# **Experiment 3**

# **Radical Copolymerization of Styrene and Methyl**

# Methacrylate

In the polymerization of a mixture of two or more monomers, the rates at which different monomers add to the growing chain determine the composition and hence the properties of the resulting copolymer. The order as well as the ratio of amounts in which monomers add are determined by their relative reactivities in the chain-growth step, which in turn are influenced by the nature of the end of the growing chain, depending on which monomer was added previously. Among the possibilities are random and regular addition as well as block formation.

In condensation copolymerization, the reactivities of functional groups are often independent of other considerations and the results are trivial: Random addition occurs in the same ratio as the concentrations of the monomers in the mixture. The situations for free-radical and other types of chain polymerization are similar, and the following discussion is limited to the free-radical case.

With two monomers present, there are four possible propagation reactions, assuming that growth is influenced only by the nature of the end of the growing chain and of the monomer:

$$M_1 \bullet + M_1 \longrightarrow M_1 \bullet \qquad (a)$$

1

1

k22

$$M_1 \bullet + M_2 \xrightarrow{k_{12}} M_2 \bullet \tag{b}$$

$$M_2 \bullet + M_1 \xrightarrow{K_{21}} M_1 \bullet \qquad (c)$$

$$M_2 \bullet + M_2 \longrightarrow M_2 \bullet$$
 (d)

With the definition of reactivity ratios  $r_1 = \frac{k_{11}}{k_{12}}$  and  $r_2 = \frac{k_{22}}{k_{21}}$  and the

application of the steady-state assumption, one can derive a copolymer equation relating the instantaneous composition of copolymer being formed,  $\frac{d[M_1]}{d[M_2]}$  to the monomer

concentrations in the feed:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])}$$
(1)

The reactivity ratios  $r_1$  and  $r_2$  are ratios of the rate constants for a given radical adding its own monomer to that for the same radical adding the other monomer. A value of r > 1 means that the radical prefers to add its own monomer, and vice versa.

Copolymerizations are classified according to values of the product  $r_1 r_2$ . When  $r_1r_2 = 0$ , neither monomer radical will add its own monomer, and propagation can continue only by adding first one, then the other monomer to produce an alternating copolymer. A more usual case is  $0 < r_1 r_2 < 1$ , with both reactivity ratios less than one.

When 
$$r_1 r_2 = l$$
, the copolymerization is said to be ideal, since  $r_1 = \frac{1}{r_2}$  and each radical

shows the same preference for one of the monomers. The sequence of monomers in the copolymer is completely random, determined only by the composition of the comonomer feed. When one reactivity ratio is greater than unity, the copolymer contains a larger proportion of the more reactive monomer, and as the difference in reactivity of the two

monomers increases, it becomes more and more difficult to produce copolymers containing appreciable amounts of both monomers.

It has become apparent in recent years that the methods used to analyze experimental results may have a strong influence on the magnitudes and reliability of reactivity ratios calculated from binary copolymerizations.

In principle, the measurement of reactivity ratios appears to be straightforward provided the equation linking feed and copolymer compositions fits the data obtained by analyzing the compositions of copolymers formed from several different concentrations of monomers. If a differential form of the copolymer equation (1) is used with initial feed composition values, it is necessary to keep the total conversion to polymer in each experiment less than about 5 per cent so as to minimize the drift of copolymer makeup. Ten or more per cent of the monomers can be converted to polymer in a single run without significant calculation error if the arithmetic averages of the final and initial monomer concentrations are used in these differential copolymer equations. The extent of reaction at which this procedure becomes unreliable depends on the relative magnitudes of the reactivity ratios, except, of course, for the case of azeotropic feed mixtures. This expedient is safe in general so long as the concentration of each unreacted monomer is linearly related to reaction time. Alternatively, it is quite feasible to fit the experimental feed and polymer compositions to an integrated form of the copolymer Equation (1), although the calculations are slightly more cumbersome than with the differential form.

The fitting of corresponding feed and copolymer compositions to the copolymer Equation (1) to obtain reactivity ratio values is not without pitfalls. Many of the available

 $r_1$  and  $r_2$  values in the literature are defective because of unsuspected problems, which are involved in estimation procedures, use of inappropriate mathematical models to link polymer and feed compositions and experimental or analytical difficulties.

Two procedures for extracting reactivity ratios from differential forms of the copolymer Equation (1) are mentioned in the following paragraphs. These methods are arithmetically correct but they do not give reliable results because of the nature of the experimental uncertainties in reactivity ratio measurements.

