Supporting material for students registered to subject:

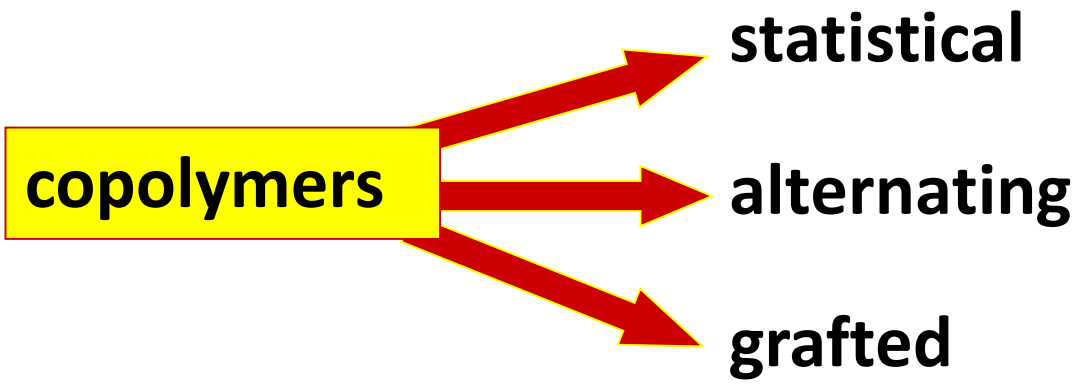
Macromolecular chemistry S112003

Teacher: Jan Merna, Department of Polymers, Institute of Chemical Technology ,Prague

Sources:

Prokopová I.: Makromolekulární chemie, VŠCHT Praha, 2007. (educational text in Czech)
Merna J.: Polymers Instantly, educational text in English, freely accessible from http://merna.eu/teaching/macromolecular-chemistry/
Encyclopedia of Polymer Science and Technology, J.Wiley Sons, Interscience, Publ., New York, 1964-1991

Radical copolymerization



Copolymerization equation

- relationship between composition of reaction mixture and composition of copolymer

– at monomer conversion < 5%

(relation between instantaneous composition of reaction mixture and composition of copolymer)

Copolymerization parameters

- Express relative reactivity of radical P_1 towards monomer M_1 and M_2, resp. radical P_2 towards monomer M_2 a M_1

$$P_1\cdot + M_1 \xrightarrow{k_{11}} P_1M_1$$
$$P_1\cdot + M_2 \xrightarrow{k_{12}} P_1M_2$$
$$P_2\cdot + M_1 \xrightarrow{k_{21}} P_2M_1$$
$$P_2\cdot + M_2 \xrightarrow{k_{22}} P_2M_2$$

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

Penultimative effect: r1, r1´, r2,r2´

Copolymerization behavior of pair of monomers M_1 M_2:

$r_1 r_2 = 0$ alternating copolymerization

$r_1 r_2 = 1$ ideal copolymerization

$r_1 r_2 >> 1$ block copolymers (only ionic polymn.)

$r_1 >> 1, r_2 >> 1$ ⇨ two homopolymers are formed preferentially (radical p.)

Deriving the copolymerization equation

$[P^*]$=const.

$d[P_1^*]/dt = d[P_2^*]/dt$

$k_{12}\,[P_{1*}]\,[M_2] = k_{21}\,[P_{2*}]\,[M_1]$

$[P_{1*}]/[P_{2*}] = (k_{21}\,[M_1])/(k_{12}\,[M_2])$ eq.1

$-d[M_1]/dt = k_{11}\,P_1\,M_1 + k_{21}\,P_2\,M_1$
$-d[M_2]/dt = k_{22}\,P_2\,M_2 + k_{12}\,P_1\,M_2$

Reacted monomer = incorporated monomer unit

$m_1/m_2 = d[M_1]/d[M_2] = (k_{11}\,P_1\,M_1 + k_{21}\,P_2\,M_1)/(k_{22}\,P_2\,M_2 + k_{12}\,P_1\,M_2)$ eq.2

