reaction was a simple condensation reaction.

Gamma irradiation (Co 60, 1500 Cu) of the chelated and unchelated polymers at a dose rate of 0.35 Mrad/hr up to a total dose of 85.1/Mrads at room temperature in air produced essentially no change in the esr signal, thus demonstrating the exceptional resistance of these polymers to high energy radiation. While there was practically no change in the viscosity in the high molecular weight polymer the viscosity of the low molecular weight polymer in one case had increased by 100%.

Acknowledgment. The authors thank Professor C. S. Marvel for the continuing interest and advice in this work. They also appreciate the stimulating discussions with Dr. Anton Peterlin. They are indebted to Mr. R. Fava for most of the conductivity measurements and the Langley Research Center of the National Aeronautics and Space Administration for the loan of the esr spectrometer. The support of this work by the Camille and Henry Dreyfus Foundation is gratefully acknowledged.

The Control of Copolymer Composition Distributions in Batch and Tubular Reactors

W. H. Ray and C. E. Gall

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada. *Received April 10, 1969*

ABSTRACT: In this paper, the problem of maintaining a specified copolymer composition distribution in a batch reactor is considered. The advantages of temperature control, rather than monomer addition are discussed, and the necessary and sufficient conditions for temperature control in the face of monomer depletion are derived. Examples are worked to illustrate the results for a practical range of temperatures.

In this paper we are considering the composition of a copolymer resulting from polymerization carried out in a batch or plug-flow tubular reactor. If the reactants are well mixed initially, the temperature is considered uniform in the reactor at every residence time, and the chain length is very long, then the composition of polymer produced at any instant in the reactor can be represented by[1]

$$F_1 = \frac{(r_1 - 1)f_1^2 + f_1}{(r_1 - r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2} \qquad (1)$$

where F_1 = mole fraction of monomer M_1 polymer, f_1 = mole fraction of monomer M_1 in solution = $M_1/(M_1 + M_2)$, r_1 = reactivity ratio of monomer $M_1 = k_{11}/k_{12}$, r_2 = reactivity ratio of monomer $M_2 = k_{22}/k_{21}$, and where the k_{ij} are the propagation rate constants for the propagation steps

$$P_{n,m} + M_1 \xrightarrow[k_{11}]{} P_{n+1,m}$$

$$P_{n,m} + M_2 \xrightarrow[k_{12}]{} Q_{n,m+1}$$

$$Q_{n,m} + M_2 \xrightarrow[k_{22}]{} Q_{n,m+1}$$

$$Q_{n,m} + M_1 \xrightarrow[k_{21}]{} P_{n+1,m}$$

where $P_{n,m}$ = concentration of growing polymer with terminal M_1 and $Q_{n,m}$ = concentration of growing polymer with terminal M_2.

Equation 1 has been integrated[2,3] for isothermal batch reactors with depletion of monomer to give the copolymer composition distribution (CCD) under these conditions. Except for the rare case where M_1 and M_2 disappear in such a way that f_1 remains constant, the CCD will not be monodisperse due to variations in f_1 with total monomer conversion. O'Driscoll and Knorr[3,4] aptly illustrate the CCD which can be expected in these cases.

If one wished to produce a polymer with monodisperse CCD, he could (i) add additional amounts of the most reactive monomer as the reaction progresses to maintain f_1 constant, or (ii) adjust the reactor temperature (which affects the values of r_1 and r_2) so as to keep F_1 constant in the face of changes in f_1. Control scheme i is quite simple conceptually and would only require careful addition of one monomer species, but suffers from the requirement that the added monomer must be perfectly mixed with the (often quite viscous) polymer in order to produce a monodisperse CCD. Any imperfections in the mixing will produce a widened CCD.[3,4] Control scheme ii is not as simple conceptually (as it requires the selection of a temperature at each f_1 to give the correct combination of r_1 and r_2 for constant F_1) and in fact will not always work for all systems. Nevertheless it has the enormous practical advantage that no material is added to the polymer so that only temperature uniformity is required at all times. Since it is much easier to design reactors for very viscous materials with good temperature control than with perfect micromixing, control scheme ii looks very attractive indeed.

