

Formation of homogeneously branched polymers using terminal double bond polymerization

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A method of synthesizing homogeneously branched polymers using long-chain branching through terminal double bond polymerization is considered theoretically. It was found that the homogeneously branched polymers can be obtained by conducting polymerizations that involve both creation and dissipation of terminal double bonds in a continuous stirred-tank reactor (CSTR). Because the analytical expressions for the full molecular weight distribution (MWD) as well as the fractional MWDs containing 0, 1, 2, etc., branch points can be determined, such polymer molecules are regarded as polymers with a well defined branched structure. When the same polymerization reactions are conducted in a batch reactor, or in a CSTR operated under non-steady state, the homogeneous structure cannot be formed. The heterogeneity in the distribution of branch points can make the weight-average molecular weight larger or smaller compared with the homogeneously branched polymers, depending on the branching density distribution even at the same average branching density level. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: random branching; molecular weight distribution; branching density distribution)

NOMENCLATURE

C_m	monomer transfer constant ($= k_{fm}/k_p$)	n_p	number fraction distribution of the primary polymer molecule
C_{fp}	polymer transfer constant ($= k_{fp}/k_p$, where k_{fp} is the rate constant for chain transfer to polymer)	$[P]$	total concentration of the live (active) polymer molecules
C_{fT}	transfer constant for chain transfer agent ($= k_{fT}/k_p$)	$P_{r,i}$	active polymer molecule that does not possess a terminal double bond with chain length r containing i branch points
C_β	parameter for the production of terminal double bonds by β -hydride elimination used in equation (48), ($C_\beta = k_\beta/(k_p [M]_0)$)	$P_{r,i}^-$	active polymer molecule that possesses a terminal double bond with chain length r containing i branch points
CTA, [CTA]	chain transfer agent and its concentration	$P_{connect}^*(\xi)$	probability that the chain end of a primary chain whose residence time is ξ is connected to a backbone polymer chain (equation (15))
$D_{r,i}$	dead polymer molecule that does not possess a terminal double bond with chain length r containing i branch points	$P_{react}^*(\xi)$	probability that the terminal double bond located on the primary chain whose residence time is ξ has reacted (equation (9))
$D_{r,i}^-$	dead polymer molecule that possesses a terminal double bond with chain length r containing i branch points	$P_a^*(\xi_B \xi_A)$	probability that the chain end of A (whose residence time is ξ_A) is connected to the backbone polymer chain B (whose residence time is between ξ_B and ξ_A , with $\xi_B < \xi_A$)
$E(\xi)$	residence time distribution (equation (24))	$P_i^*(\xi_C \xi_A)$	probability that the backbone polymer chain A (whose residence time is ξ_A) is connected to the branch chain C (whose residence time is between ξ_A and ξ_C , with $\xi_A < \xi_C$)
$F(\xi)$	cumulative distribution function of $E(\xi)$, i.e. $F(\xi) = \int_0^\xi E(\xi)d\xi$ (equation (13))	\bar{P}_N, \bar{P}_W	number- and weight-average chain lengths
K	terminal double bond reactivity ($= k_p^*/k_p$)	$\bar{P}_{N,k}, \bar{P}_{W,k}$	number- and weight-average chain lengths of the fractional MWD containing k branch points
k	number of branch points in a polymer molecule		
k_{fm}	rate constant for chain transfer to monomer		
k_{fT}	rate constant for chain transfer to chain transfer agent, CTA		
k_p	propagation rate constant		
k_p^*	rate constant for terminal double bond polymerization		
k_β	rate constant for β -hydride elimination		
$M, [M]$	monomer and its concentration		

$\bar{P}_{np}, \bar{P}_{wp}$	number- and weight-average chain lengths of the primary polymer molecules
Q_i	i th moment of the chain length distribution of the polymer molecules without a terminal double bond
Q_i^-	i th moment of the chain length distribution of the polymer molecules with a terminal double bond.
Q_i^T	i th moment of the chain length distribution, $Q_i^T = Q_i + Q_i^-$
R_p	polymerization rate
R_p^*	rate of the terminal double bond polymerization
r	chain length (degree of polymerization)
t	time
\bar{t}	mean residence time
$W(r)$	weight fraction distribution
$W_k(r)$	fractional weight-based chain length distribution containing k branch points
w_p	weight fraction distribution of the primary polymer molecules
x	monomer conversion
y	random number between 0 and unity
<i>Greek letters</i>	
δ	mole fraction of the terminal double bonds within the primary polymer molecules at the time of their formation, defined by equation (7)
θ	conversion at which the given primary polymer molecule was formed (batch polymerization)
ξ	reduced residence time, $\xi = t/\bar{t}$
ρ	branching density
$\bar{\rho}$	average branching density
$\bar{\rho}_k$	average branching density of the polymer molecules that contain k branch points
$\bar{\rho}_r$	average branching density of the polymer molecules whose chain length is r
Φ^-	fraction of the unreacted terminal double bonds within the monomeric units bound into polymer molecules
ϕ	ratio between the rate of chain transfer to chain transfer agent (CTA) and the propagation rate ($\phi = C_{fT}[CTA]/[M]$, equation (10))
ψ	conversion at the present time (for batch polymerization)

INTRODUCTION

As early as 1949, Zimm and Stockmayer¹ proposed the theoretical functional forms for the radius of gyration for several standard branched structures including homogeneously branched polymers whose primary polymer chains (chains obtained if all branch points were cut) conform to the most probable distribution. For example, suppose such homogeneously branched polymers are fractionated into a series of samples, each of a different but equal molecular weights. By using the average number of branch points per polymer molecule in a given fraction \bar{m} , the root-mean-square radius of gyration for the polymer fraction is given by¹:

$$\sqrt{\langle s^2 \rangle} = \sqrt{\langle s^2 \rangle}_{\text{linear}} \left\{ \left(1 + \frac{\bar{m}}{7} \right)^{0.5} + \frac{4\bar{m}}{9\pi} \right\}^{-0.25} \quad (1)$$

where $\sqrt{\langle s^2 \rangle}_{\text{linear}}$ is the root-mean-square radius of gyration for the linear polymer molecules whose number of segments is the same as the branched polymers. Equation (1) has been applied extensively to analyse polymers with long-chain branches, in particular, by size exclusion chromatography (s.e.c.).

Recently, another important property of homogeneously branched polymers have been revealed. The analytical solution for the full weight fraction distribution ($W(r)$) for the homogeneously branched polymers has been derived as follows^{2,3}:

$$W(r) = \left(\frac{1 - \rho \bar{P}_{np}}{\bar{P}_{np}} \right) \left(\frac{I_1 \left(2r \sqrt{\rho / \bar{P}_{np}} \right)}{\sqrt{\rho \bar{P}_{np}}} \right) \times \exp \left\{ - \left(\frac{\rho \bar{P}_{np} + 1}{\bar{P}_{np}} \right) r \right\} \quad (2)$$

where I_m is the modified Bessel function of the first kind and r is the chain length (degree of polymerization). Furthermore, the above equation can be fractionated by the number of branch points in each polymer to obtain the fractional weight-based distribution containing k branch points ($W_k(r)$) as shown below^{2,3}:

$$W_k(r) = \left(\frac{1 - \rho \bar{P}_{np}}{\bar{P}_{np}} \right) \exp \left\{ - \left(\frac{\rho \bar{P}_{np} + 1}{\bar{P}_{np}} \right) r \right\} \times \left(\frac{r}{\bar{P}_{np}} \right)^{2k+1} \frac{(\rho \bar{P}_{np})^k}{k!(k+1)!} \quad (3)$$

Obviously, $W(r)$ is given by:

$$W(r) = \sum_{k=0}^{\infty} W_k(r) \quad (4)$$

On the basis of the W_k function, very detailed structural information of the homogeneously branched polymer molecules were obtained², such as the number- and weight-average chain lengths of the polymers containing k branch points, the average branching density as a function of the number of branch points and that of the chain length. Because very detailed structural information can be obtained, the homogeneously branched polymer molecules can be regarded as polymers with a well defined branched structure. Such polymer molecules could be used as a polymer standard, for example, to prepare a calibration curve for the s.e.c. analysis for branched polymer molecules.

