

Chapter II

ラジカル共重合、リビングラジカル重合、界面重縮合

—連鎖重合、リビング重合、逐次重合の代表例として—

Radical Copolymerization, Living Radical Polymerization, and Interfacial

Polycondensation

-As Representatives of Chain-Growth Polymerization,

Living Polymerization, and Step-Growth Polymerization-

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1. Introduction

Polymers constitute widely used materials such as plastics, rubbers, and fibers, which are indispensable in our daily lives. The properties of a polymer depend not only on the structures of its constituent monomers but also on characteristics such as the polymer chain length, chain-end groups, stereochemistry, monomer composition, and monomer sequence (Figure 1). Therefore, it is possible to tune the polymer properties by various means to achieve desired functionality for their applications.

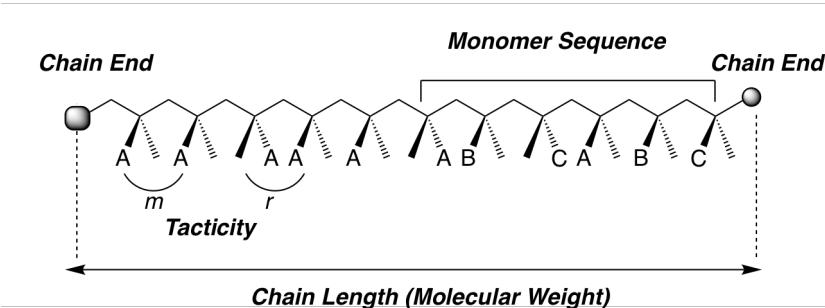


Figure 1. Primary structures of vinyl polymers.

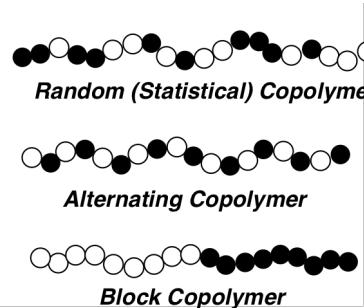


Figure 2. Various copolymers.

There are various polymerization methods and they are categorized into two large families, namely, chain-growth polymerization and step-growth polymerization. Radical polymerization is one of the most extensively used chain-growth polymerizations in laboratories and industries and produces various general purpose resins because it allows efficient polymerization or copolymerization of a wide variety of vinyl monomers into high-molecular-weight polymers even under mild conditions. In this section, you will learn about radical copolymerization, which enables the synthesis of copolymers with diverse properties, and living radical polymerization, which allows control over the molecular weight of the resulting polymers. In addition, you will study interfacial polycondensation, which is one of the most efficient step-growth polymerization methods to synthesize high-molecular-weight polyamide or nylon.

1.1 Radical Copolymerization (Chain-Growth Polymerization)

Copolymerization is useful for preparing polymers with tunable properties depending on the comonomer compositions and sequences. Copolymers can be subdivided into different categories based on the monomer sequence distributions and architectures, such as random (statistical) copolymers, alternating copolymers, and block copolymers (Figure 2). As the properties of the copolymers depend on the comonomer compositions and sequence distributions, it is important to have knowledge of the structures of the copolymers as well as the means to control copolymerization for an efficient design of the polymer materials.

Radical polymerization is the most effective strategy for the synthesis of various copolymers from almost all vinyl monomers because of the highly reactive radical propagating species. The

comonomer compositions and distributions depend on the electronic and steric factors of the comonomers as well as their feed ratios. If comonomer reactivities in radical copolymerization are known, the comonomer compositions and distributions can be predicted.

The main purpose of the first part of this exercise is therefore directed toward measuring comonomer reactivity ratios in the radical copolymerization of methyl methacrylate and styrene.

1.2 Living Radical Polymerization (Living Polymerization)

In chain-growth polymerizations, including radical polymerization, there are essentially four elementary reactions, *i.e.*, initiation, propagation, termination, and chain transfer. The rates of the four reactions determine the molecular weights and their distributions of the resulting polymers. It is worth noting that the termination and chain transfer steps make it difficult to control the molecular weight in chain-growth polymerization.

However, living polymerization, which is free from termination and chain transfer, allows for control over the chain lengths and chain-end groups of the polymers (Figure 3). In living polymerization, all chains generated via initiation can continue their propagation because of the absence of termination and chain transfer. Therefore, the molecular weight increases in direct proportion to monomer conversion and agrees with the calculated value, assuming that one molecule of initiator generates one polymer chain. Accordingly, the molecular weight distribution is narrow and obeys the Poisson distribution theoretically. In addition, living polymerization enables a precise synthesis of well-defined polymers, such as end-functional polymers, block copolymers, and star polymers, which are utilized as functional materials.