In this paper we will first explore the range of values of F_1, f_1, over which temperature control is possible, then give simple graphical techniques for computing these parameters for each f_1, and finally treat some ex-

---

(1) I. Skeist, *J. Amer. Chem. Soc.*, **68**, 1781 (1946).

(2) V. Meyer and G. Lowry, *J. Polym. Sci., Part A*, 3, 2843 (1965).

(3) K. F. O'Driscoll and R. Knorr, *Macromolecules*, 1, 367 (1968).

(4) K. F. O'Driscoll and R. Knorr, paper presented at A.I.Ch.E. Meeting, Cleveland, Ohio, May 1969.

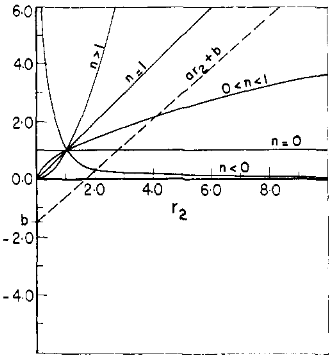

Figure 1. Graphical solution to eq 13.

amples from the literature to show the range of temperatures which might be required in practice.

Conditions for Temperature Control

In order to determine if temperature control is possible we must ask what conditions on r_1 and r_2 are required. Setting $F_1 = F_{10}$ and rearranging eq 1 we get the condition

$$r_1 = \delta(f_1, F_{10})r_2 + \beta(f_1, F_{10}) \tag{2}$$

which must be satisfied at constant F_{10} for all f_1. The quantities δ, β become

$$\delta(f_1, F_{10}) = \left(\frac{F_{10}}{1 - F_{10}}\right)\left(\frac{1 - f_1}{f_1}\right)^2 = \frac{\mathrm{h}(f_1)^2}{\mathrm{h}(F_{10})} \tag{3}$$

$$\beta(f_1, F_{10}) = \left(\frac{1 - 2F_{10}}{1 - F_{10}}\right)\left(\frac{1 - f_1}{f_1}\right) = -\{\mathrm{h}[\mathrm{h}(F_{10})]\}\mathrm{h}(f_1) \tag{4}$$

where h is defined by

$$\mathrm{h}(x) = \frac{1 - x}{x} \tag{5}$$

If we can find r_1, r_2 which satisfy eq 2 for all F_{10}, f_1 of interest, then temperature control is possible. However, we must first determine the relation between r_1, r_2 and temperature.

Let us assume the Arrhenius form for K_{ij} so that

$$K_{ij} = A_{ij} \exp\{-E_{ij}/RT\} \tag{6}$$

and

$$r_1 = \frac{A_{11}}{A_{12}} \exp\{-(E_{11} - E_{12})/RT\} \tag{7}$$

$$r_2 = \frac{A_{22}}{A_{21}} \exp\{-(E_{22} - E_{21})/RT\} \tag{8}$$

Now if we let $\Delta E_1 = E_{11} - E_{12}$, $\Delta E_2 = E_{22} - E_{21}$, $\alpha = \dfrac{\Delta E_2}{\Delta E_1}$, and $\tau = \dfrac{\Delta E_1}{RT}$

then

$$\frac{r_1}{r_{10}} = \exp(-[\tau - \tau_0]) \tag{9}$$

$$\frac{r_2}{r_{20}} = \exp(-\alpha[\tau - \tau_0]) \tag{10}$$

where r_{10}, r_{20} are the values of r_1, r_2 at the initial reactor temperature T_0. Combining eq 9 and 10 we get

$$\frac{r_1}{r_{10}} = \left(\frac{r_2}{r_{20}}\right)^{1/\alpha} = \exp(-[\tau - \tau_0]) \tag{11}$$

or

$$r_1 = \rho r_2^{\,n} \tag{12}$$

where

$$\rho = \frac{r_{10}}{(r_{20})^n}$$

($n = 1/\alpha$). We see that eq 12 now relates r_1 and r_2 and depends on the activation energies of the propagation steps. The existence of a simultaneous solution of eq 2 and 12 will then guarantee that temperature control is possible. That is, when the equation