The problem is, however, how to synthesize such homogeneously branched polymers. In order for equations (1)–(3) to be valid, (a) the primary polymer chains must follow the most probable distribution, (b) the probability of possessing a branch unit must be the same for all units, and (c) each branch point is connected to any primary chain with equal probability, i.e. the primary chains must be connected randomly.

For example, consider a batch free-radical polymerization that involves chain transfer to polymers. Note that in this type of branch formation, the branch points are formed on the primary chains formed earlier. The primary chains formed in the earlier stages of polymerization are subjected to branching reactions for a longer period of time; therefore, the branching density of these chains would be larger than those formed in the later stages of polymerization. Such history-dependent

processes result in the formation of a heterogeneously branched structure⁴. This is a clear violation of the requirement (b).

Figure 1 shows the comparison of the distribution of branching density when the reduced average branching density is $\bar{\rho}/C_{fp} = 1$ for a free-radical polymerization that involves chain transfer to polymer. Here, C_{fp} is the polymer transfer constant, and $\bar{\rho}$ is the average branching density. When primary chains with different branching densities exist, we can distinguish the primary chains by the level of branching density. The y-axis shows the weight fraction of the primary polymer molecules whose branching density is smaller than ρ that is given by the value shown on the x-axis. In a batch polymerization, the conversion is set to be $x = 0.7968$ in order to give $\bar{\rho}/C_{fp} = 1$. The branching density of the primary chains formed right at $x = 0.7968$ is 0, because primary chains formed later do not exist. On the other hand, the primary chains formed at $x = 0$ are expected to possess the largest branching density, ρ_{max} , which can be identified by the x-axis value at which $W_{cum} = 1$. The batch polymerization produces primary chains with a wide variety of branching density levels, from 0 to ρ_{max} , as shown in Figure 1.

The calculated results for the continuous polymerization in a stirred-tank reactor (continuous stirred-tank reactor; CSTR) are also shown in Figure 1. Note that when we use the term 'CSTR' in the present report, we assume that the reactor is ideally micromixed and is under steady state, otherwise mentioned. Because the average branching density, $\bar{\rho}$ is set to be the same both for a batch reactor and a CSTR, the conversion level (x) is different. In the calculation, the primary chain lengths are assumed large enough to neglect the statistical deviations due to finite chain lengths (because the variance of the branching density of the primary chains is inversely proportional to the chain length). The fundamental equations to calculate the branching density distribution can be found elsewhere⁴. The branched polymer molecules formed in a CSTR possess a very large variation in branching density due to a large residence time distribution.

On the other hand, the use of a CSTR ensures that the primary chain length distribution follows the most probable distribution⁵ (requirement (a) is satisfied), provided bimolecular termination by combination is not involved and the probability of chain growth is independent of chain length (i.e. chain-length-dependent kinetics can be neglected). Therefore, if one chooses the reaction mechanism in which the probability of

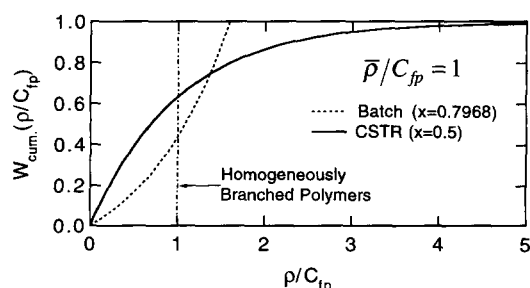


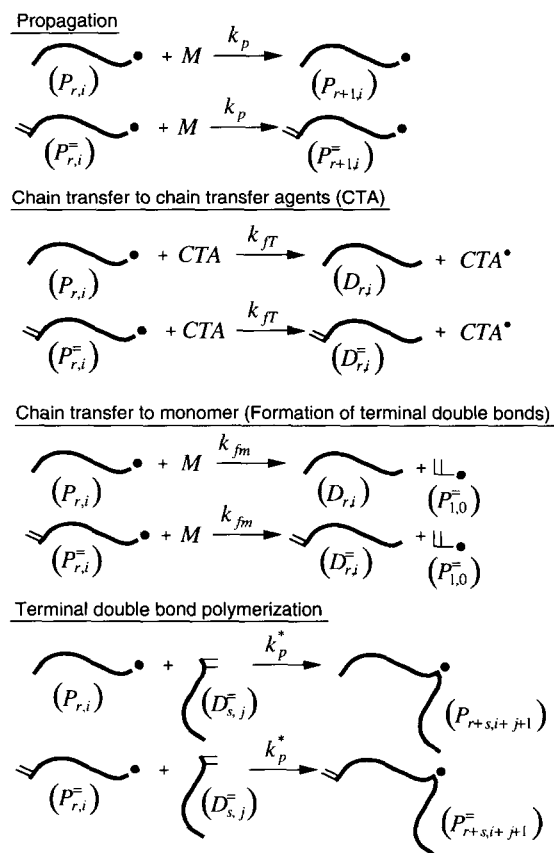
Figure 1 Distribution of branch points formed in a batch reactor and a CSTR as well as the homogeneously branched polymers. The y-axis shows the cumulative weight fraction of the primary polymer molecules whose branching density is smaller than ρ

incorporating branch points is the same along the primary chains, it would be possible to synthesize branched polymer molecules that satisfy the requirements (a) and (b) by using a CSTR.

Consider a polymerization system that involves both the production of active terminal double bonds and the consumption of them through terminal double bond polymerization (TDBP). In this process, the branch points are introduced on the newly formed primary chains during their growth. A notable advantage of using a CSTR is that the concentration of any functional group, including that of the terminal double bonds, is kept constant as long as the CSTR is under steady state. Therefore, the probability of branch formation through TDBP is the same during the growth of a polymer chain. For example, consider a free-radical polymerization in which active terminal double bonds are formed by chain transfer to monomer as shown in Scheme 1.

In Scheme 1, $P_{r,i}$ is the polymer radical with chain length r containing i branch points (without a terminal double bond), $D_{r,i}$ is the dead polymer molecule with chain length r containing i branch points (without a terminal double bond), and $P_{r,i}^-$ and $D_{r,i}^-$ are those with a terminal double bond. CTA and CTA^{*} are used to designate chain transfer agents with and without a radical centre, respectively, and CTA^{*} can reinitiate polymerization without changing polymerization rate. In the schematic representation of Scheme 1, only linear chains (with and without an active centre) are shown; however, these linear chains should be regarded as a part of polymer molecules that contain i (or j) branch points.

Note that the polymer molecules that contain more



Scheme 1

than one terminal double bond cannot be formed in the present reaction scheme. Furthermore, because polymer radical concentration is very low in usual free-radical polymerizations, the TDBP to consume a terminal double bond located on a polymer radical ($P_{r,i}^-$) can be neglected. In the present scheme, it is assumed that the dead polymer chain formation is transfer-dominated, so the initiation and termination reactions can be neglected in terms of the formation of the molecular weight distribution (MWD). According to the present polymerization scheme, the expected branching density along the primary chain is the same for all primary chains in a CSTR, so the requirements (a) and (b) are fulfilled.

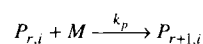
In reality, however, when active terminal double bonds are formed via chain transfer to monomer (cf. vinyl acetate polymerization), usually chain transfer to polymer is also involved, although we intentionally neglected the occurrence of chain transfer to polymers in *Scheme 1*. As mentioned earlier, chain transfer to polymers can form chains with different branching densities. A way to avoid the formation of the heterogeneously branched structure due to chain transfer to polymer would be the use of the free-radical copolymerization with chain transfer monomers⁶⁻⁸ (monomers with high transfer coefficients with a polymerizable double bond in it), such as the copolymerization of styrene with vinylbenzylthiol (whose chain transfer constant is as high as $C_{fp} = 25$)⁶. Because the chain transfer constant of the chain transfer monomer is high, most chain transfer monomers are incorporated into polymer chains via chain transfer reactions and form terminal double bonds. Even when some of the chain transfer monomers are incorporated first by propagation, the distribution of branch chain would be still considered random, provided the product of the reactivity ratios $r_1 r_2$ is (close to) unity and (almost) all pendant transferable groups have already been reacted. (Note that the copolymer composition drift during polymerization does not occur in a CSTR.) In the present report, however, we consider homopolymerizations that follow *Scheme 1* in order to simplify the discussion, and the investigations on the copolymerizations with the chain transfer monomers are reported separately⁹.

