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Copolymerization with Chain Transfer Monomer. 1. Distribution of Branch Points

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ABSTRACT: A theoretical investigation is conducted on a batch free-radical copolymerization in which one type of monomer possesses a high chain transfer constant with a polymerizable double bond in it, which is called the chain transfer monomer. When the chemical structures of the polymerizable double bonds are the same for the monomer pair, the reactivity ratios may be close to unity. In such cases, the probability of possessing a branch point may become the same for all units bound to polymer molecules at any stage of polymerization, irrespective of the magnitude of the chain transfer constant. On the other hand, a homogeneously branched structure cannot be formed except when the chain transfer constant is unity, because the primary chains formed at different stages of polymerization are not connected randomly. The present reaction system could be used to investigate the effect of detailed structural differences on the physical properties of branched polymer systems.

Introduction

Long-chain branches have significant effects on the various properties of polymers and polymer solutions even when their frequency is rather small.[1] The control of branched structure is, therefore, of great importance to produce higher quality polymers. The representative reaction mechanisms to form long-chain branches in free-radical polymerizations are chain transfer to polymer (CTP) and the terminal double-bond polymerization (TDBP). For example, the long-chain branches in poly(vinyl acetate) are usually attributed to both CTP and TDBP,[2−4] partly because the growing polymer radicals can abstract the hydrogen from the acetoxy methyl group on both polymer (CTP) and monomer (to form active terminal double bonds). Various types of mathematical languages have been used to analyze such types of polymerization systems, such as the method of moments,[4−6] the cascade theory,[7] and the random sampling technique.[8,9]

In this and the subsequent report,[10] we consider the branched polymer structure formed by a free-radical copolymerization with chain transfer monomer. The chain transfer monomer is a type of monomer whose chain transfer constant is very high with a polymerizable double bond in it.[11−13] Examples of such polymerization systems may involve free-radical copolymerization of styrene with vinylbenzenethiol (chain transfer constant, $C_{\mathrm{fm}} = 25$) or with vinylbenzyl bromide ($C_{\mathrm{fm}} = 0.015$), as reported by Tung et al.,[11] provided side reactions could be suppressed.

In the present reaction system, long-chain branches are formed both by CTP and TDBP, as in the case of vinyl acetate polymerization. When a chain transfer monomer (CTM) is first incorporated into polymer chains by chain transfer to monomer, a polymer chain with a polymerizable terminal double bond is formed. This terminal double bond may be used to form a polymer with long-chain branching through the TDBP. On the other hand, if a CTM polymerizes first, a long-chain branch is formed by CTP. The average branching frequency can be controlled by changing the molar ratio of the comonomers.

Table 1. Elementary Reactions

propagation
$\mathrm{R}_r^i + \mathrm{M}_m \rightarrow \mathrm{R}_{r+1}^m$ (rate constant, $k_{\mathrm{p},im}$)
chain transfer to monomer (M_2)
$\mathrm{R}_r^i + \mathrm{M}_2 \rightarrow \mathrm{P}_r + \mathrm{M}_2^\bullet$ ($k_{\mathrm{fm},i}$)
chain transfer to chain transfer agents (CTA)
$\mathrm{R}_r^i + \mathrm{CTA} \rightarrow \mathrm{P}_r + \mathrm{CTA}^\bullet$ ($k_{\mathrm{fT},i}$)
chain transfer to polymer
$\mathrm{R}_r^i + \mathrm{P}_s \rightarrow \mathrm{P}_r + {\mathrm{R}_s}^3$ ($k_{\mathrm{fp},i}$)
terminal double-bond polymerization
$\mathrm{R}_r^i + {}^{=}\mathrm{P}_s \rightarrow {\mathrm{R}_{r+s}}^4$ (k_i^*)
bimolecular termination by disproportionation
$\mathrm{R}_r^i + \mathrm{R}_s^j \rightarrow \mathrm{P}_r + \mathrm{P}_s$ ($k_{\mathrm{td},ij}$)
bimolecular termination by combination
$\mathrm{R}_r^i + \mathrm{R}_s^j \rightarrow \mathrm{P}_{r+s}$ ($k_{\mathrm{tc},ij}$)
$i, j = 1, 2, 3, 4$
$m = 1, 2$

In nonlinear polymers, the same average branching density does not guarantee formation of the identical branched structure. In particular, free-radical polymerizations are kinetically controlled; therefore, the formed branched structures are highly history-dependent, which usually results in a nonrandom distribution of branch points.[8,9,14−16] For example, consider a batch free-radical homopolymerization that involves chain transfer to polymer. In this case, the primary chains formed at earlier stages of polymerization are subjected to branching reactions for a longer period of time; therefore, the branching density of these chains is expected to be larger than those formed in the later stages of polymerization. A logical consequence of such a thought experiment is that the expected branching density of each primary polymer molecule is dependent on the birth time of the primary chains.