The *method of intersections*<sup>1</sup> has been widely used for computing reactivity ratios from data fitted to the differential copolymer Equation (1). In this procedure, Equation (1) is recast into the form:

$$r_{2} = \frac{[M_{1}]}{[M_{2}]} \left[ \frac{d[M_{1}]}{d[M_{2}]} \left( 1 + \frac{[M_{1}]}{[M_{2}]} r_{1} \right) - 1 \right]$$
(2)

Corresponding experimental values of  $[M_1]$ ,  $[M_2]$ ,  $d[M_1]$  and  $d[M_2]$  are substituted into Equation (2) and  $r_2$  is plotted as a function of assumed values of  $r_1$ . Each experiment yields one straight line in the  $r_1r_2$  plane and the intersection region of such lines from different feed composition experiments is assumed to give the best values of  $r_1$  and  $r_2$ . The same basic technique may be applied to the integrated form of the copolymer Equation (1). The intersection point, which corresponds to the "best" values of r1 and r2, is selected imprecisely and subjectively by this technique. Each experiment yields a straight line and each such line can intersect one line from every other experiment. Thus

*n* experiments yield  $\frac{n(n-1)}{2}$  intersections and even one "wild" experiment produces

(n-1) unreliable intersections. Various attempts to eliminate subjectivity and reject dubious data on a rational basis have not been successful.

Alternatively<sup>2</sup> the simple copolymer Equation (1) can be solved in a linear

graphical manner by substituting  $x = \frac{[M_1]}{[M_2]}$ ,  $y = \frac{d[M_1]}{d[M_2]}$  so that Equation (1) becomes:

$$y = x \frac{1 + r_1 x}{r_2 + x}$$
(3)

Equation (3) can be linearized in the alternative form:

$$G = \frac{x(y-1)}{y} = r_1 F - r_2 \tag{4}$$

where  $F = \frac{x^2}{y}$ . Linear least squares fits to Equation (4) yield one reactivity ratio as the

intercept and the other as the slope of the plotted line. The experimental data are however unequally weighted by these equations and the values obtained at low  $[M_2]$  in Equation (4) have the greatest influence on the slope of a line corresponding to these equations. Equation (4) is also not symmetrical in  $r_1$  and  $r_2$ .

#### A. Polymerization

The reactivity ratios  $r_1$  and  $r_2$  will be determined for the copolymerization of methyl methacrylate (MMA) and styrene (Sty). The following data are given for styrene and methyl methacrylate.

	Styrene	Methyl Methacrylate
ρ (g/mL)	0.909	0.936
Mw (g/mol)	104.15	100.12
Q	1.00	0.74
е	-0.80	0.40

Table 1: Physical parameters for styrene and methyl methacrylate.

**Safety Considerations**: Dangerous chemicals are used in this experiment. AIBN (2,2'azodiisobutyronitrile) is highly toxic and the monomers are toxic and irritant as well as highly flammable. Adequate ventilation is essential (always work under the fumehood). Safety glasses must be worn in the laboratory at all times.

 Five solutions will be prepared with styrene molar compositions of 40mole%, 60mole%, 70mole%, 80mole% and 100mole. Add 20mL of monomers to the 50mL round bottom flasks according to Equations (5) and (6).

$$m_{sty} = \frac{20 \times x \times Mw(Sty)}{\frac{(1-x) \times Mw(MMA)}{r_{MMA}} + \frac{x \times Mw(Sty)}{r_{Sty}}}$$
(5)

$$m_{MMA} = \frac{20 \times (1 - x) \times Mw(MMA)}{\frac{(1 - x) \times Mw(MMA)}{r_{MMA}} + \frac{x \times Mw(Sty)}{r_{Sty}}}$$
(6)

where *x* is the styrene mole% (0 < x < 1).

- 2. Further add 20mg of initiator AIBN to each flask.
- 3. Since oxygen is a powerful inhibitor, the solutions are degassed by bubbling nitrogen for 20 minutes. The round bottom flasks are fitted with a rubber septum, which is then pierced with one long needle and one short needle. The long needle dips into the solution and ensures that nitrogen bubbles through the mixture. The short needle has its tip above the solution and ensures that nitrogen can exit the flask. The five samples are degassed simultaneously (ask demonstrator).
- 4. While the samples are degassing, prepare five water baths at  $70^{\circ}$ C.
- 5. When the degassing is over, remove *first* the short needle, and then the long one from the flask. Keep the long needle attached to the tube so that the pressure does not drop inside the other flasks.
- Put the flasks in the 70°C waterbaths at approximately three minutes intervals. Stagger the starts of the reaction times so you can remove and chill the samples one at a time.
- 7. After reacting for twenty minutes, the samples are removed from the waterbaths and are cooled immediately in an icebed.
- 8. The polymers are precipitated by pouring the mixtures into 300 mL methanol.
- 9. The solids are recovered by filtration on a Buchner funnel.