Another promising polymerization reaction scheme that involves both formation and consumption of terminal double bonds was reported recently. Polyolefins containing long-chain branches are reported to be synthesized by using certain metallocene catalysts such as Dow Chemical's constrained geometry catalyst^{10,11}. It is speculated that the elimination of the facile β -hydride forms terminal vinyl unsaturation¹¹. The polymerization scheme proposed¹¹ is shown in *Scheme 2*.

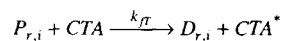
Note that *Schemes 1* and *2* are equivalent and can form the same MWD if $C_m (= k_{fm}/k_p)$ in *Scheme 1* and $k_3/(k_p[M]_0)$ in *Scheme 2* are the same in a CSTR.

Under both *Schemes 1* and *2*, the expected branching density should be the same for all primary chains formed in a CSTR (operated under steady state). However, it is possible to form heterogeneously branched polymers by connecting primary chains non-randomly, even when the expected branching density is the same for all primary chains¹². Therefore, we need to examine the branched polymer structure carefully. In the present report, we examine whether the above reaction schemes really provide the homogeneously branched structure by comparing equations (2) and (3) with the Monte Carlo

Propagation

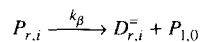


Chain transfer to chain transfer agents (CTA)

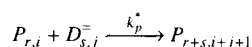


β -Hydride elimination

(Formation of terminal double bonds)



Terminal double bond polymerization



Scheme 2

simulations in which the chemical processes that occur during *Scheme 1* or *2* are fully accounted for. We further investigate heterogeneously branched structure formed in a batch reactor, and compare the MWD with the homogeneously branched polymers.

POLYMERIZATION IN A CONTINUOUS STIRRED-TANK REACTOR

The fraction of the unreacted terminal double bonds within the monomeric units bound into polymer molecules whose residence time since their formation is t , $\Phi^-(t)$ is given by¹³:

$$\frac{d\Phi^-(t)}{dt} = -k_p^* \Phi^-(t) [P] \quad (5)$$

where $[P]$ is the total concentration of the live (active) polymer molecules. In *Scheme 1*, the terminal double bonds are formed by chain transfer to monomer, and therefore, the Φ^- value of the primary polymer molecules at the time of their formation, $\Phi^-(0)$ is given by:

$$\Phi^-(0) = C_m \quad (6a)$$

On the other hand, in *Scheme 2*, the terminal double bonds are formed due to β -hydride elimination, so $\Phi^-(0)$ is given by:

$$\Phi^-(0) = \frac{k_3}{k_p [M]_0 (1-x)} \quad (6b)$$

where $[M]_0$ is the monomer feed concentration, and x is the monomer conversion to polymer. In order to unify the expression, we introduce δ defined as follows:

$$\delta = \begin{cases} C_m & \text{(for Scheme 1)} \\ k_3 / \{k_p [M]_0 (1-x)\} & \text{(for Scheme 2)} \end{cases} \quad (7)$$

By using δ , the initial condition for equation (5) is given by $\Phi^-(0) = \delta$. Then, equation (5) can be solved to give¹³:

$$\Phi^-(\xi) = \delta \exp \left\{ -K \left(\frac{x}{1-x} \right) \xi \right\} \quad (8)$$

where K shows the terminal double bond reactivity ($= k_p^*/k_p$), ξ is the reduced residence time ($= t/\bar{t}$), and \bar{t} is the mean residence time.

Therefore, the probability that the terminal double

bond located on the primary chain whose residence time is ξ has reacted, $P_{\text{react}}^*(\xi)$ is given by:

$$P_{\text{react}}^*(\xi) = 1 - \Phi^-(\xi)/\delta = 1 - \exp\left\{-K\left(\frac{x}{1-x}\right)\xi\right\} \quad (9)$$

Equation (9) clearly shows that the reaction probability of the terminal double bonds is dependent on the residence time and, therefore, the connection among primary polymer chains is not random in terms of the residence time of the primary polymer molecules, which appears to be a violation of the requirement (c). Therefore, the formation of homogeneously branched structure in a CSTR is not a trivial problem, but needs to be proven.

Monte Carlo simulation based on the random sampling technique

We use the Monte Carlo simulation based on the random sampling technique in which the history of the nonlinear structure development is fully accounted for¹³. In the random sampling technique, polymer molecules are sampled randomly from the infinite number of polymer molecules involved in the reaction mixture, and the statistical properties of the whole population is estimated. For simpler cases, the random sampling technique can lead to the analytical solutions^{2,3,14,15}. For more general cases, it is straightforward to combine this technique with the Monte Carlo method to obtain a very powerful simulator that can be applied virtually any type of nonlinear polymerizations irrespective of the reactor types used^{2,3,13-28}. Because the fundamental equations as well as the simulation method that can be applied to the present reaction schemes was reported earlier¹³, here we show the simulation procedure briefly by using a simple example.

We randomly select a monomeric unit bound to polymer molecules, and determine the size and the structure of the polymer molecule that contains this particular monomeric unit. In this selection process, the sampling is made on the weight basis, so the MWD obtained with the present simulation is the weight fraction distribution. Suppose our randomly selected polymer molecule possesses the structure shown in *Figure 2*. This polymer molecule consists of three primary polymer molecules. The circles on **A** and **B** are the branch points formed via TDBP. Suppose we randomly selected a monomeric unit bound to the primary polymer **A**, and we now construct the whole branched structure shown in *Figure 2*. In a CSTR, one obtains the instantaneous chain length distribution (produced in a very small time interval in a batch

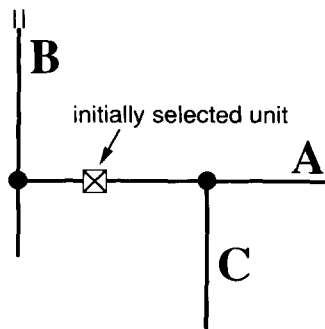


Figure 2 Example of a branched polymer molecule

reactor) for chain-growth linear polymerization⁵, i.e. the chain length distribution of the primary polymer molecules for the present case. In both reaction schemes, the primary polymer molecules follow the most probable distribution⁵. In the present sampling process, the selection is made on a weight basis; therefore, the primary polymer, **A** follows the weight-based chain length distribution, $w_p(r)$ shown below:

$$w_p(r) = (\delta + \phi)^2 r \exp\{-(\delta + \phi)r\} \quad (10)$$

where $\phi = C_{IT}[CTA]/[M]$. The chain lengths that follow the weight-based most probable distribution can be generated by using two random numbers, y_1 and y_2 , between 0 and unity as follows^{14,28}:

$$r = \text{ceiling}\left\{\left\{1/(\delta + \phi)\right\} \ln(1/y_1)\right\} + \text{ceiling}\left\{\left\{1/(\delta + \phi)\right\} \ln(1/y_2)\right\} - 1 \quad (11)$$

where $\text{ceiling}[a]$ means the closest integer greater than a .

In order to investigate the connection rule between primary polymer molecules, we need to determine the residence time of each primary polymer molecule, because the probability of reaction for the terminal double bond is dependent on the residence time as shown in equation (9). The residence time of the primary chain **A** can be determined as follows. The residence time distribution in a CSTR is given by:

$$E(\xi) = \exp(-\xi) \quad (12)$$

Therefore, the probability that the residence time of a randomly selected primary polymer molecule is shorter than ξ , is given by:

$$F(\xi) = \int_0^\xi E(\xi) d\xi = 1 - \exp(-\xi) \quad (13)$$

As a consequence, the residence time of **A**, ξ_A can be determined from the following transformation by using a random number between 0 and unity, y as follows:

$$\xi_A = \ln\{1/(1-y)\} \quad (14a)$$

or equivalently:

$$\xi_A = \ln(1/y) \quad (14b)$$

The probability that the chain end of **A** is connected is given by:

$$P_{\text{connect}}^*(\xi_A) = \frac{\delta}{\delta + \phi} P_{\text{react}}^*(\xi_A) \quad (15)$$

The ratio, $\delta/(\delta + \phi)$ indicates the probability that the chain end possesses terminal double bonds at the time of the formation of the primary polymer molecule. If the random number between 0 and unity, y satisfies the following inequality, the chain end of **A** is connected.

$$y < \frac{\delta}{\delta + \phi} \left[1 - \exp\left\{-K\left(\frac{x}{1-x}\right)\xi_A\right\} \right] \quad (16)$$