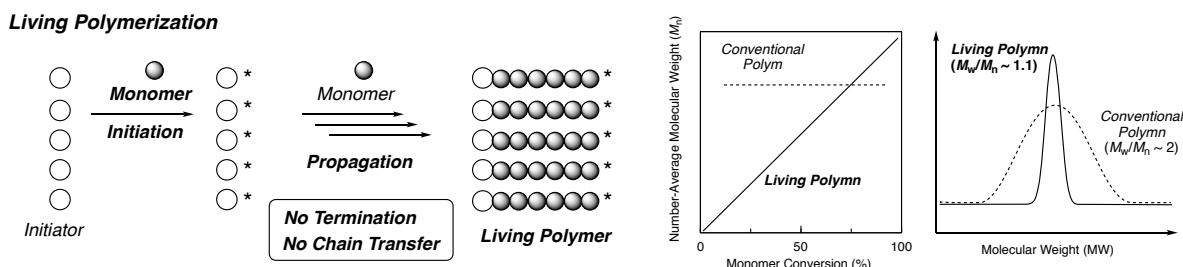
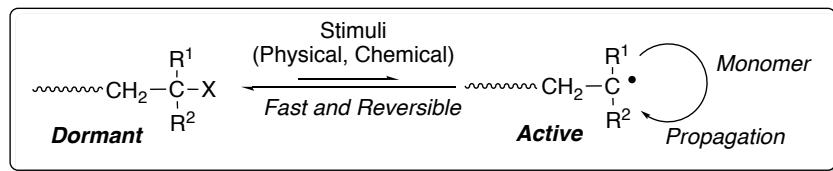


Figure 3. Living polymerization.

Living radical polymerization was discovered in the 1990s by introducing dormant species that are in equilibrium with the propagating radical species (Figure 4). Among the various living radical polymerization systems, nitroxide-mediated polymerization (NMP) is the simplest and based on the reversible thermal activation of alkoxyamine ($\text{C}-\text{ON}$) into the propagating radical and stable nitroxide radical.

In the second part, you will conduct living radical polymerization using an alkoxyamine and differentiate between conventional and living radical polymerizations.



Nitroxide-Mediated Polymerization (NMP)

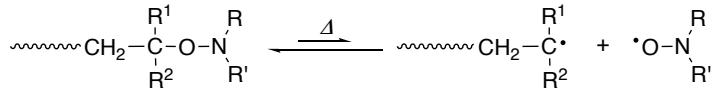


Figure 4. Living radical polymerization and nitroxide-mediated polymerization (NMP).

1.3 Interfacial Polycondensation (Step-Growth Polymerization)

Polycondensation is a typical step-growth polymerization, which proceeds via repetitive condensation reactions between two functional groups at the chain ends of the monomers and the resulting oligomers and polymers. Engineering plastics such as polyesters, polyamides, and polycarbonates are usually prepared via polycondensation. To produce high-molecular-weight polymers by polycondensation, the two functional groups should be generally stoichiometric because they react at the 1:1 molar ratio. However, if you use the interfacial polymerization method, you can easily obtain the high-molecular-weight polyamide.

In the third part, you will perform interfacial polycondensation of hexamethylenediamine and sebacoyl chloride.

2. Experiments

This section describes the radical copolymerization of methyl methacrylate (MMA) and styrene (St) using 2,2'-azobisisobutyronitrile (AIBN) to evaluate the monomer reactivity ratios and living radical polymerization in the presence of a nitroxide (2,2,6,6-tetramethylpiperidine 1-oxyl, TEMPO) to compare the molecular weights obtained by conventional and living radical polymerizations.

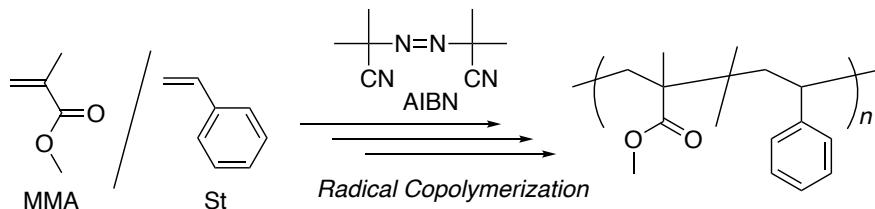
Caution: The reaction conditions are different for each group. Check the table given below.

