Branching by Copolymerization of Monovinyl and Divinyl Monomers in Continuous-Flow Stirred Reactors

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Synopsis

The effect on molecular weight distribution of copolymerization with divinyl monomers, which leads to branch points in an otherwise linear polymer, is calculated for a continuous-flow stirred reactor. It is found that steady state operation of the reactor becomes impossible at a degree of branching equal to only half that which causes gelation in a batch reactor. In steady state operation the ratio of weight to number average degree of polymerization cannot exceed 7, this ratio being 2 in the absence of branching. The classical result that the fraction of mers coupled at the gel point is $1/(\overline{DP}_w)_0$, where $(\overline{DP}_w)_0$ is the weight-average degree of polymerization without branching, does not apply in a CFSR at any steady state conversion. Such deviations appear in batch reactions only when gelation occurs at high conversions.
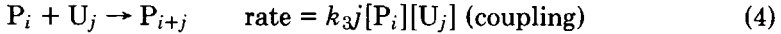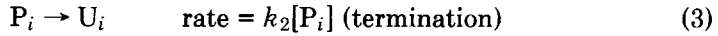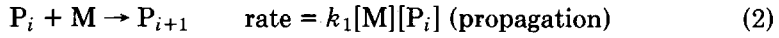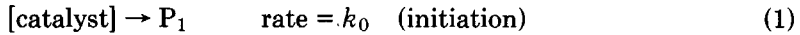
INTRODUCTION

Branching reactions during polymerization generally lead to a broadened molecular weight distribution and eventually, in some cases at least, to network formation. The relationships between distribution breadth, branching frequency, and conversion depend on the branching mechanism. They also depend on the type of polymerization reactor: different distributions are obtained in batch reactors (or plug-flow tubular reactors) and continuous-flow stirred reactors (CFSR). In a recent paper,[1] hereafter referred to as I, the equations describing tetrafunctional crosslinking of preformed polymers in a CFSR were presented. Comparisons were made with results for the same system in a batch reactor and for trifunctional branching by polymer transfer in a CFSR. The model in I did not consider polymerization which is discussed in this paper for the case of copolymerization with divinyl monomers. These results necessarily reduce to a most probable distribution of molecular weights ($\overline{M}_w/\overline{M}_n = 2$) in the absence of branching, and thus the flexibility with regard to initial distribution which appeared in I is lost. On the other hand, the linking statistics in the crosslinking and copolymerization causes are different. This produces some significant changes in the CFSR products, both in the distribution breadths attainable without gelation for steady state operation and in the relationship between gel point conversion and crosslinking density.

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ANALYSIS

We will consider the following set of reactions to represent copolymerization of difunctional and tetrafunctional (monovinyl and divinyl) monomers. All rates and concentrations are expressed in moles/volume:

$$[\text{catalyst}] \rightarrow P_1 \qquad \text{rate} = k_0 \quad \text{(initiation)} \tag{1}$$

$$P_i + M \rightarrow P_{i+1} \qquad \text{rate} = k_1[M][P_i] \quad \text{(propagation)} \tag{2}$$

$$P_i \rightarrow U_i \qquad \text{rate} = k_2[P_i] \quad \text{(termination)} \tag{3}$$

$$P_i + U_j \rightarrow P_{i+j} \qquad \text{rate} = k_3 j[P_i][U_j] \quad \text{(coupling)} \tag{4}$$

where $[P_i]$ = concentration of i-mer growing polymer molecules, $[U_i]$ = concentration of i-mer terminated polymer molecules, and $[M]$ = total monomer concentration. Coupling occurs when a growing chain adds the second double bond of a divinyl monomer which was incorporated earlier in another chain. The chains are large and assumed to contain many unreacted double bonds. Thus, the factor j appears in the coupling rate because the number of potential coupling sites on a terminated chain is proportional to its size, and k_3 is a composite constant proportional to the fraction of divinyl mers in terminated chains.

In the subsequent development of branching equations the following assumptions have been made:

(1) Reaction rate constants (k_1, k_2, and k_3) are independent of polymer size.

(2) Chain coupling gives a negligible depletion of enchained double bonds.

(3) The mean lifetime of the active species is very short so that $[U] \gg [P]$, where $[U]$ and $[P]$ are the terminated and active chain concentrations. This permits neglecting reactions between active species and the contribution of active species to the moments of the molecular weight distribution.

(4) All coupling reactions are intermolecular.

With the above assumptions and approximations, a material balance on each of the various species in a perfectly mixed CFSR with mean residence time θ gives the following equations:

$$\frac{d[M]}{dt} + \frac{[M] - [M]_0}{\theta} = -k_1[M] \sum_{i=1}^{\infty} [P_i] \tag{5}$$

$$\frac{d[U_i]}{dt} + \frac{[U_i]}{\theta} = k_2[P_i] - k_3 i[U_i] \sum_{j=1}^{\infty} [P_j] \tag{6}$$

$$\frac{d[P_1]}{dt} + \frac{[P_1]}{\theta} = k_0 - \left(k_1[M] + k_2 + k_3 \sum_{i=1}^{\infty} i[U_i] \right)[P_1] \tag{7}$$

$$\frac{d[P_i]}{dt} + \frac{[P_i]}{\theta} = k_1[M][P_{i-1}] - \left(k_1[M] + k_2 + k_3 \sum_{i=1}^{\infty} i[U_i] \right)[P_i]$$
$$+ k_3 \sum_{j=1}^{i-1} j[U_j][P_{i-j}] \tag{8}$$

in which eq. (6) applies for $i \geq 1$ and eq. (8) for $i \geq 2$. At steady state the time derivatives are zero. Equations for a batch reactor are obtained by setting the flow terms (those containing θ) equal to zero. The moments of U_i and P_i are defined as

$$Q_n = \sum_{i=1}^{\infty} i^n [U_i] \tag{9}$$

$$Y_n = \sum_{i=1}^{\infty} i^n [P_i] \tag{10}$$

and the average D.P.'s of the product polymer are

$$\overline{D.P._n} = \frac{Q_1 + Y_1}{Q_0 + Y_0} \approx \frac{Q_1}{Q_0} \tag{11}$$

$$\overline{D.P._w} = \frac{Q_2 + Y_2}{Q_1 + Y_1} \approx \frac{Q_2}{Q_1} \tag{12}$$

since $[U] \gg [P]$. Fractional conversion x is $([M]_0 - [M])/[M]_0$, which is equal to $Q_1/[M]_0$.