In the present case, the chain end of **A** is connected to the primary chain **B**. In the long-chain branching formed through TDBP, the backbone polymer chain **B** must be formed after the formation of the branch chain **A**. The

probability that the chain end of **A** is connected to the backbone polymer chain **B** whose residence time is from ξ_B to ξ_A , $P_a^*(\xi_B|\xi_A)$ is given by¹³:

$$P_a^*(\xi_B|\xi_A) = \frac{P_{\text{react}}^*(\xi_A - \xi_B)}{P_{\text{react}}^*(\xi_A)} \quad (17)$$

(Note that a typographical error exists in equation (15) of ref. 13.) If one uses the same y value used in equation (16), one can determine the residence time of primary chain **B** as follows:

$$\xi_B = \xi_A + \{(1-x)/(Kx)\} \ln\{1 - y(\delta + \phi)/\delta\} \quad (18)$$

Then we determine the chain length of **B**. Because any monomeric unit on chain **B** can become the branching point with equal probability, the selection of primary chain **B** is made on the weight basis. Therefore, the chain length of **B** can again be determined from equation (11). The possibility of end connection for **B** must be examined by using $P_{\text{connect}}^*(\xi_B)$; however, no backbone polymer chain is connected to **B** in the present case. In this type of chain connection, the primary chains formed later (smaller residence times) are connected.

Next, consider the connection of primary chains formed earlier (larger residence time). This type of connection is formed during the formation of the given primary polymer molecule. The probability of reaction with a terminal double bond, which is equal to the branching density, is given by:

$$\rho = R_p^*/R_p = K\bar{\Phi}^-x/(1-x) \quad (19)$$

where R_p is the polymerization rate, R_p^* is the rate of TDBP, and $\bar{\Phi}^-$ is the mole fraction of the unreacted terminal double bonds in a CSTR, which is given by:

$$\begin{aligned} \bar{\Phi}^- &= \int_0^\infty E(\xi)\Phi^-(\xi)d\xi \\ &= \frac{\delta}{1 + Kx/(1-x)} \end{aligned} \quad (20)$$

By substituting equation (20) into equation (19), one obtains:

$$\rho = \frac{\delta Kx}{1-x + Kx} \quad (21)$$

Therefore, the probability that the primary chain with chain length r possesses n branch points is given by the following binomial distribution:

$$p(n) = \binom{r}{n} \rho^n (1-\rho)^{r-n} \quad (22)$$

The number of connected branch chains must be examined for both chain **A** and **B**. In the present example, only one branch chain (**C**) exists on chain **A**.

The residence time of **C** can be determined from the following conditional probability, i.e. the probability that the primary chain with residence time ξ_A is connected to the branch chain whose residence time is between ξ_A and ξ_C is given by¹³:

$$\begin{aligned} P_i^*(\xi_C|\xi_A) &= \frac{\int_0^{\xi_C - \xi_A} E(\xi)\Phi^-(\xi)d\xi}{\int_0^\infty E(\xi)\Phi^-(\xi)d\xi} \\ &= 1 - \exp\left\{-\left(\frac{1-x + Kx}{1-x}\right)(\xi_C - \xi_A)\right\} \end{aligned} \quad (23)$$

Therefore, by using a random number, y , ξ_C can be determined as follows:

$$\xi_C = \xi_A + \frac{(1-x)\ln(1/y)}{1-x + Kx} \quad (24)$$

The chain length of **C** is determined from the number fraction distribution of the primary polymer molecules, because only the chain end can be connected. In the present case, the number fraction distribution of the primary chains is given by:

$$n_p(r) = (\delta + \phi) \exp\{-(\delta + \phi)r\} \quad (25)$$

Therefore, the chain length r can be obtained from the following transformation^{14,28}:

$$r = \text{ceiling}\{[1/(\delta + \phi)] \ln(1/y)\} \quad (26)$$

The number of branch chains connected to primary chain **C** must also be examined by using equation (22), but no further chains are connected in the present example. At this stage, we have determined the size and structure of one polymer molecule. By simulating a large number of polymer molecules, i.e. by taking a large number of polymer samples, the statistical properties of the whole population can be determined effectively. In this method, because one can observe the structure of each polymer molecule directly, virtually any information can be obtained^{2,19,22,23}. (For example, one can find the structure of homogeneously branched polymers visually in refs 2 and 23.) Furthermore, the present simulation is made on the weight basis: therefore, much smaller numbers of simulations for the polymer molecules are required to obtain weight-average chain length with sufficient accuracy (usually about 5×10^3 polymer molecules are enough), compared with the conventional Monte Carlo simulations that employ a finite reaction system in order to represent an infinite system approximately²⁹⁻³³ where the simulation is conducted on a number basis.

Simulation results

Figure 3 shows the simulated results for the weight fraction distribution formed under conditions, $\delta = 2 \times 10^{-3}$, $K = 1$, $x = 0.5$, and $C_{IT} = 0$. Under these reaction conditions, the number-average chain length of the primary polymer molecules is $\bar{P}_{np} = 500$, and the branching density is $\rho = 1 \times 10^{-3}$. The Monte Carlo simulation was made for 4×10^4 polymer molecules. The

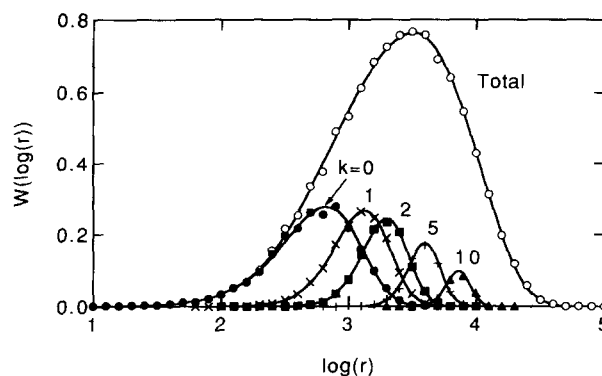


Figure 3 Fractional weight-based distribution of polymers containing k branch points and the whole weight fraction distribution when $\bar{P}_{np} = 500$ and $\rho = 1 \times 10^{-3}$

solid curves show the theoretical distribution of the homogeneously branched polymers calculated from equations (2) and (3). Both the whole MWD and the fractional MWD containing k branch points agree satisfactorily with the Monte Carlo simulation results in which the chemical reaction processes of *Schemes 1* or *2* are carefully accounted for.

The number- and weight-average chain length for randomly branched polymer molecules are given by^{2,3}:

$$\bar{P}_N = \bar{P}_{np} / (1 - \rho \bar{P}_{np}) \quad (27)$$

$$\bar{P}_W = \frac{1}{1 - \rho \bar{P}_{np}} \left\{ \bar{P}_{wp} + \rho \bar{P}_{np} \left(1 + \frac{\bar{P}_{wp} - 1}{1 - \rho \bar{P}_{np}} \right) \right\}$$

$$\cong \frac{\bar{P}_{wp}}{(1 - \rho \bar{P}_{np})^2} \quad (\bar{P}_{wp} \gg 1) \quad (28)$$

where \bar{P}_{wp} is the weight-average chain length of the primary polymer molecules. Note that equations (27) and (28) are valid irrespective of the primary chain length distribution. In the present example, equations (27) and (28) give $\bar{P}_N = 1 \times 10^3$ and $\bar{P}_W = 4 \times 10^3$. From the Monte Carlo simulations, we obtained $\bar{P}_N = 1.001 \times 10^3$ and $\bar{P}_W = 4.012 \times 10^3$, which agrees reasonably well with the analytical solution for the homogeneously branched polymers.

On the basis of equation (3), it was shown that the number- and weight-average chain length of the MWD containing k branch points are given by the following equations²:

$$\bar{P}_{N,k} = \frac{(2k+1)\bar{P}_{np}}{1 + \rho \bar{P}_{np}} \quad (29)$$

$$\bar{P}_{W,k} = \frac{(k+1)\bar{P}_{wp}}{1 + \rho \bar{P}_{np}} \quad (30)$$

Figure 4 shows the comparison with the Monte Carlo simulation results. The solid lines are calculated from equations (29) and (30), while the symbols show the Monte Carlo simulation results. Complete agreement is confirmed.