The obtained dates are shared with other groups to calculate the monomer reactivity ratios.

Group	Feed Ratio		Amount			
	MMA	St	MMA	St	AIBN Solution*	St-TEMPO Solution*
A	8	2	3.59 mL (33.6 mmol)	0.97 mL (8.40 mmol)	1.34 mL (AIBN: 0.06 mmol)	1.34 mL (St-TEMPO: 0.42 mmol)
B	7	3	3.14 mL (29.4 mmol)	1.45 mL (12.6 mmol)		
C (F)	5	5	2.25 mL (21.0 mmol)	2.41 mL (21.0 mmol)		
D (G)	3	7	1.34 mL (12.6 mmol)	3.38 mL (29.4 mmol)		
E	2	8	0.90 mL (8.40 mmol)	3.86 mL (33.6 mmol)		

*These solutions are prepared by the teaching assistant (TA).

2-1. Radical Copolymerization of MMA and St



Polymerization

The following procedure is for Group C. Change the amounts according to the table if you are not in Group C.

Add MMA (2.25 mL, 21.0 mmol), St (2.41 mL, 21.0 mmol), and the AIBN solution (1.34 mL of 44.8 mM in toluene, 0.06 mmol) to a test tube with a magnetic stir bar using a micropipette. Then, seal the test tube with a rubber septum. Place the tube in a 0 °C bath, and evacuate and refill it with N₂ gas three times. This step is performed by the TA. Ask the TA for help after you have prepared the solution. After degassing the test tube, place it in a stirring 80 °C oil bath and note the time. After 30 min, take out the test tube from the oil bath and place it in a 0 °C bath to quench the polymerization.

Isolation

Add methanol (180 mL) to a 500 mL beaker with a magnetic stir bar. Pipette the quenched solution dropwise slowly into methanol under stirring. The polymer should precipitate out of the solution. Filter the solution with a Buchner funnel and suction flask. Dissolve the obtained solid with CHCl₃ (6 mL). Pipette the solution dropwise slowly into 180 mL of methanol again under stirring. Filter the solution with a Buchner funnel and a suction flask. Weigh the obtained products. Submit the polymer to the TA, who will perform size-exclusion chromatography (SEC) and measure the ¹H NMR of the sample later.

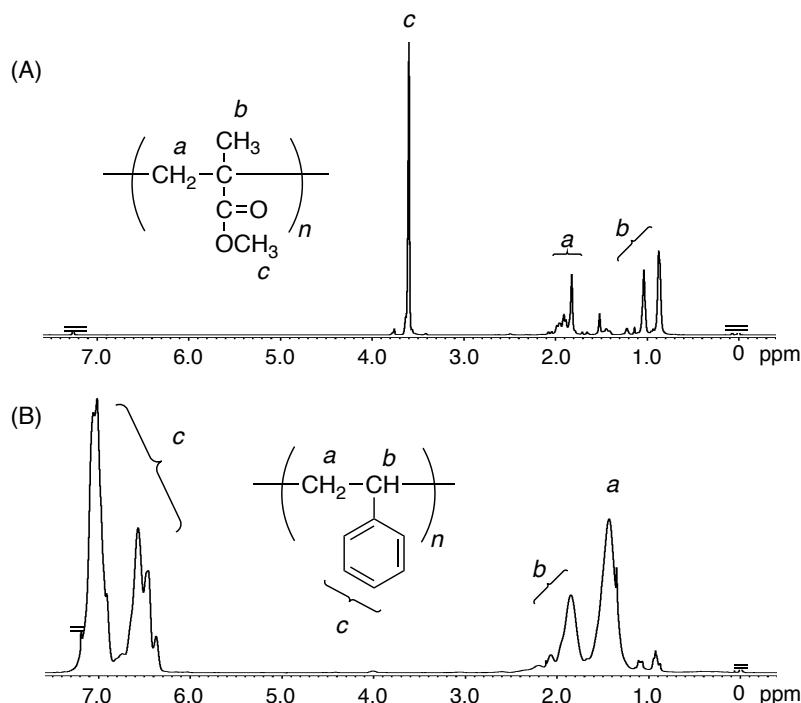
Answer the following questions:

1. Calculate the yield of the copolymer.
2. Assign each signal in the ¹H NMR spectra to the corresponding proton of the copolymer structures by referring to the ¹H NMR spectra of the homopolymers (Figure 5).
3. Calculate the copolymer composition of the product using the integral ratios of MMA and St units in the ¹H NMR spectra. (Share the obtained composition with the other groups for the next question.)
4. Calculate the monomer reactivity ratios (r_1 and r_2) using the Fineman-Ross method.
5. Draw a copolymer composition curve using the obtained monomer reactivity ratios and plot the experimental data. Compare the obtained values with the reported ones.
6. If you are interested, calculate the monomer reactivity ratios using the Kelen-Tüdös method

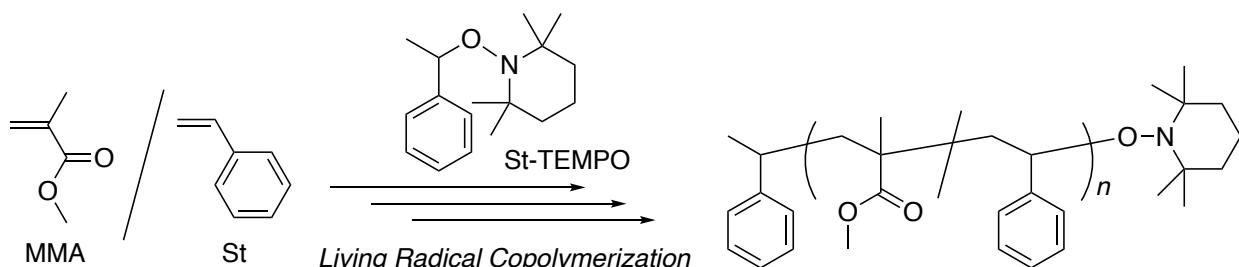
and compare the results with those obtained using the Fineman-Ross method.

7. What is a requirement for alternating copolymerization in terms of the monomer reactivity ratios?

Suggest a combination of monomers to obtain alternating copolymers in radical copolymerization.



2-2. Nitroxide-Mediated Living Radical Copolymerization of MMA and St



Polymerization

The following procedure is for Group C. Change the amount according to the table if you are not in Group C.

Add MMA (2.25 mL, 21.0 mmol), St (2.41 mL, 21.0 mmol), and the St-TEMPO solution (1.34 mL of 313 mM St-TEMPO in toluene, St-TEMPO: 0.42 mmol) to a test tube with a magnetic stir bar using a micropipette. Then, seal the test tube with a rubber septum. Place the tube in a 0 °C bath, and evacuate and refill it with N₂ gas three times. *This step is performed by the TA. Ask the TA for help after you have prepared the solution.* After degassing the test tube, place it in a stirring 120 °C oil bath and note the time. After 24 h, take out the test tube from the oil bath and place it in a 0 °C bath to quench the polymerization.

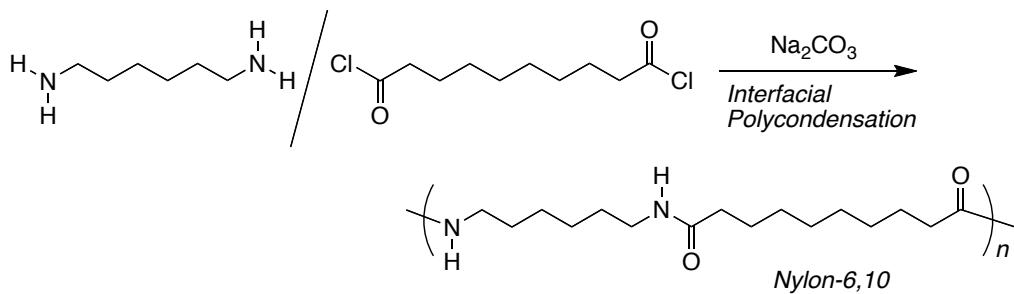
Isolation

Dilute the quenched solution with CHCl₃ (4 mL). Add methanol (240 mL) to a 500 mL beaker with a magnetic stir bar. Pipette the diluted solution *dropwise slowly* into methanol under stirring. The polymers should precipitate out of the solution. Filter the solution with a Buchner funnel and suction flask. Weigh the obtained products. Submit the obtained polymer to the TA, who will measure the SEC of the sample later.

