Polymer chemistry and macromolecular engineering
Fall 2024
Assignment 5

1. Consider the following monomer reactivity ratios for the copolymerization of several different pairs of monomers:

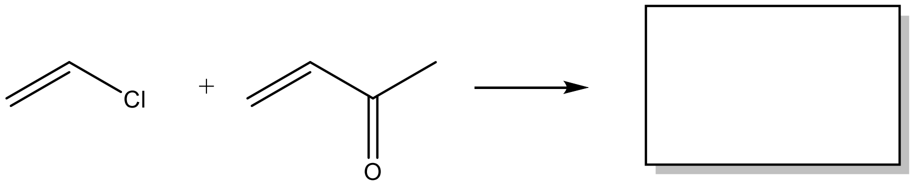
Case	r_1	r_2
1	0.1	0.2
2	0.1	10
3	0.1	3
4	0	0.3
5	0	0
6	0.8	2
7	1	15

What is the composition of the copolymer that would be formed at low conversion from equimolar mixtures of the two monomers in each case? What can you say about the microstructure of the copolymers that are formed?

Case	r_1	r_2	F_1: percentage monomer 1	r_1r_2: microstructure
1	0.1	0.2	0.478	0.02 alt
2	0.1	10	0.091	1 ideal
3	0.1	3	0.216	0.3 “ideal”
4	0	0.3	0.435	0 alt
5	0	0	0.500	0 alt
6	0.8	2	0.375	1.6 “ideal”
7	1	15	0.111	15 block

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad f_1 = f_2 = 0.5$$

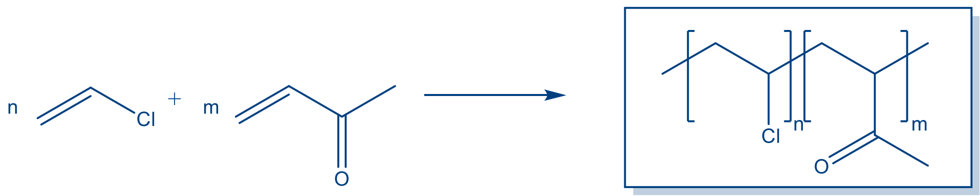
2. Two equivalent volumes of methyl vinyl ketone and vinyl chloride are polymerized via free radical chain polymerization at 70 °C.



density:	0.911 g/mL	0.841 g/mL
molecular weight:	62.5 g/mol	70.1 g/mol

a) Draw the structure of the copolymer.
b) What is the mole fraction of methyl vinyl ketone and vinyl chloride in the copolymer given that their reactivity ratios are 8.3 and 0.1, respectively, under a steady-state assumption?
c) Which type of copolymer is obtained from the copolymerization of these two monomers?
d) How could a random copolymer, which contains equimolar quantities of the two monomers be obtained? Explain.

a.



b.

$$Methyl\ vinyl\ ketone: x * \frac{0.841}{70.1} = 0.01199x\ mol\ \rightarrow 12.0x\ mmol$$

$$Vinyl\ chloride: x * \frac{0.911}{62.5} = 0.01458x\ mol\ \rightarrow 14.6x\ mmol$$

As “x” is the same volume used for methyl vinyl ketone and vinyl chloride:

$$f1 = \frac{12.0}{12.0 + 14.6} = 0.45$$

$$f2 = \frac{14.6}{12.0 + 14.6} = 0.55$$

$$\frac{F1}{F2} = \frac{f1(r1f1 + f2)}{f2(r2f2 + f1)}$$

$$\frac{F1}{F2} = \frac{0.45(8.3 * 0.45 + 0.55)}{0.55(0.1 * 0.55 + 0.45)} = \frac{0.45 * 4.285}{0.55 * 0.505} = \frac{1.93}{0.28}$$

$F_1 = 0.87$, $F_2 = 0.13$

c. $r_1 > 1$, i.e. M_1 prefers to homopolymerize. $r_2 < 1$ – i.e. M_2 prefers to cross-propagate. The result is a gradient block copolymer.

d. Consider a random copolymer with $F_1 = F_2$

$$\frac{F_1}{F_2} = \frac{f_1(r_1 f_1 + f_2)}{f_2(r_2 f_2 + f_1)}$$

$$1 = \frac{f_1(8.3 f_1 + f_2)}{f_2(0.1 f_2 + f_1)} = \frac{8.3{f_1}^2 + f_1 f_2}{0.1{f_1}^2 + f_1 f_2}$$

$$0.1{f_2}^2 + f_1 f_2 = 8.3{f_1}^2 + f_1 f_2$$

$$0.1{f_2}^2 = 8.3{f_1}^2$$

$$0.012{f_2}^2 = {f_1}^2$$

$$0.11 = \frac{f_1}{f_2}$$

It is possible to vary the concentration of the monomers. The co-polymerization of methyl vinyl ketone and vinyl chloride with a molar feed ratio of 1 to 9.09 would lead to a random copolymer.

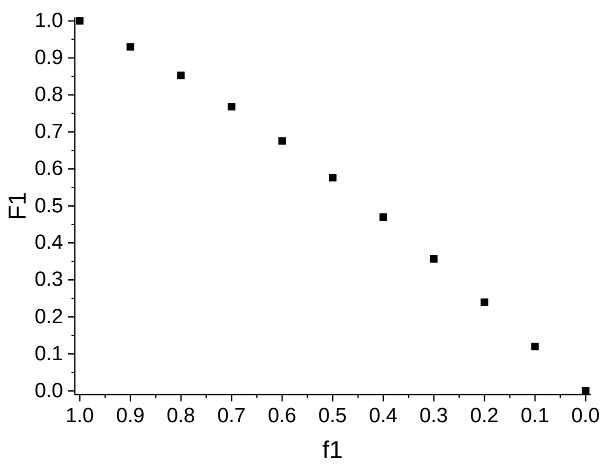
3. Draw plots of the initial composition of copolymers prepared via radical polymerization for the following sets of co-monomer. What type of copolymers are these?
   a) Acrylonitrile ($r_1 = 1.5$) and methyl acrylate ($r_2 = 0.84$):
   b) Acrylonitrile ($r_1 = 0.02$) and styrene ($r_2 = 0.29$):

a)

$$\frac{F1}{F2} = \frac{f1(r1f1 + f2)}{f2(r2f2 + f1)}$$

Replace the molar fractions f1 and f2 with random values to obtain F1 and plot.

a) $r_1 * r_2 = 1.5 * 0.84 = 1.26$ “ideal” copolymer



b) $r_1 * r_2 = 0.02 * 0.29 = 0.0058$ alternating copolymer