As a final examination for the validity of the speculation that the present reaction schemes lead to homogeneously branched structure, we investigated the branching density as a function of k and r . For homogeneously branched polymers, the average branching density of the polymer molecules that contain k

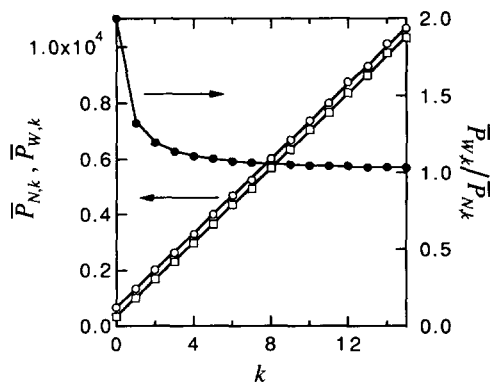


Figure 4 Average chain lengths of polymer fraction containing k branch points

branch points is given by²:

$$\bar{\rho}_k = \frac{k(1 + \rho \bar{P}_{np})}{(2k+1)\bar{P}_{np}} \quad (31)$$

On the other hand, the average branching density of the polymer molecules whose chain length is r is given by²:

$$\bar{\rho}_r = \frac{\sqrt{\rho/\bar{P}_{np}} I_2 \left(2r \sqrt{\rho/\bar{P}_{np}} \right)}{I_1 \left(2r \sqrt{\rho/\bar{P}_{np}} \right)} \quad (32)$$

Figure 5 shows the comparison with the Monte Carlo simulation results, and complete agreement is obtained. From Figures 3–5, it can be concluded that homogeneously branched polymers are formed by conducting the polymerization shown in *Scheme 1* or *2* in a CSTR.

In the above example, the chain transfer reaction to CTA that does not form terminal double bonds is not included. In practice, however, use of an appropriate solvent may be required to decrease the viscosity of the reaction medium, in order to obtain the ideally micro-mixed, steady-state condition. In the solution polymerization, chain transfer reactions to solvent may need to be accounted for. Therefore, if homogeneously branched polymers cannot be synthesized with the presence of CTA, the production of homogeneously branched polymers in a CSTR may be difficult to accomplish.

In order to investigate the effect of chain transfer to CTA, we made another Monte Carlo simulation under conditions, $\delta = 1.5 \times 10^{-3}$, $K = 0.5$, $x = 0.8$, and $\phi = 5 \times 10^{-4}$. Under these reaction conditions, \bar{P}_{np} and ρ are the same as the previous example, and therefore, the MWD becomes the same as the previous case if homogeneously branched structure is formed.

Figure 6 shows the comparison of the weight fraction distribution. Again, complete agreement is confirmed, and it is shown that homogeneously branched structure is formed irrespective of the existence of CTAs.

In the present reaction system, the connection among

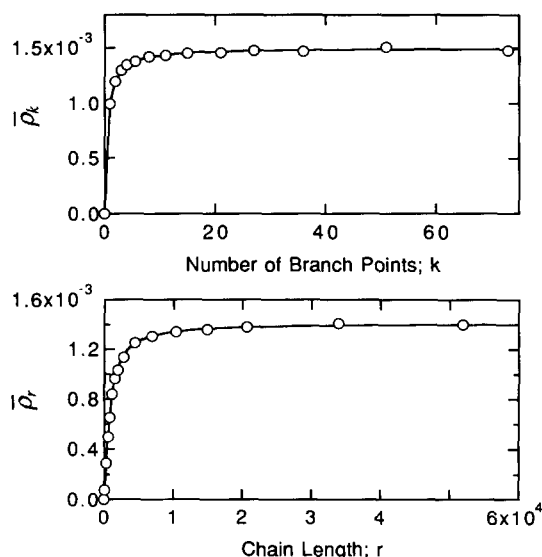


Figure 5 Branching density as a function of k and r . The circular keys are the average branching density within small intervals of k and r obtained from the Monte Carlo simulation results, while the solid curves are the analytical solution for the homogeneously branched polymers (equations (31) and (32))

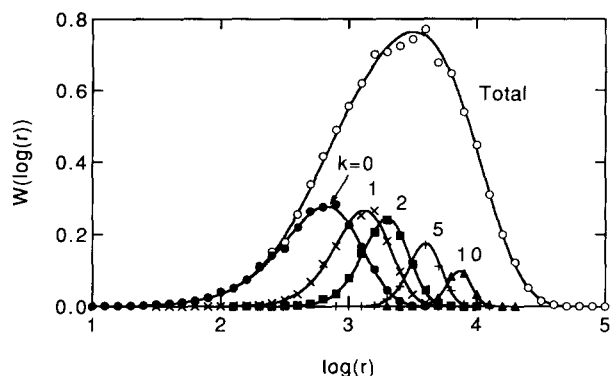


Figure 6 Fractional weight-based distribution of polymers containing k branch points and the whole weight fraction distribution when chain transfer reactions to CTA are involved

primary chains is nonrandom with respect to the residence time of the primary polymer molecules, as clearly shown in equation (9). Then, why does the present reaction system produce homogeneously branched polymers? One needs to realize that the primary chain length distribution, which is formed instantaneously, is independent of the residence time. Therefore, the same molecular constitution is obtained irrespective of the chain connection rule, as long as the branching density is the same for all chains. The discrimination of the primary chains with respect to the residence time is required only for the purpose of following the reaction scheme exactly, and such discrimination is immaterial in terms of the resulting branched polymers.

Comment on the method of moments

The method of moments has been used widely to predict the average molecular weights in free-radical polymerization that involves branching and cross-linking³⁴⁻³⁹. Conventional method of moments neglects the existence of polymer molecules with more than one active centre, i.e. the effect of polyradicals is neglected. It was shown that such assumption can be acceptable for batch polymerizations except for the vicinity of gel point^{16,17,20,21,40}; however, such assumption can lead to involve significant errors for other types of reactor operations such as a CSTR¹³ especially when branching frequency is high.

In *Scheme 2*, it is impossible to form polymer molecules with more than one active centre. On the other hand, in *Scheme 1*, the formation of polyradicals is not totally prohibited, because a polymer radical may react with a terminal double bond located on a polymer radical ($P_{r,i}^-$). However, because the lifetime of a primary polymer radical is very short and the concentration of polymer radicals is extremely small, it would be reasonable to neglect the radical attack on $P_{r,i}^-$. Therefore, the method of moments could be used for the present reaction schemes.

For a CSTR, Nagasubramanian and Graessley³⁶ obtained analytical solutions for the number- and weight-average chain length for free-radical polymerizations that involve both chain transfer to polymer and TDBP by using the method of moments. When chain transfer to polymer is involved, the obtained results for \bar{P}_W may be erroneous because the effects of polyradicals must be accounted for properly¹³. On the other hand, their equations could be applied for the cases that

involve only TDBP. The equations for the number- and weight-average chain lengths reduce to the following equations³⁶:

$$\bar{P}_N = \frac{(1-x+Kx)}{\delta(1-x) + \phi(1-x+Kx)} \quad (33)$$

$$\bar{P}_W = \frac{2(1-x+KQ_1^-)^2}{(\delta+\phi)(1-x)^2} \quad (34)$$

where Q_1^- is the first order moment of the polymer molecules that contain a terminal double bond, which is given by:

$$Q_1^- = \frac{\delta x(1-x)}{\delta(1-x) + \phi(1-x+Kx)} \quad (35)$$

(Note that in our notation, $C_s[S]$ used in ref. 36 is given by $C_s[S] = \phi(1-x)$. Furthermore, note that equation (35) in ref. 36 involves a typographical error.)

In the present reaction schemes, the branching density is given by equation (21) and the number-average chain length of the primary polymer molecules, \bar{P}_{np} is given by:

$$\bar{P}_{np} = 1/(\delta + \phi) \quad (36)$$

Therefore, equation (33) can be rewritten by using \bar{P}_{np} and ρ as follows:

$$\begin{aligned} \frac{1}{\bar{P}_N} &= \delta + \phi + \left(\frac{1-x}{1-x+Kx} - 1 \right) \delta \\ &= \delta + \phi - \frac{\delta Kx}{1-x+Kx} \\ &= \frac{1}{\bar{P}_{np}} - \rho \end{aligned} \quad (37)$$

Equation (37) agrees with the analytical solution for the homogeneously branched polymers given by equation (27).

