ρ would mean $1/r_1$ is increased by electron-withdrawing substituents.) Substituents increase the reactivity of styrene in the approximate order

$$\underset{(-0.27)}{p\text{-OCH}_3} > \underset{(-0.17)}{p\text{-CH}_3} > \underset{(0)}{p\text{-H}} > \underset{(+0.23)}{p\text{-Cl}} > \underset{(+0.37)}{m\text{-Cl}} > \underset{(+0.71)}{m\text{-NO}_2}$$

Effect of solvent

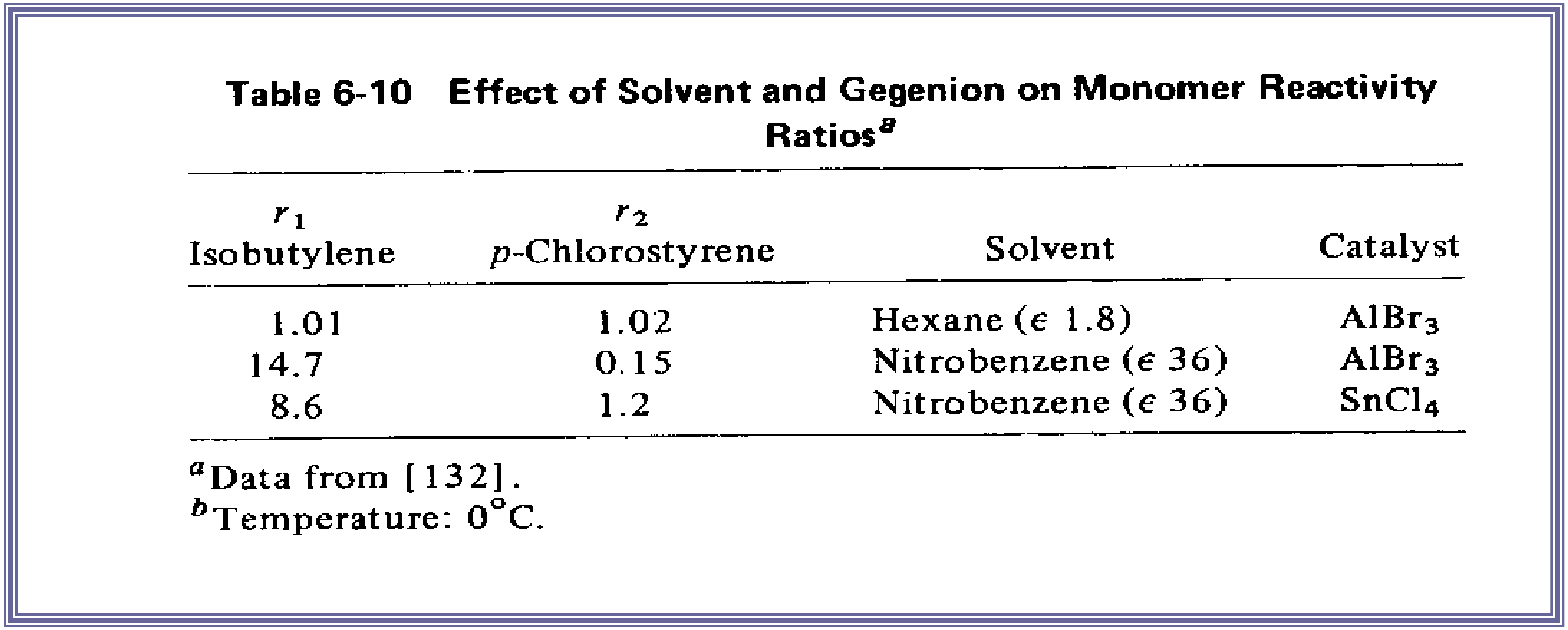


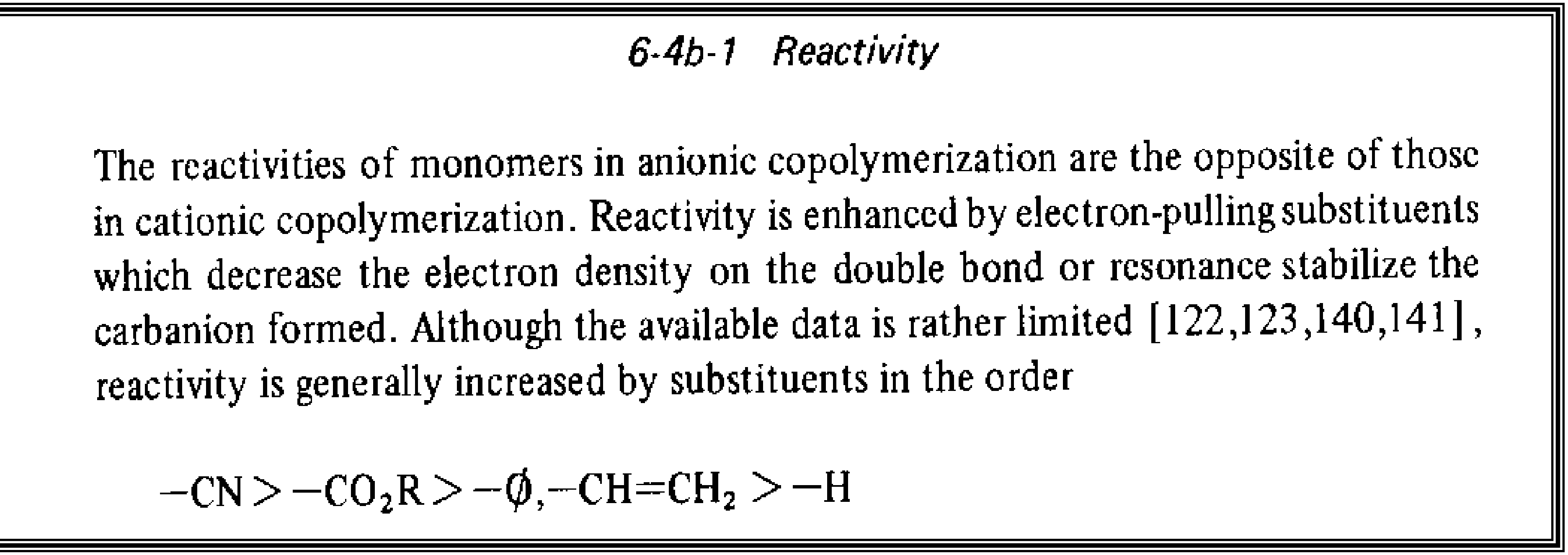
Table 6-10 Effect of Solvent and Gegenion on Monomer Reactivity Ratios[a]

r_1 Isobutylene	r_2 *p*-Chlorostyrene	Solvent	Catalyst
1.01	1.02	Hexane (ϵ 1.8)	$AlBr_3$
14.7	0.15	Nitrobenzene (ϵ 36)	$AlBr_3$
8.6	1.2	Nitrobenzene (ϵ 36)	$SnCl_4$

[a] Data from [132].

[b] Temperature: 0°C.

ANIONIC COPOLYMERISATION



6-4b-1 Reactivity

The reactivities of monomers in anionic copolymerization are the opposite of those in cationic copolymerization. Reactivity is enhanced by electron-pulling substituents which decrease the electron density on the double bond or resonance stabilize the carbanion formed. Although the available data is rather limited [122,123,140,141], reactivity is generally increased by substituents in the order