In the present report, we investigate the branched structure formation in the copolymerization with chain transfer monomer, by focusing our attention on the distribution of the branch points among primary chains. Also to be discussed are the conditions required to form a homogeneously branched polymer system in the present reaction scheme.

Elementary Reactions

By assuming that the terminal model for copolymerization kinetics is applicable, the elementary reactions considered here can be summarized as shown in Table 1. In the table, M_1 is the monomer whose chain transfer

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constant is much smaller than M_2, and M_2 is the chain transfer monomer. The subscripts, r and s show the chain length (degree of polymerization) of the polymeric species, P_r is the dead polymer molecule with chain length r, and R_r^i is the polymer radical of type i with chain length r. Both P_r and R_r^i include those with and without terminal double bonds in the present notation. When we need to distinguish polymeric molecules with terminal double bonds explicitly, we use ${}^{=}P_r$ and ${}^{=}R_r^i$. For polymer radicals, we have four types of radicals; R_r^1 and R_r^2 are formed by propagation reactions whose active center is located on M_1 and M_2, respectively, R_r^3 is formed by chain transfer reaction to polymer, and R_r^4 is formed by addition of a radical to the terminal double bond.

We neglect the TDBP that consumes a terminal double bond located on a polymer radical, ${}^{=}R_r^i$, because the concentration of polymer radicals is much smaller than that for dead polymers. A further assumption is that the active terminal double bonds are formed only by chain transfer to monomer, M_2. Bimolecular termination by disproportionation produces terminal double bonds; however, these double bonds are often 1,2-disubstituted and are inactive toward free-radical polymerization, although the disproportionation mechanisms for many types of monomer are not clear. Note that these two assumptions are not essential to the present theory, and they are used just for simplicity.

In order to simplify the rate expressions, we use the pseudokinetic rate constants[17−21] defined below:

$$k_{\mathrm{p}} = \sum_{m=1}^{2} \sum_{i=1}^{4} k_{\mathrm{p},im} \phi_i^{\bullet} f_m \tag{1}$$

$$k_{\mathrm{fm}} = \sum_{i=1}^{4} k_{\mathrm{fm},i} \phi_i^{\bullet} \tag{2}$$

$$k_{\mathrm{fT}} = \sum_{i=1}^{4} k_{\mathrm{fT},i} \phi_i^{\bullet} \tag{3}$$

$$k_{\mathrm{fp}} = \sum_{i=1}^{4} k_{\mathrm{fp},i} \phi_i^{\bullet} \tag{4}$$

$$k^* = \sum_{i=1}^{4} k_i^* \phi_i^{\bullet} \tag{5}$$

$$k_{\mathrm{td}} = \sum_{j=1}^{4} \sum_{i=1}^{4} k_{\mathrm{td},ij} \phi_i^{\bullet} \phi_j^{\bullet} \tag{6}$$

$$k_{\mathrm{tc}} = \sum_{j=1}^{4} \sum_{i=1}^{4} k_{\mathrm{tc},ij} \phi_i^{\bullet} \phi_j^{\bullet} \tag{7}$$

where $\phi_i^{\bullet}$ and f_m are the mole fraction of polymer radical of type i and of monomer of type m in the reaction mixture, which are given by

$$\phi_i^{\bullet} = \sum_{r=1}^{\infty} [R_r^i] / \sum_{j=1}^{4} \sum_{r=1}^{\infty} [R_r^j] \tag{8}$$

$$f_1 = [M_1]/([M_1] + [M_2]) \tag{9}$$

In general, the pseudokinetic rate constants defined above change with the progress of polymerization. On the other hand, however, if the mole fraction of M_2 is much smaller than unity, the change of the pseudokinetic rate constants would be negligibly small, and they could be considered constant. Another reaction condition in which the pseudokinetic rate constants could be considered true constants is the case where the chemical structures of the polymerizable double bonds are the same for the monomer pair, such as the case of styrene and vinylbenzenethiol. In such cases, a reasonable speculation would be that the reactivity of all types of double bonds are equal and that the reactivity of radicals of type 1, 2, and 4 are equal. Therefore, if the reactivity of the polymer radical of type 3 does not differ significantly from other types of polymer radicals, the pseudokinetic rate constants could be considered as true constants. Note that the reasonable estimates for the latter case would be as follows:

$$r_1 = r_2 = 1 \tag{10}$$

$$K = k^*/k_{\mathrm{p}} = 1 \tag{11}$$

$$C_{\mathrm{fm}} = C_{\mathrm{fp}} \tag{12}$$

where r_1 and r_2 are the reactivity ratios, K shows the terminal double-bond reactivity, C_{fm} is the monomer transfer constant ($=k_{\mathrm{fm}}/k_{\mathrm{p}}$), and C_{fp} is the polymer transfer constant ($=k_{\mathrm{fp}}/k_{\mathrm{p}}$). We will show later that the probability of possessing a branch point becomes the same for all units under this special condition.