On the other hand, equation (34) can be modified as follows. From equations (33), (35), and (37), Q_1^- is given by:

$$Q_1^- = \bar{P}_N \frac{(1-x)\delta x}{1-x+Kx} \quad (38)$$

Therefore:

$$1-x+KQ_1^- = (1-x)(1+\rho\bar{P}_N) = \frac{1-x}{1-\rho\bar{P}_{np}} \quad (39)$$

By substituting equation (39) into equation (34), one obtains:

$$\bar{P}_W = \frac{2\bar{P}_{np}}{(1-\rho\bar{P}_{np})^2} \quad (40)$$

Because the primary polymer molecules conform to the most probable distribution, $\bar{P}_{wp} = 2\bar{P}_{np}$. Therefore, the method of moments can give the same weight-average chain length as that given by equation (28).

On the basis of the above discussion, it can be concluded that the method of moments can be used to obtain the number- and weight-average chain lengths for the present reaction schemes.

PRODUCTION OF HETEROGENEOUSLY
BRANCHED POLYMERS BY USING BATCH
POLYMERIZATION

In the previous section, it was shown that *Scheme 1* or *2* leads to homogeneously branched polymers, if it is conducted in a CSTR (operated under steady state). On the other hand, during non-steady state operation of a CSTR, the molar ratio between the terminal double bonds and monomeric double bonds may change, which clearly gives different branching densities among primary polymer molecules depending on the time of their formation. Therefore, homogeneously branched polymer molecules cannot be formed under non-steady state operations, contrary to the earlier speculation¹¹. It may also be worth noting here that the use of equations (2) and (3) is also limited by the assumption that the primary polymer molecules follow the most probable distribution. Therefore, if the most probable distributions with different average chain lengths are superposed (which may be caused due to the chain length drift during non-steady state operation of a CSTR or a batch reactor), equations (2) and (3) cannot be used.

In this section, we investigate the branched structure formed in a batch reactor, and the effect of heterogeneity in the distribution of branch points as well as the effect of chain length drift is clarified.

Monte Carlo simulation in a batch reactor

Because the derivation of fundamental equations as well as the simulation algorithm has already been described²¹, we show the simulation method briefly by using the branched polymer shown in *Figure 2* again. For a batch polymerization, it is convenient to use conversion as an independent variable. Suppose that we randomly select a polymer molecule from the reaction mixture when the conversion at the present time is $x = \psi$. Because the weight of polymer formed in the conversion interval Δx is the same irrespective of the conversion level, the conversion at which the primary polymer molecule **A** was formed (the birth conversion θ) can be determined by selecting the birth conversion θ_A from 0 to ψ randomly. Once the birth conversion of **A** is settled, then we determine the chain length of **A**. This can be done by generating a random number that follows the instantaneous weight-based chain length distribution of the primary polymer molecules formed at $x = \theta$. In the present case, the chain length of **A** is given by:

$$r = \text{ceiling}[\{1/[\delta(\theta_A) + \phi(\theta_A)]\} \ln(1/y_1)] \\ + \text{ceiling}[\{1/[\delta(\theta_A) + \phi(\theta_A)]\} \ln(1/y_2)] - 1 \quad (41)$$

Compare with equation (11). In a batch polymerization, the parameters, δ and ϕ may change during polymerization, so one has to use the parameters right at the given conversion level.

The probability that the chain end of **A** is connected with another backbone chain (**B**) via TDBP is given by²¹:

$$P_{\text{connect}}^*(\theta_A, \psi) = \left(\frac{\delta(\theta_A)}{\delta(\theta_A) + \phi(\theta_A)} \right) \left\{ 1 - \left(\frac{1 - \psi}{1 - \theta_A} \right)^K \right\} \quad (42)$$

In the present case, **B** is connected to **A**. The birth conversion of **B**, θ_B ($\theta_A < \theta_B < \psi$) can be determined from the following conditional probability, i.e. the

probability that **B** is formed in the conversion interval θ_A to θ_B is given by²¹:

$$P_a^*(\theta_B|\theta_A) = \frac{P_{\text{connect}}^*(\theta_A, \theta_B)}{P_{\text{connect}}^*(\theta_A, \psi)} \\ = \frac{1 - \{(1 - \theta_B)/(1 - \theta_A)\}^K}{1 - \{(1 - \psi)/(1 - \theta_A)\}^K} \quad (43)$$

The chain length of **B** can be determined from equation (41) by using θ_B instead of θ_A . The possibility of end connection for **B** must be examined by using $P_{\text{connect}}^*(\theta_B, \psi)$; however, no chain is connected in the present example.

The number of the branch chains connected to **A** via TDBP during the formation of **A** can be determined from the following binomial distribution:

$$p(n) = \binom{r}{n} \{\rho(\theta_A)\}^n \{1 - \rho(\theta_A)\}^{r-n} \quad (44)$$

The branching density of the primary polymer molecules that were formed at $x = \theta$ is given by²¹:

$$\rho(\theta) = \frac{R_p^*(\theta)}{R_p(\theta)} = \frac{K}{1 - \theta} \int_0^\theta \Phi^-(x, \theta) dx \quad (45)$$

where the mole fraction of unreacted terminal double bonds within the primary polymer molecules that were formed at conversion θ , $\Phi^-(\theta, \psi)$ is given by²¹:

$$\Phi^-(\theta, \psi) = \delta(\theta) \left(\frac{1 - \psi}{1 - \theta} \right)^K \quad (46)$$

Under *Scheme 1*, $\delta(\theta) = C_m$; therefore, $\rho(\theta)$ is given by:

$$\rho(\theta) = \begin{cases} \frac{KC_m}{1 - K} \left\{ \left(\frac{1}{1 - \theta} \right)^{1-K} - 1 \right\} & (K \neq 1) \\ C_m \ln\{1/(1 - \theta)\} & (K = 1) \end{cases} \quad (47)$$

Under *Scheme 2*, $\delta(\theta) = k_\beta/\{k_p[M]_0(1 - \theta)\}$; therefore, $\rho(\theta)$ is given by:

$$\rho(\theta) = \frac{C_\beta}{1 - \theta} \{1 - (1 - \theta)^K\} \quad (48)$$

where $C_\beta = k_\beta/(k_p[M]_0)$.

In the present case, the primary chain **C** is connected to **A**. The birth conversion of **C**, θ_C ($0 < \theta_C < \theta_A$) can be determined from the following conditional probability, i.e. the probability that **C** is formed in the conversion interval 0 to θ_C is given by²¹:

$$P_i^*(\theta_C|\theta_A) = \frac{\int_0^{\theta_C} \Phi^-(x, \theta_A) dx}{\int_0^{\theta_A} \Phi^-(x, \theta_A) dx} \quad (49)$$

For *Scheme 1*, $P_i^*(\theta_C|\theta_A)$ is given by:

$$P_i^*(\theta_C|\theta_A) = \begin{cases} \frac{1 - (1 - \theta_C)^{1-K}}{1 - (1 - \theta_A)^{1-K}} & (K \neq 1) \\ \frac{\ln(1 - \theta_C)}{\ln(1 - \theta_A)} & (K = 1) \end{cases} \quad (50)$$

For *Scheme 2*, $P_i^*(\theta_C|\theta_A)$ is given by:

$$P_i^*(\theta_C|\theta_A) = \frac{(1 - \theta_C)^{-K} - 1}{(1 - \theta_A)^{-K} - 1} \quad (51)$$

The chain length of **C** can be determined from the number fraction distribution of the primary polymer molecules formed at $x = \theta_C$; therefore, it can be obtained from the following equation by using a random number, y ($0 < y < 1$):

$$r = \text{ceiling}[\{1/[\delta(\theta_C) + \phi(\theta_C)]\} \ln(1/y)] \quad (52)$$

Obviously, equation (44) must also be examined for primary chains **B** and **C**; however, no other branch chains are connected in the present case, and the simulation for this polymer molecule ends. By taking a large number of polymer molecules, the statistical properties of the whole reaction mixture can be estimated effectively.