$$-CN > -CO_2R > -\emptyset, -CH{=}CH_2 > -H$$

EFFECT OF SOLVENT

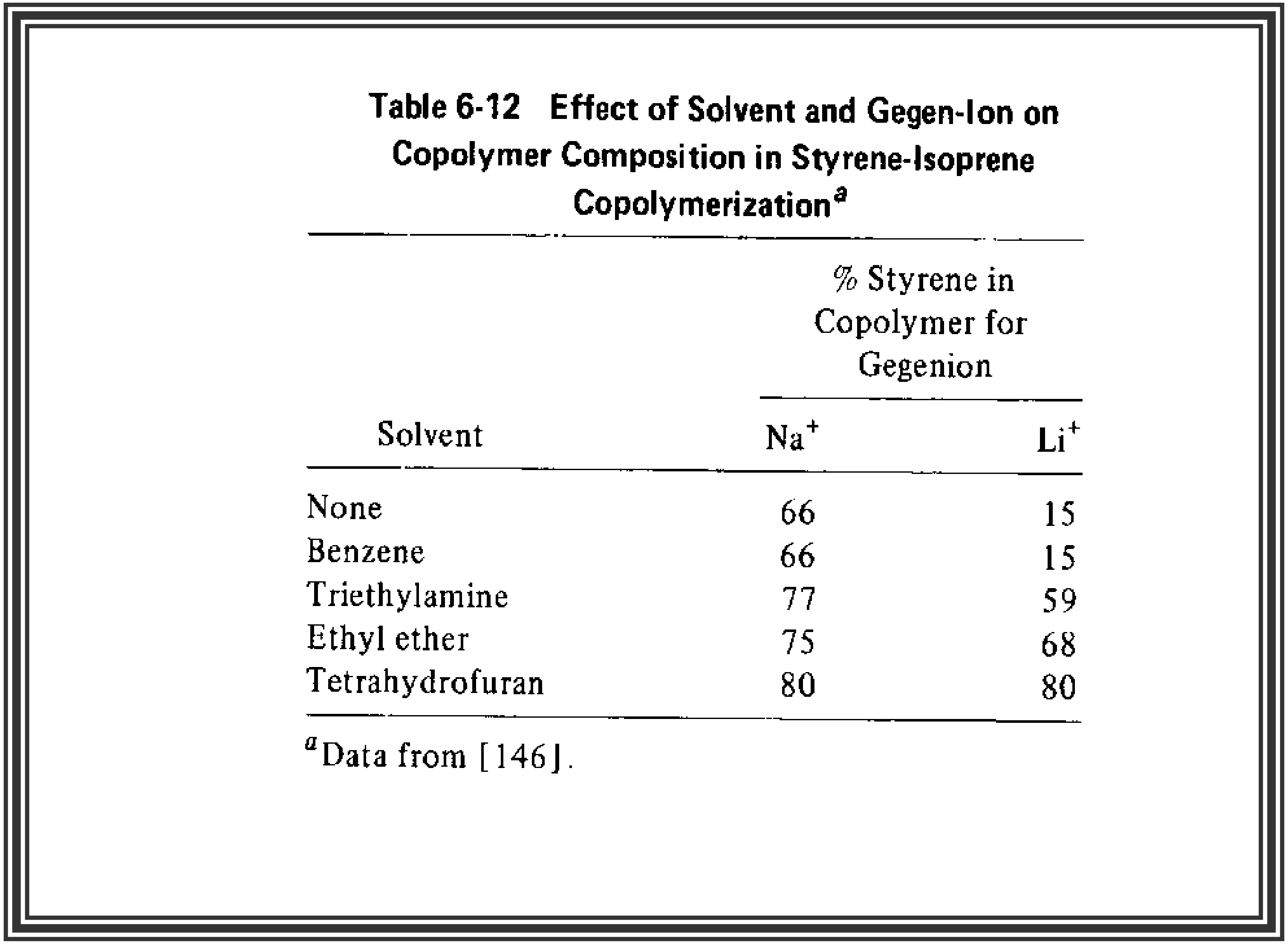


Table 6-12 Effect of Solvent and Gegen-Ion on Copolymer Composition in Styrene-Isoprene Copolymerization[a]

Solvent	% Styrene in Copolymer for Gegenion	
	Na^+	Li^+
None	66	15
Benzene	66	15
Triethylamine	77	59
Ethyl ether	75	68
Tetrahydrofuran	80	80

[a] Data from [146].