$$r_2^{\,n} = ar_2 + b \tag{13}$$

where $a = \delta/\rho$, $b = \beta/\rho$, has a real positive solution, then temperature control is possible. Examination of a, b, n show that physically $0 < a < \infty$, $-\infty < b < \infty$, $-\infty < n < \infty$. In Figure 1, the existence of a solution to eq 13 is seen to be equivalent to the intersection of curves representing the left and right sides of eq 13. It is shown in the appendix that the necessary and sufficient conditions for eq 13 to have at least one real positive root are

$$\begin{array}{ll} n < 0 & \text{all } a \text{ and } b \text{ permitted} \\ 0 \le n < 1 & b \le a^{n/n-1}\left[\dfrac{1 - n}{(n)^{n/n-1}}\right] \\ n \ge 1 & b \ge a^{n/n-1}\left[\dfrac{1 - n}{(n)^{n/n-1}}\right] \end{array} \tag{14}$$

This indicates quite precisely the combination of parameters a, b, n for which temperature control is possible. An additional property which study of Figure 1 makes clear is that for $n > 1$ and $b < 0$ condition 14 being satisfied implies always two solutions to eq 13. Similarly for $0 \le n < 1$ and $b > 0$ two solutions to eq 13 exist if any exist. Thus single solutions exist only in the cases where $n > 1$, $b > 0$ and $n < 1$, $b < 0$ and we see from eq 14 that these last conditions are also sufficient.

Let us now indicate a simple graphical means of calculating the parameters a and b for each f_1 for fixed f_{10}, because eq 3 and 4 have the special form that uses only factors of the function h, then Figure 2 is all that is required for computing the coefficients a and b in eq 13. Curve 1 allows the calculation of $\mathrm{h}(F_{10})$ and b multiplied by the constant factor $-\rho/\mathrm{h}[\mathrm{h}(F_{10})]$. Curve 2 allows the calculation of a multiplied by the constant factor $\rho\mathrm{h}\cdot(F_{10})$. Thus Figure 2 shows explicitly the dependence of a and b on f_1, and we can quickly check to see if temperature control is possible.

Examples

In order to see what range of temperature is required, a few practical examples are worked.

i. **Example 1 ($n < 0$).** Mayo and Walling[5] report

---

(5) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

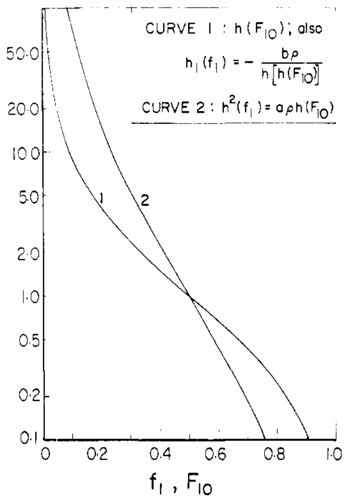

Figure 2. Graphical calculation of a, $h(F_{10})$, and b.

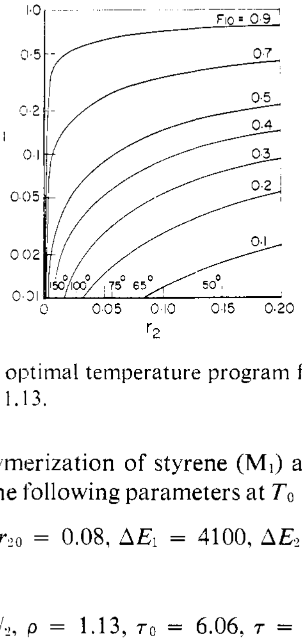

Figure 3. The optimal temperature program for example 1, $\alpha = -2.0$, $\rho = 1.13$.