Incidentally, the average branching density can be obtained from:

$$\bar{\rho}(\psi) = \frac{1}{\psi} \int_0^\psi \rho(\theta, \psi) d\theta \quad (53)$$

Therefore, for Scheme 1:

$$\bar{\rho}(\psi) = \begin{cases} \frac{C_m}{1-K} \left\{ \frac{1 - (1-\psi)^K}{\psi} - K \right\} & (K \neq 1) \\ \frac{C_m}{\psi} \{ (1-\psi)[\ln(1-\psi) - 1] + 1 \} & (K = 1) \end{cases} \quad (54)$$

For Scheme 2:

$$\bar{\rho}(\psi) = \frac{C_\beta}{K\psi} \left\{ K \ln\left(\frac{1}{1-\psi}\right) - [1 - (1-\psi)^K] \right\} \quad (55)$$

Effect of heterogeneous distribution of branch points on the formed MWD

Under Scheme 1, the primary polymer chain length drift does not occur, provided no chain transfer agents (CTA) exist or by using an ideal CTA with $C_{fT} = 1$. Even for such reaction systems, the formation of a non-homogeneous distribution of branch points is inevitable owing to a history dependent branch chain formation. Therefore, by using these types of reaction systems, it is possible to investigate the effect of heterogeneous distribution of branch points without changing the primary chain length distribution.

In this section we use two reaction conditions: (a) $K = 1$, $C_m = 2 \times 10^{-3}$, $C_{fT} = 0$; and (b) $K = 0.5$, $C_m = 1.5 \times 10^{-3}$, $C_{fT} = 1$, $[CTA]_0/[M]_0 = 5 \times 10^{-4}$ where $[CTA]_0$ is the initial concentration of CTA. Figure 7 shows the branching density distribution as a function of the birth conversion. In both cases, the average branching density, $\bar{\rho}$ is set to be 1×10^{-3} , and therefore, the conversion at the present time, ψ is different [$\psi = 0.715$ for (a) and $\psi = 0.96$ for (b)]. As shown in Figure 7, the primary chains formed in the later stages of polymerization possess larger branching densities than those formed in the earlier stages of polymerization. Figure 8 shows the cumulative weight fraction of the primary polymer molecules whose branching density is smaller than ρ . It is shown clearly that the branched structure formed in a batch polymerization is heterogeneous.

For the present reaction systems, the conventional method of moments can be used to obtain the number- and weight-average chain length as discussed earlier. For

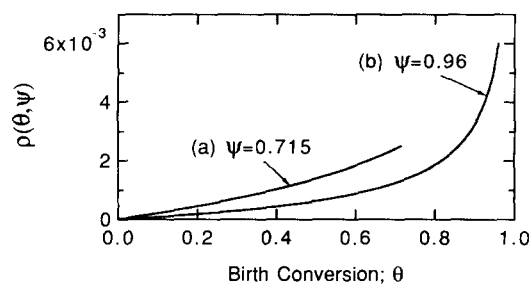


Figure 7 Expected branching density of the primary polymer molecule as a function of the birth conversion of it, θ under conditions (a) and (b) shown in the text, when the average branching density of the whole reaction mixture is $\bar{\rho} = 1 \times 10^{-3}$

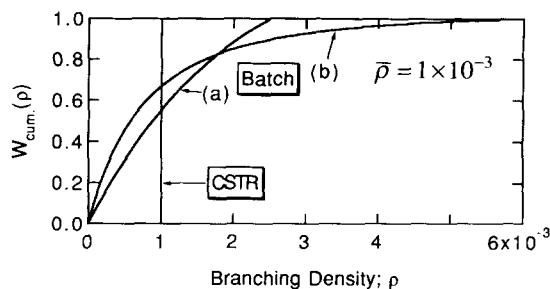


Figure 8 Distribution of branch points formed in a batch reactor [conditions (a) and (b)] and a CSTR. The y -axis shows the cumulative weight fraction of primary polymer molecules whose branching density is smaller than ρ

a batch polymerization, the moment equations are given by³⁶:

$$\frac{dQ_0^-}{dx} = \delta - \frac{KQ_0^-}{1-x} \quad (56)$$

$$\frac{dQ_0}{dx} = \phi \quad (57)$$

$$\frac{dQ_1^-}{dx} = \bar{P}_{np} \left(\delta - \frac{KQ_1^- \phi}{1-x} \right) \quad (58)$$

$$\frac{dQ_1^T}{dx} = 1 \quad (59)$$

$$\frac{dQ_2^T}{dx} = \bar{P}_{wp} \left(\frac{1-x + KQ_1^-}{1-x} \right)^2 \quad (60)$$

where Q_i is the i th moment of polymer distribution without a terminal double bond, and when the superscripts = and T are used, they indicate the moment for polymer molecules with a terminal double bond and that for total polymers, respectively ($Q_i^T = Q_i + Q_i^-$). Note that \bar{P}_{np} and \bar{P}_{wp} used above are the averages for the primary polymer molecules formed at the given instance, i.e.:

$$\bar{P}_{np} = 1/[\delta(x) + \phi(x)] \quad (61)$$

$$\bar{P}_{wp} = 2/[\delta(x) + \phi(x)] \quad (62)$$

The number- and weight-average chain length of the whole polymer molecules can be obtained from the

moments as follows:

$$\bar{P}_N = Q_1^T / Q_0^T \quad (63)$$

$$\bar{P}_W = Q_2^T / Q_1^T \quad (64)$$

Figure 9 shows the calculated average chain lengths both for a batch and a CSTR at the same average branching density levels. Note that $\bar{P}_{np} = 500$ for all cases (both for a batch and a CSTR) in the present example, and both conditions (a) and (b) give the same \bar{P}_N and \bar{P}_W in a CSTR at the same branching density level. The symbols indicate the Monte Carlo simulation results at $\bar{\rho} = 1 \times 10^{-3}$ for batch polymerizations. The Monte Carlo simulation results agree completely with the moment equations, and it is confirmed that the method of moments can be used for the present reaction systems. The number-average chain lengths (\bar{P}_N) are the same for all conditions. Under condition (a), the weight-average chain length (\bar{P}_W) is smaller than that for a CSTR, i.e. homogeneously branched polymers. On the other hand, under condition (b), the weight-average chain length becomes larger than the homogeneously branched polymers at the same branching density level. Therefore, it can be concluded that the weight-average chain length can be made larger or smaller due to the heterogeneous distribution of the branch points.

Figure 10 shows the comparison of the full weight fraction distribution at $\bar{\rho} = 1 \times 10^{-3}$. The MWD profiles are changed due to the heterogeneous branched structure. Figure 11 shows both full and fractional MWD containing k branch points. The solid curves are

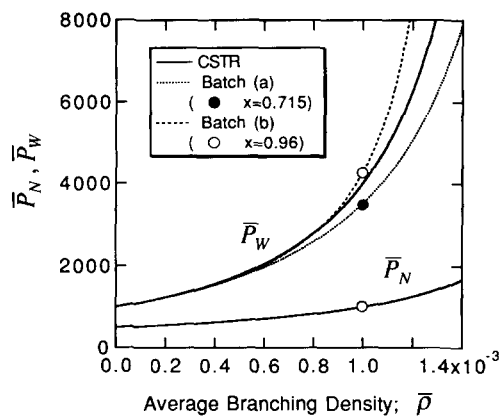


Figure 9 Average chain length development under conditions (a) and (b) in a batch reactor and a CSTR. For a CSTR, both conditions give the same average chain lengths. The circles indicate the Monte Carlo simulation results at $\bar{\rho} = 1 \times 10^{-3}$ for batch polymerizations, while the curves are calculated from the method of moments

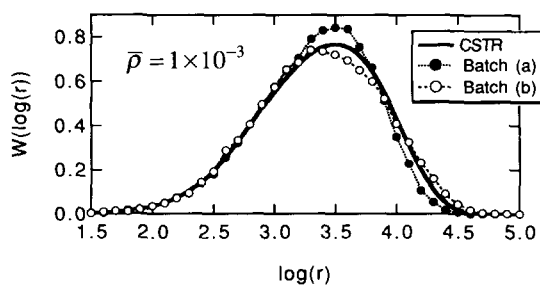


Figure 10 Comparison of the weight fraction distributions at the same average branching density level ($\bar{\rho} = 1 \times 10^{-3}$)

the MWD for the homogeneously branched polymers. Clear structural differences are shown.