Combining eq. 1 and 2 + substitution for r_1 and r_2 $\mathbf{r_1 = \frac{k_{11}}{k_{12}}}$ $\mathbf{r_2 = \frac{k_{22}}{k_{21}}}$

$$\frac{[m_1]}{[m_2]} = \frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]}$$

Copolymerization equation

$$\frac{[m_1]}{[m_2]} = \frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]}$$

For copolymerization of monomers M_1 and M_2:

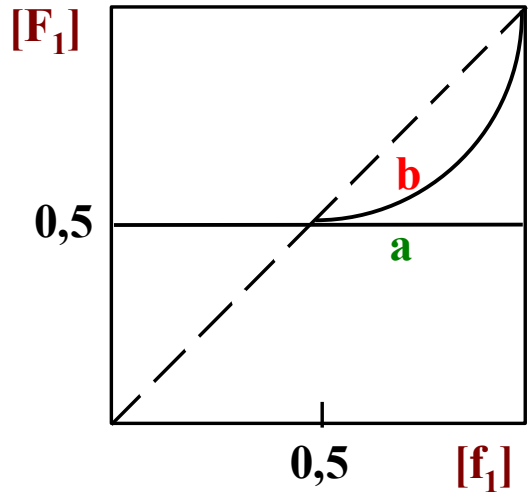
$[m_1]$, $[m_2]$ concentration of structural units of monomers M_1, M_2 in macromolecules of copolymer

$[M_1]$, $[M_2]$ instantaneous concentration of monomers M_1, M_2 in reaction feed

r_1, r_2 copolymerization parameters

Copolymerization diagrams

Alternating copolymerization, $r_1\ r_2 = 0$



F_1 molar fraction of structural units of monomer M_1 in copolymer

f_1 molar fraction of monomer M_1

Copolymerization diagram of alternating copolymerization

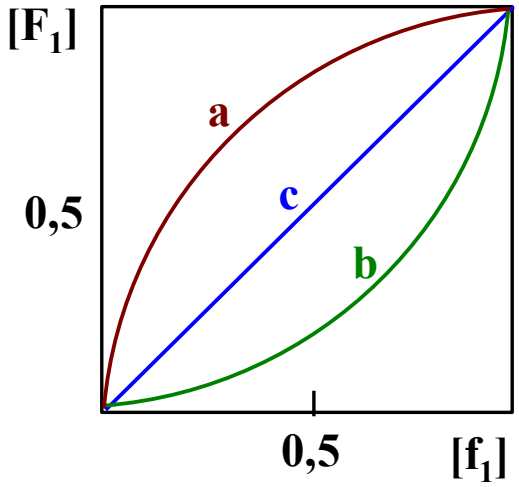
a) $r_1 = r_2 = 0$

b) $r_1 = 0.1$; $r_2 = 0$

$$F_1 = \frac{[m_1]}{[m_1]+[m_2]} \quad ; \quad f_1 = \frac{[M_1]}{[M_1]+[M_2]}$$

Ideal copolymerization, $r_1 r_2 = 1$

From condition $r_1 r_2 = 1$ follows:



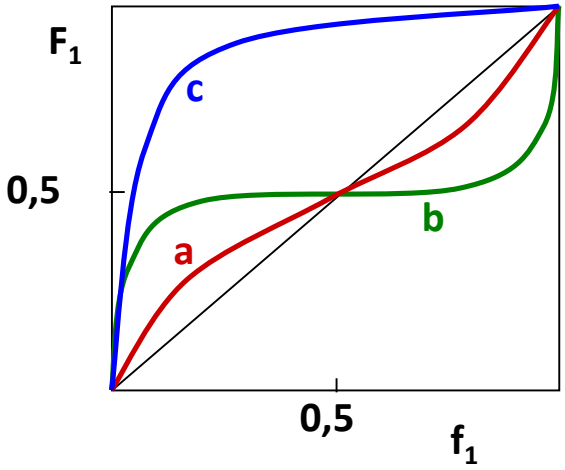
$$r_1 = \frac{1}{r_2}, \quad \Rightarrow \quad \frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}}$$