for the copolymerization of styrene (M_1) and dichlorostyrene (M_2) the following parameters at $T_0 = 65°$

$$r_{10} = 0.32,\ r_{20} = 0.08,\ \Delta E_1 = 4100,\ \Delta E_2 = -8200$$

which lead to

$$n = -{}^1/_2,\ \rho = 1.13,\ \tau_0 = 6.06,\ \tau = 2050/T$$

Since $n < 0$, we know that temperature control is always possible, but we must determine for what values of f_1 it is practical. Let us assume $50° < T < 150°$ and determine the range of f_1 which can be compensated for. Rearranging eq 1 and solving for f_1 we get

$$f_1 = \{[2(r_2 - 1)F_{10} + 1] \pm ([2(r_2 - 1)F_{10} + 1]^2 - 4F_{10}r_2[(F_{10} - 1)\rho r_2^n + F_{10}(r_2 - 2) + 1])^{1/2}\}/\{2[(F_{10} - 1)\rho r_2^n + F_{10}(r_2 - 2) + 1]\} \quad (15)$$

which was used to construct Figure 3. For a selection of F_{10} values the range of possible f_1 which can be compensated for with temperature within the limits given above is shown. For example, if it is desired to keep $F_{10} = 0.7$, then the range $0.11 \leq f_1 \leq 0.40$ can be exactly compensated for by temperature control with $50° \leq T \leq 150°$.

ii. Example 2 ($n > 0$). When $n > 0$, in addition to having a single solution to eq 13, there is the possibility of having either no solutions or two solutions. In the former circumstance, temperature control is impossible and in the latter we have a choice between two temperature control policies. Mayo and Walling[6] report for the system dichlorostyrene–acrylonitrile the following parameters at $T_0 = 65°$

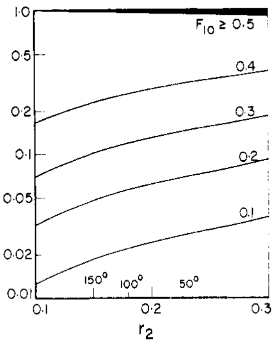

Figure 4. The optimal temperature program for example 2 $\alpha = {}^1/_3$, $\rho = 0.118$.

$$r_{10} = 0.07,\ r_{20} = 0.21,\ \Delta E_1 = -3300,\ \Delta E_2 = -1100$$

which lead to

$$n = 3,\ \rho = 0.118,\ \tau_0 = -4.88,\ \tau = -1650/T$$

By solving eq 15 for several values of F_{10}, we can generate the curves shown in Figure 4. From the curves we see that for $F_{10} \geq 0.5$ only values of f_1 very close to 1.0 can be compensated for within the temperature range $50° \leq T \leq 150°$. However, for $F_{10} < 0.5$, the behavior is much like the previous example; *e.g.*, for $F_{10} = 0.3$ the range $0.10 \leq f_1 \leq 0.15$ can be exactly compensated for.

It is perhaps worth noting that Figures 3 and 4 are a useful way to analyze specific copolymerization systems because they show explicitly F_1 as a function of temperature and monomer composition.

Summary

We have shown the necessary and sufficient conditions for maintaining a monodisperse CCD in a batch or tubular reactor through temperature control and have illustrated through examples what the optimal temperature control policy should be. Although the use of eq 14 makes things very precise, some rules of thumb can be extracted.

i. A single temperature for each f_1 is always guaranteed for

$$(F_{10} < 0.5,\ n > 1),\ (F_{10} > 0.5,\ 0 \leq n < 1),$$

and for (all F_{10}, $n < 0$).

ii. Either two temperatures or no temperature for each f_1 (depending on eq 14) is the result when ($F_{10} > 0.5, n > 1$), or ($F_{10} < 0.5, 0 \leq n < 1$).

The results presented here are also useful for applications where it is desired that the CCD have a certain specified polydisperse composition. In this case, both f_1 and F_{10} will be functions of residence time—f_1 through the monomer disappearance equations and F_{10} from the CCD specifications. The required temperature policy could then be calculated from the above equations.