Answer the following questions:

1. Calculate the theoretical molecular weight of the obtained polymers under the specified conditions using the yield of the copolymer.
2. Compare the molecular weight obtained by SEC with the theoretical value. Additionally, compare the molecular weight and its distribution with those obtained by free radical copolymerization in 2-1.
3. Describe the initiation and propagation steps in this living radical polymerization.

2-3. Interfacial Polycondensation of Hexamethylenediamine and Sebacoyl Chloride



Polymerization and Isolation

Add Na₂CO₃·10H₂O (2.5 g) and hexamethylenediamine (2.0 g, 17 mmol) to a 100 mL beaker. Dissolve the solids with distilled water (50 mL).

Add carbon tetrachloride (50 mL) and sebacoyl chloride (5.0 mL, 23 mmol) to another 500 mL beaker.

Ask the TA to watch the following procedures after you have prepared the solutions.

Carefully add the aqueous solution of hexamethylenediamine to the CCl₄ solution of sebacoyl chloride *attempting to not mix the two layers by tilling the beaker of the aqueous solution slightly and pouring the solution down the side of the beaker along a stirring rod*.

At the interface, the reaction should occur with one of the products being nylon. Use forceps to pull the nylon from the interface and wind the polymer around the stirring rod vertically from the center of the beaker as shown in Figure 6. Continue to wind the polymer onto the stirring rod. When all of the nylon has been collected, put the polymer into the large glass container of water

to wash. Leave the polymer in the water for 10 min, remove it, and allow the polymer to dry overnight under air. Weigh the obtained products.

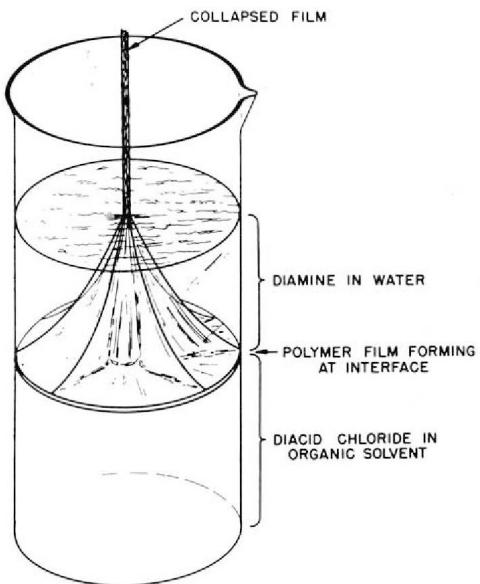


Figure 6. Polyamide film being removed from interface (*J. Chem. Educ.* **1959**, *36*, 182–184).

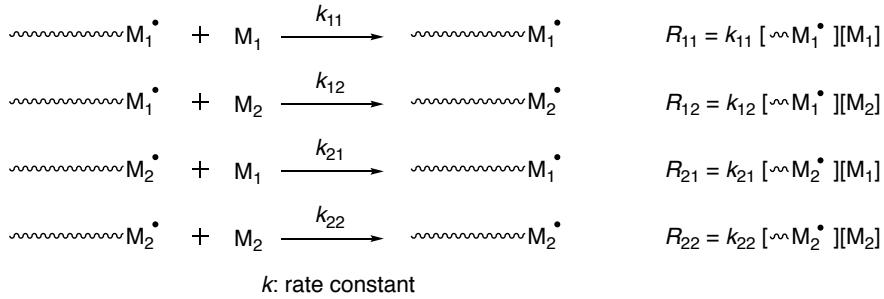
Answer the following questions:

1. Calculate the yield of the polymer.
2. Suggest a mechanism of this polymerization.
3. Why is the nylon formed at the interface?
4. Why does the polycondensation proceed well to result in the high-molecular-weight polymer even though the two components are nonstoichiometric?

3. Appendix

3-1. Copolymer Composition Equation and Monomer Reactivity Ratio in Terminal Model

The simplest model to analyze statistical copolymerization is the terminal model, in which the propagation rates are determined by the concentrations of the monomer and terminal monomer unit at the propagating radical. According to this model, the propagations in radical copolymerization of two monomers (M_1 and M_2) can be described by the following four equations.



The rates of each monomer consumption are determined by equations (1) and (2).

$$-\frac{d[M_1]}{dt} = k_{11}[\sim M_1^\bullet][M_1] + k_{21}[\sim M_2^\bullet][M_1] \quad (1)$$

$$-\frac{d[M_2]}{dt} = k_{12}[\sim M_1^\bullet][M_2] + k_{22}[\sim M_2^\bullet][M_2] \quad (2)$$

Then, the ratio of the rates at which the two monomers enter the copolymer, *i.e.*, the instantaneous copolymer composition, is described as in equation (3).