By using the pseudokinetic rate constants, the rate expressions for the elementary reactions are given by eqs 13−19.

Propagation rate:

$$v_{\mathrm{p}} = k_{\mathrm{p}}[R^{\bullet}][M] \tag{13}$$

where $[R^{\bullet}]$ is the total polymer radical concentration ($= \sum_{i=1}^{4} \sum_{r=1}^{\infty} [R_r^i]$), and [M] is the total monomer concentration ($=[M_1] + [M_2]$).

Rate of chain transfer to monomer:

$$v_{\mathrm{fm}} = k_{\mathrm{fm}}[R^{\bullet}][M] f_2 \tag{14}$$

Note that M_2 monomers are incorporated into polymer chains by both propagation and chain transfer to monomer in the present reaction scheme. On the other hand, however, we consider only the cases where long primary chains are formed in the present report, i.e., v_{p} is much larger than v_{fm}. Therefore, the polymerization rate is given by $v_{\mathrm{p}} + v_{\mathrm{fm}} \cong v_{\mathrm{p}}$.

Rate of chain transfer to CTA:

$$v_{\mathrm{fT}} = k_{\mathrm{fT}}[R^{\bullet}][\mathrm{CTA}] \tag{15}$$

Rate of CTP:

$$v_{\mathrm{fp}} = k_{\mathrm{fp}}[R^{\bullet}] Q_1 (\bar{F}_2 - \bar{\rho}) \tag{16}$$

where Q_1 is the first-order moment of polymer molecules ($= \sum_{r=1}^{\infty} r[P_r]$), $\bar{F}_2$ is the accumulated mole fraction of M_2 in the copolymer chains incorporated by propagation, and $\bar{\rho}$ is the accumulated branching density formed by CTP. The quantity $(\bar{F}_2 - \bar{\rho})$ shows the mole fraction of units that possess chain transfer functional groups in the polymer.

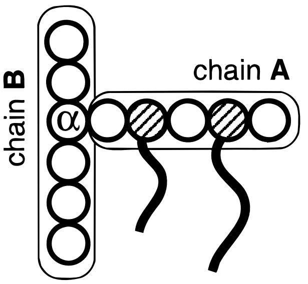

Figure 1. Schematic example of a branched polymer molecule.

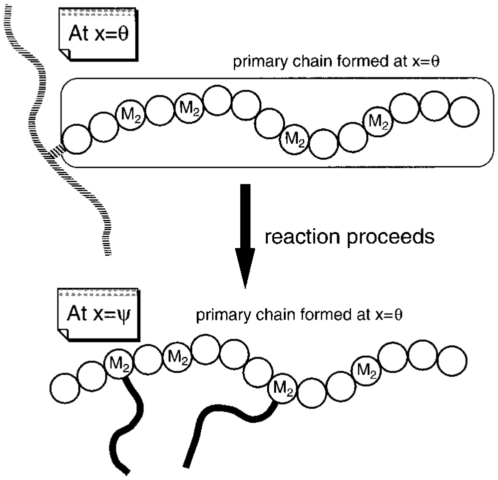

Figure 2. Schematic representation of the branch chain formation on a primary polymer molecule via CTP. The branch chains are formed on the M_2 units bound to the polymer chain after it was born ($x = \theta$).

Rate of TDBP:

$$v^* = k^*[R^\bullet]Q_1\bar{\Phi}^{=} \tag{17}$$

where $\bar{\Phi}^{=}$ is the fraction of terminal double bonds within all units bound to the polymer.

Rate of bimolecular termination by disproportionation, v_{td}, and by combination, v_{tc}:

$$v_{td} = k_{td}[R^\bullet]^2 \tag{18}$$

$$v_{tc} = k_{tc}[R^\bullet]^2 \tag{19}$$

Any type of structural information resulting from the present reaction scheme can be expressed by using the rate equations given by eqs 13–19.