Finally, the problem of maintaining a specified CCD (possibly monodisperse) as closely as possible when the temperature calculated from the equations above is beyond practical bounds (*e.g.*, $T < 50°$, or $T > 150°$) can

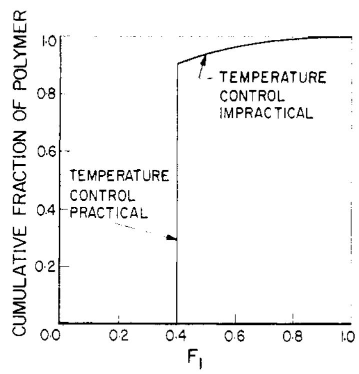

Figure 5. The copolymer composition distribution when complete compensation is impractical.

be treated, by picking the initial monomer concentrations so that the greatest volume of polymer is produced in the region where temperature compensation is possible. Figure 5 illustrates the shape of the CCD in this case when a monodisperse polymer is desired.

Although the temperature variations proposed will tend to widen the molecular weight distribution (MWD), it is felt that this temperature control scheme has great practical advantage for control of copolymerization reactors when MWD effects are not critical and the required heat transfer is allowed for at the design stage.

Appendix

Let us determine the conditions under which eq 13 has positive real solutions. Let

$$g(r_2) = r_2^n - ar_2 - b \qquad (16)$$

Since

$$g'(r_2) = nr_2^{n-1} - a \qquad (17)$$

$$g''(r_2) = n(n-1)r_2^{n-2} \qquad (18)$$

we can now determine the character of $g(r_2)$.

i. $n < 0$**.** In this case $g(0) \rightarrow \infty$, $g(r_2 \rightarrow \infty) \rightarrow -\infty$, $g''(r_2) > 0$ (*i.e.*, g is strictly convex) so that there is one and only one root to eq 16 when $n < 0$.

ii. $0 \leq n < 1$**.** In this case $g(0) = -b$

$$\lim_{r_2 \rightarrow \infty} g(r_2) \rightarrow -\infty$$

and g is strictly concave so that if $b < 0$, then there is one only one root to eq 16 and when $b \geq 0$ there is either zero or two roots to eq 16 depending on the value of $g(r_2)$ when it attains its maximum. The maximum value of $g(r_2)$ (gotten by setting eq 17 to zero) is given by

$$g_m = a^{n/n-1}\left[\frac{1-n}{(n)^{n/n-1}}\right] - b \qquad (19)$$

and thus $g_m \geq 0$ is required for 16 to have a solution.

iii. $n > 1$**.** In this case $g(0) = -b$

$$\lim_{r_2 \rightarrow \infty} g(r_2) \rightarrow +\infty$$

and g is strictly convex so that if $b > 0$ there is one and only one solution to eq 16. For $b \leq 0$ we must require the minimum value of g, eq 19, to be nonpositive for eq 16 to have a solution.

Acknowledgment. The authors are indebted to Mr. Amar Mohan for performing the calculations and to the Department of University Affairs of Ontario for research support.

Telomerization by Free Radical Mercaptan Chain Transfer. III. Chain Transfer Constants and Stereospecificity in the Methyl Acrylate–Ethanethiol System[1]

G. P. Scott and F. J. Foster

Department of Chemistry, University of South Dakota, Vermillion, South Dakota.
Received April 7, 1969

ABSTRACT: Previous determinations of methyl acrylate–ethanethiol chain transfer constants have been refined and extended to five-unit radicals. Values higher than C_1 are nearly constant and essentially equal to the average for long chains; therefore no reactivity minimum exists, and telomer addition steps are suitable kinetic models for polymerization. Three-unit diastereomers have been separated and quantitatively measured. The isotactic and syndiotactic mole fractions were found to be nearly equal and constant over wide ranges of monomer–mercaptan ratio and temperature, showing that the two modes of addition differ little in entropy and enthalpy of activation.

Studies of free-radical telomerization are useful in elucidating details of corresponding polymerizations. However the inherent advantage offered by direct observation of pure monodisperse fractions may be offset by complicating end-group effects unless these are thoroughly understood. This paper is concerned with application of the telomer approach to investigation of free-radical additions of methyl acrylate; at the outset it was thought that a serious complicating end-group effect might exist.

In 1964, rough measurements of the chain transfer constants for the first three methyl acrylate–ethanethiol

---

(1) Reported in part at the Midwest Regional Meeting of the American Chemical Society, Manhattan, Kansas, Nov 1968.