- The solids are redissolved in approximately 10mL of HPLC grade tetrahydrofuran (THF) and the solutions reprecipitated into about 50 mL of HPLC grade methanol.
- 11. The solids are filtered again on a Buchner funnel. The recovered solids are washed with some distilled water to remove remaining traces of methanol and THF.
- The samples are placed in 20mL scintillation flasks in a preheated 70<sup>o</sup>C oven for 30 minutes.

### B. <u>UV/Vis Spectroscopy</u>

The styrene content of each sample is estimated by absorption measurements. Methyl methacrylate does not absorb in the UV (at 240-280nm) where styrene absorbs (cf. Figure 1). Thus an absorption spectrum of each copolymer sample yields the styrene concentration of the solution. From the knowledge of the weight content of the copolymer solution, it is possible to estimate the molar fractions of styrene and methyl methacrylate that have been incorporated into the copolymer.

- 1. 10mg of each copolymer sample is dissolved in 10mL of **HPLC grade** THF. The exact weights of the copolymers must be recorded. The polymer samples must be completely dissolved before carrying out any absorption measurement. Use the small stirrer bars to ensure complete dissolution.
- An absorption spectrum of each solution is taken from 200nm to 350nm on a Beckman 640B spectrophotometer (ask TA for assistance). A blank of the pure THF is taken before scanning the copolymer sample for background correction.
- 3. For each sample, the absorption at 270nm (Abs(270nm) is the styrene absorption) is recorded as well as the absorption at 350nm (Abs(350nm) is some residual

absorption resulting from the background correction). The quantity Abs(270nm)-Abs(350nm) is taken as the real absorption of the solution at 270nm.



Figure 1: Absorption spectrum of a polystyrene solution in THF with a styrene concentration equal to  $9.5 \times 10^{-3} \text{ molL}^{-1}$ .

4. The styrene concentration can be estimated by using the Beer-Lambert law which states that:

$$Abs(\mathbf{l}) = \mathbf{e}(\mathbf{l}) C L \tag{7}$$

where  $\mathbf{e}(\lambda)$  is the extinction coefficient (expressed in M<sup>1</sup>cm<sup>-1</sup>) of the chromophore (styrene) at the considered wavelength  $\mathbf{I}$ , C is the chromophore concentration (in molL<sup>-1</sup>) and L in the optical path length of the cuvette (expressed in cm, L=1cm). Since the polymer weight of the solution made of pure polystyrene is known as well as the molar mass of styrene (104.15gmol<sup>-1</sup>), the styrene molar concentration of the solution is also known. The absorption spectrum yields the absorption of this solution at 270nm. Combining [*Sty*] with *Abs*(270nm) in Equation (7) yields  $\mathbf{e}_{Sty}(270nm)$ .  $\mathbf{e}_{Sty}(270nm)$  can be used to estimate the styrene concentration of all other copolymer solutions.

5. The fraction of styrene that has been incorporated into the copolymer is calculated using Equation (8) for each copolymer sample.

$$x = \frac{M_{MMA}}{\frac{m}{V} \frac{\boldsymbol{e}_{Sty}(270\,nm)}{Abs(270\,nm)} + M_{MMA} - M_{Sty}}$$
(8)

where m is the polymer mass and V is the THF volume used to make the polymer solution.

### Discussion

- 1. Explain and derive Equations (5), (6) and (8).
- 2. Use the *Linear Method* (Equation (4)) to estimate the reactivity ratios for the copolymerization of styrene with methyl methacrylate using styrene as  $M_1$  and methyl methacrylate as  $M_2$ .

3. Using the Q and e values listed in Table 1 for styrene and methyl methacrylate, calculate  $r_1$  and  $r_2$  for the copolymerization of these two monomers and compare these values to those obtained experimentally. Comment on the reasons for discrepancies, if any.

### References

- (1) F.R. Mayo and F.M. Lewis J. Am. Chem. Soc. **1944**, 66, 1594.
- (2) M. Fineman and S.D. Ross J. Polym. Sci. 1950, 5, 269.

Apparatus 10mL pipette rubber bulb 5x50mL round bottom flask with 19/26 joints 5xcrystallization dishes 2x600mL beakers 400mL beaker rubber septa 5 medium sized stirrers 5 small stirrers 1 Buchner funnel 1 filter adapter 1 filtering flask with hose connection 5 long needles 5 short needles rubber tubing 2 ice buckets scintillation flasks pair of tweezers spatula Chemicals

distilled in glass THF HPLC grade methanol AIBN styrene methyl methacrylate