Copolymerization diagrams of ideal copolymerization

- **a) ideal non-azeotropical copolymerization $r_1 = 5$; $r_2 = 0.2$**
- **b) ideal non-azeotropical copolymerization $r_1 = 0.2$; $r_2 = 5$**
- **c) ideal azeotropical copolymerization $r_1 = r_2 = 1$**

Non-ideal copolymerization, $r_1\, r_2 \in (0;1)$

Mostly: $r_1 < 1$, $r_2 < 1$



Copolymeriztion diagrams of non-ideal copolymerization

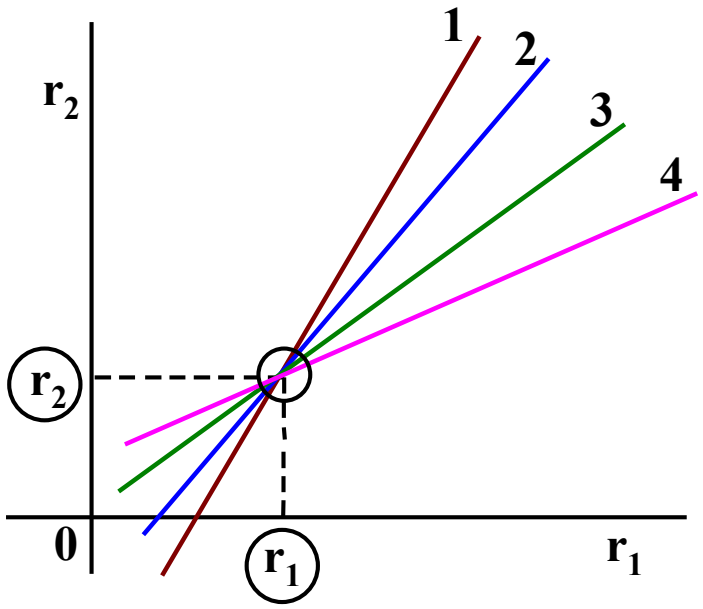
- **a) non-ideal azeotropical copolymerization $r_1 = 0{,}52$; $r_2 = 0{,}46$**
- **b) non-ideal azeotropical copolymerization $r_1 = 0{,}04$; $r_2 = 0{,}01$**
- **c) non-ideal non-azeotropical copolymerization $r_1 = 55$; $r_2 = 0{,}01$**

Determination of copolymerization parameters

Method: a) Mayo-Lewis
b) Fineman Rosse

a) $$r_2 = \frac{[M_1]}{[M_2]}\left(\frac{[m_2]}{[m_1]} - 1\right) + r_1\left(\frac{[M_1]}{[M_2]}\right)^2 \frac{[m_2]}{[m_1]}$$