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[\sim M_1^\bullet][M_1] + k_{21}[\sim M_2^\bullet][M_1]}{k_{12}[\sim M_1^\bullet][M_2] + k_{22}[\sim M_2^\bullet][M_2]} \quad (3)$$

Assuming a steady state whereby the concentrations of the two propagation radical species are constant, the rates of interconversion between the two radicals must be equal.

$$k_{21}[\sim M_2^\bullet][M_1] = k_{12}[\sim M_1^\bullet][M_2] \quad (4)$$

Equation (3) can be rearranged and combined with equation (4) to give equation (5):

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left(\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right) \quad (5)$$

where r_1 and r_2 are the monomer reactivity ratios, as defined below.

$$r_1 = \frac{k_{11}}{k_{12}} \quad (6) \quad r_2 = \frac{k_{22}}{k_{21}} \quad (7)$$

Equation (5) is known as the copolymer composition equation (Mayo-Lewis equation) that shows the instantaneous copolymer composition ($d[M_1]/d[M_2]$) at a certain monomer concentration. This equation implies that the copolymer composition can be predicted if the monomer reactivity ratios and monomer concentrations are known.

3-2. Determining Monomer Reactivity Ratios Using Fineman-Ross Method

To determine the monomer reactivity ratios experimentally, the copolymerization reactions are carried out by varying the monomer feed ratio of M_1 and M_2 . The copolymer compositions are measured for the products obtained at a low conversion (<10%), where the monomer concentrations ($[M_1]$ and $[M_2]$) are approximated to the initial ones ($[M_1]_0$ and $[M_2]_0$).

The Mayo-Lewis equation (5) can be rearranged as equation (8), where $F = [M_1]/[M_2]$ and $f = d[M_1]/d[M_2]$ refer to the monomer feed ratio and polymer composition ratio, respectively.

$$f = F \left(\frac{r_1 F + 1}{F + r_2} \right) \quad (8)$$

Equation (8) can be further rearranged as follows.

$$\frac{F(f - 1)}{f} = \frac{F^2}{f} r_1 - r_2 \quad (9)$$

Equation (9) shows a linear function of $F(f-1)/f$ to F^2/f , in which r_1 and $-r_2$ are the slope and intercept, respectively. This method is called the Fineman-Ross method. The monomer reactivity ratios, r_1 and r_2 , can be obtained by plotting and fitting the experimental data into a linear relationship using the least-squares method. The fitting can be further improved by the Kelen-Tüdös method.

Figure 6 shows several representative copolymer composition curves, which are obtained by plotting the incorporation ratio of M_1 in the produced copolymers against the monomer feed ratio of M_1 . Thus, the copolymer composition at a given monomer feed can be predicted using the monomer reactivity ratios.

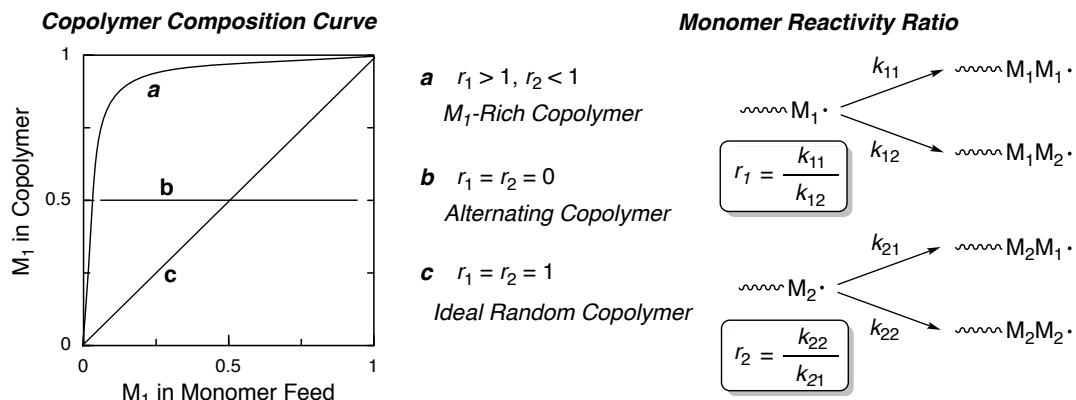


Figure 6. Representative copolymer composition curves with different monomer reactivity ratios.

4. References

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