Effect of chain length drift in heterogeneously branched polymers

Under Scheme 2, chain length drift during polymerization is inevitable in a batch polymerization, because δ is a function of conversion. Obviously, the branching density of the primary polymer molecule changes with the birth conversion, so a heterogeneously branched structure is formed. First, the following reaction condition that follows Scheme 2 is investigated: $K = 1$, $C_\beta = 1 \times 10^{-3}$, and $C_{IT} = 0$. Figure 12 shows the

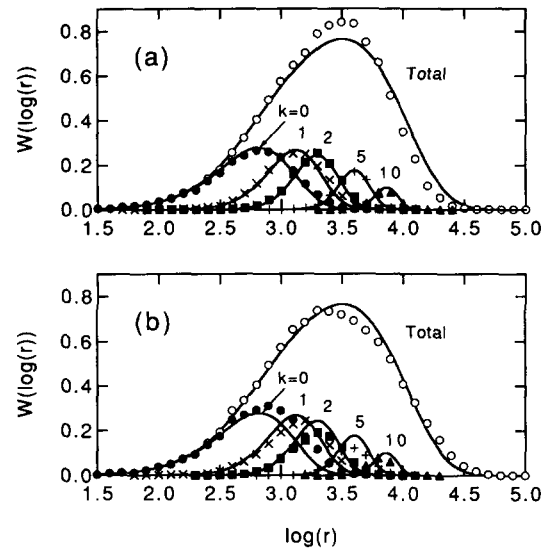


Figure 11 Comparison of the fractional weight-based chain length distribution and the whole weight fraction distribution. The symbols indicate the heterogeneously branched structure formed in a batch reactor, while the solid curves are for homogeneously branched polymers that can be formed in a CSTR at the same average branching density level ($\bar{\rho} = 1 \times 10^{-3}$)

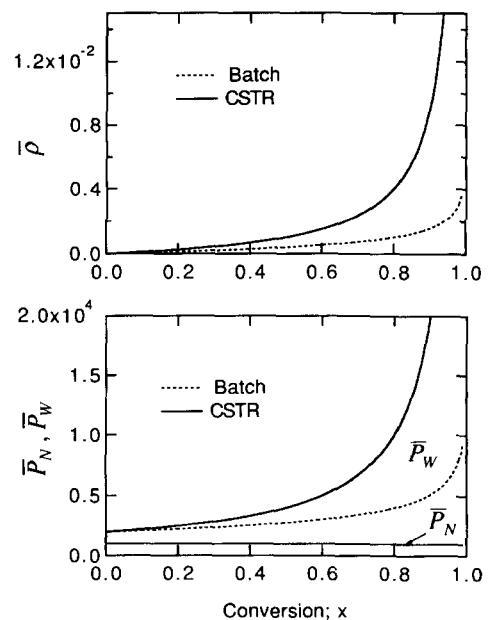


Figure 12 Development of the average branching density and the average chain lengths in a batch reactor and a CSTR for the reaction Scheme 2 with $K = 1$, $C_\beta = 1 \times 10^{-3}$, and $C_{IT} = 0$

developments of both the average branching density and the average chain lengths during polymerization. Here, comparison is made with a CSTR at the same conversion level. At the same conversion level, both $\bar{\rho}$ and \bar{P}_W are larger for a CSTR, while \bar{P}_N is the same for both types of reactor and is 1×10^3 at any conversion level.

Figure 13 shows the number- and weight-average chain lengths at the same average branching density levels. The symbols are the Monte Carlo simulation results for a batch reactor at $\bar{\rho} = 1 \times 10^{-3}$. At the same average branching density level, the difference of the reactor types on both \bar{P}_N and \bar{P}_W are very small. The effect of the heterogeneous distribution of branch points on the average chain lengths are somewhat cancelled by the chain length drift during polymerization in the present example.

Figure 14 shows the fractional MWD as well as the whole MWD for the polymerization in a batch reactor and a CSTR when the average branching density is $\bar{\rho} = 1 \times 10^{-3}$. Although \bar{P}_N and \bar{P}_W are the same for both types of reactor, the full MWD profile as well as the branched structures are completely different from each other. In the molecular weight analysis, it seems to be a

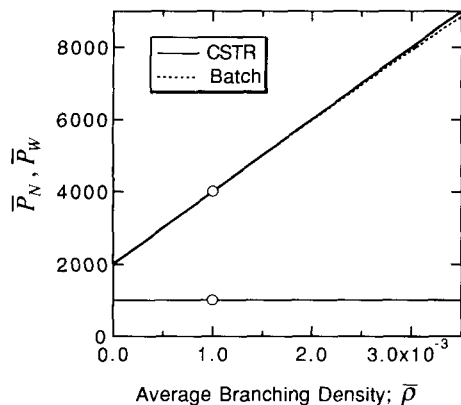


Figure 13 Number- and weight-average chain lengths as a function of the average branching density for a batch reactor and a CSTR, when $K = 1$, $C_\beta = 1 \times 10^{-3}$, and $C_{fT} = 0$. The circles indicate the Monte Carlo simulation results at $\bar{\rho} = 1 \times 10^{-3}$, while the curves are calculated from the moment equations, equations (56)–(60)

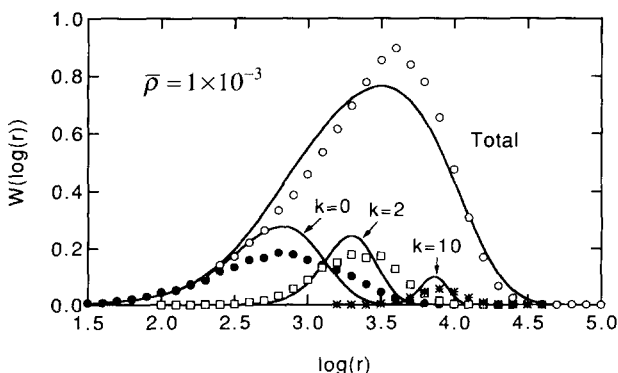


Figure 14 Comparison of the fractional weight-based chain length distribution and the whole weight fraction distribution. The symbols indicate the heterogeneously branched structure formed in a batch reactor, while the solid curves are for a homogeneously branched structure that can be formed in a CSTR at the same average branching density level ($\bar{\rho} = 1 \times 10^{-3}$)

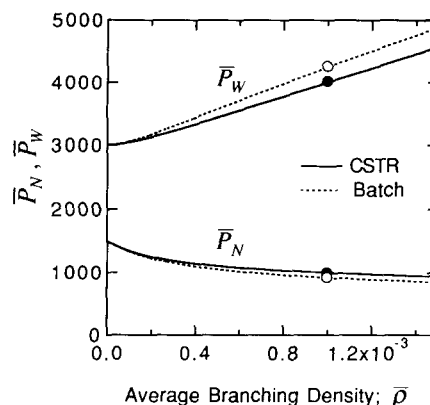


Figure 15 Number- and weight-average chain lengths as a function of the average branching density for a batch reactor and a CSTR under Scheme 2 with $K = 0.5$, $C_\beta = 6.667 \times 10^{-4}$, and $C_{fT} = 0$. The circles indicate the Monte Carlo simulation results at $\bar{\rho} = 1 \times 10^{-3}$, while the curves are calculated from the moment equations.

common practice to consider that both distributions are the same if the number- and weight-average chain lengths are the same for both distributions. Especially for nonlinear polymers, various types of distributions can be formed, and one cannot judge the distribution profiles only from the averages. Because the average molecular weights are the same for both types of polymers in the present example, one can investigate the effect of the detailed structural differences on the physical and mechanical properties by using these polymers.

Obviously, the above example is a rather special case. In general, the average molecular weight development is different depending on the reactor types used even when the average branching density level is the same as shown in Figure 15 in which $K = 0.5$, $C_\beta = 6.667 \times 10^{-4}$, and $C_{fT} = 0$.

CONCLUSIONS

It was found that the homogeneously branched polymers can be obtained by conducting chain-growth polymerizations involving both formation and consumption of terminal double bonds in a CSTR, and two types of reaction schemes are considered. Because the analytical expressions for the full MWD, the fractional MWDs containing 0, 1, 2, etc., branch points, as well as the radius of gyration have been determined for homogeneously branched polymers, such polymers show promise as polymer standards.

When the proposed polymerization reactions are conducted in a batch reactor, heterogeneously branched structures are formed. The heterogeneous distribution of branch points can make the weight-average molecular weight larger or smaller compared with the homogeneously branched polymers, depending on the branching density distribution. Besides from the heterogeneity of the branched structure, in general, the primary chain length drift occurs during batch polymerization; therefore, the formed structures can be quite complex.

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