For set of $[M_1]/[M_2]$ and $[m_2]/[m_1]$ data, we choose r_1 and calculate r_2

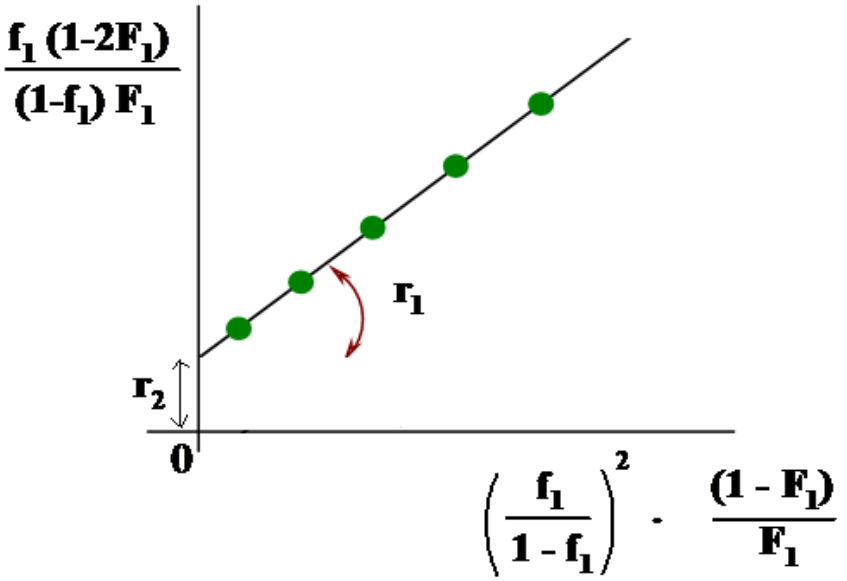


Determination of copolymerization parameters

b) $$\underbrace{\frac{f_1\,(1-2F_1)}{(1-f_1)\,F_1}}_{y} = r_2 - r_1 \underbrace{\left(\frac{f_1}{1-f_1}\right)^2 \cdot \frac{(1-F_1)}{F_1}}_{x}$$

f_1=molar fraction of units M_1 in monomer mixture

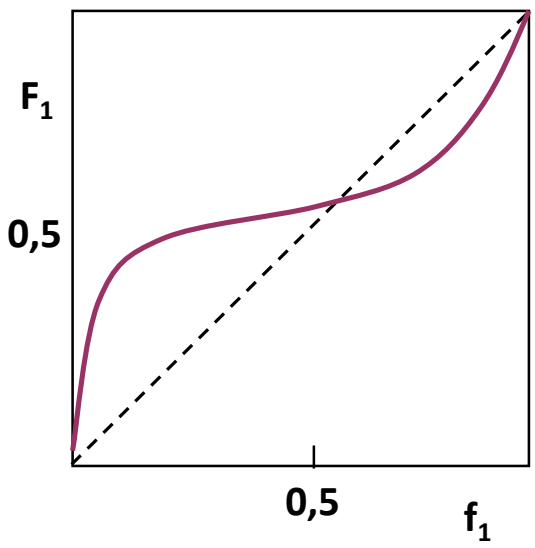
F_1=molar fraction of units M_1 in copolymer

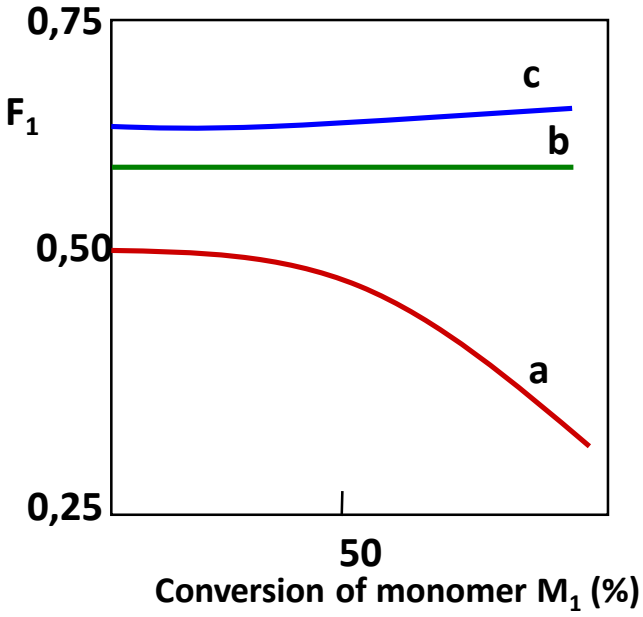


Conversion and copolymer composition

e.g..: Styrene - acrylonitril $r_1 = 0{,}4$

M_1 M_2 $r_2 = 0{,}04$





Dependence of average composition of styrene (M_1)–acrylonitrile (M_2) copolymer on conversion of M_1. Composition of reaction feed: a) 30 mol% M_1
b) 61 mol% M_1
c) 70 mol% M_1

Sequence length in copolymer

Average length of sequence of M_1 units: $\overline{l_1}$

$$\overline{l_1} = \frac{1}{p_{12}} \qquad p_{12} = \frac{v_{12}}{v_{12} + v_{11}}$$