Expressions for the moments can be obtained from eqs. (6)–(8) by multiplying through by i^n and summing. For steady state in the CFSR

$$\frac{Q_n}{\theta} = k_2 Y_n - k_3 Q_{n+1} Y_0 \tag{13}$$

$$0 = \frac{Y_n}{\theta} = k_0 - [k_1[M] + k_2 + k_3 Q_1] Y_n + k_3 \sum_{j=1}^{\infty} \sum_{i=1}^{\infty} i(i+j)^n [U_i][P_j]$$
$$+ k_1[M] \sum_{i=1}^{\infty} (i+j)^n [P_i] \quad (14)$$

The expressions obtained with $n = 0, 1,$ and 2 can be combined with eqs. (11) and (12) to give equations for $\overline{D.P._w}$ and $\overline{D.P._n}$. When $k_3 = 0$ (no coupling), the chains are linear with most probable distribution. For this case

$$(\overline{D.P._n})_0 = \frac{k_1[M] Y_0}{k_0} \tag{15a}$$

$$(\overline{D.P._w})_0 = 2(\overline{D.P._n})_0 \tag{15b}$$

The rate of coupling is $k_3 Q_1 Y_0$, and the rate of mer consumption is $k_1[M] Y_0$. Thus, the fraction of mers which participate in crosslinks (two per couple) is

$$\alpha = \frac{2k_3 Q_1}{k_1[M]} = \frac{2k_3}{k_1} \frac{x}{1-x} \tag{16}$$

When eqs. (15) and (16) are used, and for $k_0 \ll k_1[M] Y_0$ (long primary chains), the following results are obtained for steady state:

$$\overline{D.P._n} = (\overline{D.P._n})_0 \frac{1}{1 - \alpha(\overline{D.P._n})_0/2} \tag{17}$$

$$\overline{D.P._w} = 2(\overline{D.P._n})_0 \left[1 + \frac{\alpha}{2} \overline{D.P._w}\right]^2 \tag{18}$$

Equation (18) can be solved for $\overline{D.P._w}$ to give

$$\overline{D.P.}_w = \frac{2[1 - (\alpha\overline{D.P.}_w)_0 - [1 - 2\,\alpha(\overline{D.P.}_w)_0]^{1/2}]}{\alpha^2(\overline{D.P.}_w)_0} \tag{19}$$

from which it is clear that real values of $\overline{D.P.}_w$ at steady state are obtained only when $\alpha(\overline{D.P.}_n)_0 \leq 1/4$. Based on the results in paper I, we conclude that when $\alpha(\overline{D.P.}_n)_0 > 1/4$, the reactor does not reach a steady state, and that gellation occurs at some finite time after start-up. As before, a maximum $\overline{D.P.}_w/\overline{D.P.}_n$ exists for steady state operation. Substituting $\alpha(\overline{D.P.}_n)_0 = 1/4$ in eqs. (17) and (19), we obtain

$$(\overline{D.P.}_w/\overline{D.P.}_n)_{\max} = 7$$

for copolymerization coupling. This is in contrast with the earlier results for linking of preformed chains having a most probable distribution, namely, $(D.P._w/D.P._n)_{\max} = 15/4 = 3.75$.

DISCUSSION

The branching mechanisms here and in paper I lead to significantly different relationships between branching density and molecular weight distribution. Although both mechanisms lead to tetrafunctional linking, there is a qualitative difference which is related to the probability of combination of chains. For the linking of preformed chains this probability is proportional to the product of the D.P.'s of the interacting chains. In the copolymerization case the probability is proportional to the D.P. of the previously terminated chain alone. This difference combined with the residence time distribution in a CFSR permits higher branching densities and broader distributions to be obtained at steady state in the copolymerization case. Thus, in the linking of preformed chains $[(\overline{D.P.}_w)_0/(\overline{D.P.}_n)_0 = 2]$, $(\overline{D.P.}_w/\overline{D.P.}_n)_{\max} = 15/4$ and $\alpha_{\max} = 1/(4\overline{D.P.}_w)_0$, while in copolymerization $(\overline{D.P.}_w/\overline{D.P.}_n)_{\max} = 7$ and $\alpha_{\max} = 1/(2\overline{D.P.}_w)_0$. In batch, $(\overline{D.P.}_w/\overline{D.P.}_n)_{\max}$ is theoretically unlimited in both mechanisms since the reaction can be stopped anywhere short of the gel point. At the gel point, $\alpha_{\max} = 1/(\overline{D.P.}_w)_0$ for the batch linking of preformed chains. For the batch copolymerization case the product $\alpha_{\max}(\overline{D.P.}_w)_0$ is practically unity if the gel point is reached at low conversions, but it decreases progressively if gellation is delayed to higher conversions.[3] Thus, the classical criterion for gellation,[2] $\alpha(\overline{D.P.}_w)_0 = 1$, is obeyed only in the batch linking of preformed chains. It is not even a good approximation for CFSR systems.

References

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