Probability of addition of M_2 to P_1·

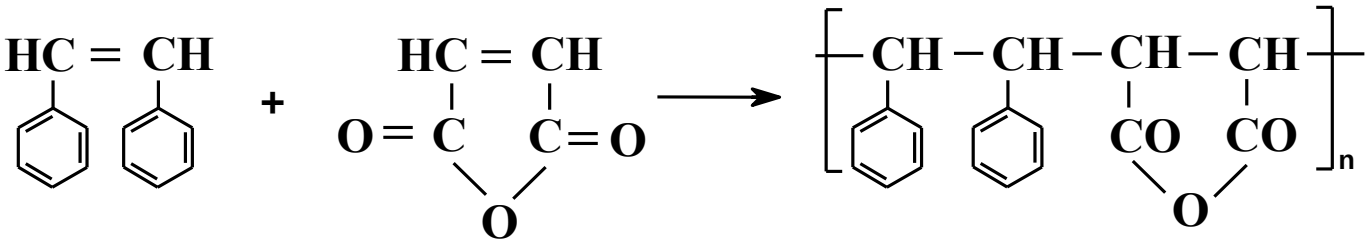
$$\overline{l_1} = \frac{k_{12}\,[P_1\cdot]\,[M_2] \;+\; k_{11}\,[P_1\cdot]\,[M_1]}{k_{12}\,[P_1\cdot]\,[M_2]} = 1 + r_1\,\frac{[M_1]}{[M_2]}$$

Stabilization of radicals

Example: Copolymerization of styrene (M_1) with various monomers (M_2):

Monomer M_2	$k_{12}.10^{-2}$ (l.mol^{-1}s^{-1})	k_{21} (l.mol^{-1}s^{-1})
methylmethacrylate	3.4	12.5
Methyl acrylate	2.3	116
Vinyl acetate	0.03	9500

Polarization effects:



Q-e scheme

- for evaluation of reactivity of a monomer independently on comonomer

Simplified assumption:

$k_{12} = P_1 Q_2 \exp(-e_1 e_2)$ $\quad$ $k_{11} = P_1 Q_1 \exp(-e_1)^2$

and analogously for k_{21} a k_{22}.

From definition of copolymerization parameters

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

it follows:

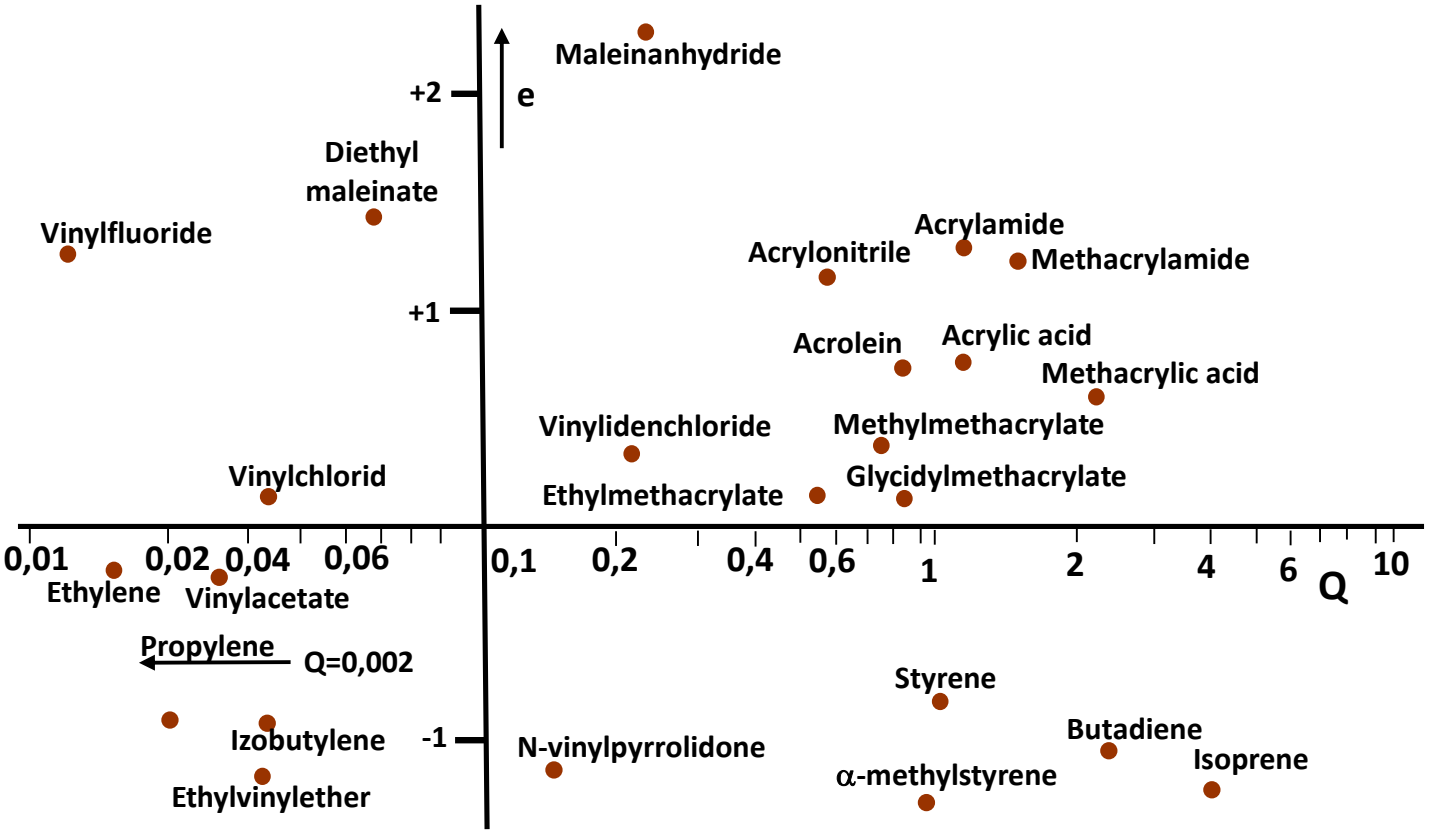
$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)] \qquad r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)]$$

Q – measure of resonance stabilization, e – measure of monomer polarization

Styrene as a standard: values Q = 1,00 and e = - 0,8

Q and e values for another monomers calculated and tabelated

Q-e scheme


Maleinanhydride
+2
e
Diethyl
maleinate
Vinylfluoride
Acrylamide
Acrylonitrile
Methacrylamide
+1
Acrolein
Acrylic acid
Methacrylic acid
Vinylidenchloride
Methylmethacrylate
Vinylchlorid
Ethylmethacrylate
Glycidylmethacrylate
0,01
0,02
0,04
0,06
0,1
0,2
0,4
0,6
1
2
4
6
10
Q
Ethylene
Vinylacetate
Propylene
Q=0,002
Styrene
Butadiene
Izobutylene
-1
N-vinylpyrrolidone
Isoprene
α-methylstyrene
Ethylvinylether

1. Draw the copolymerization diagram for pair of monomers buta-1,3-diene (M_1) and styrene (M_2), if r_1=1.39 and r_2=0.78

2. Derive the form of copolymerization equation for copolymerization in azeotropical point. Calculate azeotropical composition of monomer mixture (wt. %) for copolymerization of tetrafluorethene (M1) and ethene (M2), if r_1=0.85 and r_2=0.15.

([M_1]=95.3 wt %, [M_2]=4.7 wt%)

3.What will be the composition of a copolymer formed at low conversion of monomers that are in equimolar ratio in a feed, if

a) r_1=0.1 r_2 = 0.2
b) r_1=0.1 r_2=10
c) r_1=0 r_2=0
d) r_1=1 r_2=15

4. Calculate the copolymerization parameters of methyl-acrylate and styrene if at styrene concentration 0.7 mol% in the feed forms a copolymer containing 3.6 mol% of styrene units in the initial phase of copolymerization, at styrene concentration 24 mol% in the feed azeotropic copolymer is formed.
(r_1=0.18, r_2= 0.74)