Branching Densities of Primary Chains

In the present model, we consider the expected branching density of a primary polymer molecule by considering the history of each primary polymer molecule.[8,14] The branching density of a primary polymer molecule is the fraction of units that bear a tribranch point. The branch points are considered to belong to the backbone polymer chain. For example, the branching density of the primary chain A shown in Figure 1 is 2/5, and the branch point α is considered to belong to the primary chain B, not chain A.

Branch Points Formed by CTP. When a CTM is first incorporated into polymer chains by propagation reactions, the branch point can be formed on this unit by CTP. Figure 2 shows a schematic representation of the branch chain formation on a primary chain that is born at conversion, $x = \theta$. In order to follow the history of branch chain formation on the primary chain, one needs to determine the mole fraction of CTM (M_2) units bound to the polymer chain by propagation reactions, F_2. The instantaneous mole fraction, F_2, can be determined from the following copolymer composition equation:

$$F_2 = \frac{r_2{f_2}^2 + f_2f_1}{r_2{f_2}^2 + 2f_2f_1 + r_1{f_1}^2} \tag{20}$$

The monomer composition, f_2, can be obtained as follows. The total number of unreacted M_2 molecules in the reaction system, N_2, is given by

$$\frac{dN_2}{dt} = -V(F_2v_p + v_{fm}) \tag{21}$$

where V is the reactor volume. By using the relationship between conversion (x) and time:

$$dx/dt = k_p(1 - x)[R^\bullet] \tag{22}$$

Equation 21 can be expressed as follows:

$$\frac{df_2}{dx} = \frac{(1 - C_{fm})f_2 - F_2}{1 - x} \tag{23}$$

From eqs 20 and 23, one can calculate the copolymer composition of the primary chains formed at a given conversion level. Note that each primary polymer molecule can be considered to be formed instantaneously in the usual free-radical polymerization, because the lifetime of a radical is much smaller than the time required to obtain a high conversion of monomer to polymer.

In CTP reactions, the branch points are formed on the primary chains born earlier. From the point of view of the primary polymer molecule born at $x = \theta$, the branch points are added during the conversion interval from $x = \theta$ to the conversion at the present time, $x = \psi$ ($\theta < \psi$), as shown in Figure 2. Consider the expected density of branch points formed via CTP on the primary chains born at $x = \theta$ when the present conversion is $x = \psi$, $\rho(\theta,\psi)$. The balance equation for $\rho(\theta,\psi)$ is given by

$$\rho(\theta,\psi{+}\Delta\psi) - \rho(\theta,\psi) = k_{fp}\{F_2(\theta) - \rho(\theta,\psi)\}[R^\bullet]\Delta t \tag{24}$$

From eq 24, one obtains the fundamental equation for $\rho(\theta,\psi)$, as follows:

$$\frac{\partial\rho(\theta,\psi)}{\partial\psi} = C_{fp}\frac{F_2(\theta) - \rho(\theta,\psi)}{1 - \psi} \tag{25}$$

Because the number of branch points formed by CTP on a primary chain is zero right at the birth time of the primary chain, the initial condition for eq 25 is given by

$$\rho(\theta,\theta) = 0 \tag{26}$$

If C_{fp} is constant during polymerization one obtains the analytical solution of the expected branching density as follows:

$$\rho(\theta,\psi) = F_2(\theta)\left\{1 - \left(\frac{1 - \psi}{1 - \theta}\right)^{C_{fp}}\right\} \tag{27}$$

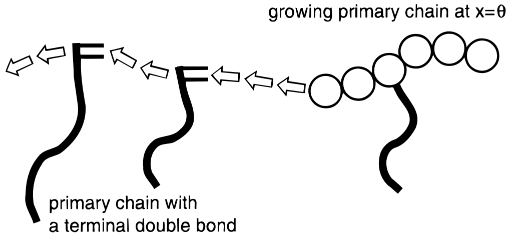

Figure 3. Schematic representation of the branch chain formation on a primary polymer molecule via TDBP. The branch chains are formed during the formation of the primary chain by adding the terminal double bonds located on other primary chains formed earlier.

Branch Points Formed by TDBP. When a CTM is first incorporated into a polymer chain by chain transfer to monomer to form a polymer chain with a terminal double bond, such a polymer chain may become a branch chain through the TDBP. Figure 3 shows a schematic representation of the branch chain formation via TDBP. The branch points on a primary chain are formed during its growth. The branching density formed via TDBP, ρ^*, is therefore given by

$$\rho^*(x) = \frac{v^*(x)}{v_{\mathrm{p}}(x)} = K\left(\frac{x}{1-x}\right)\bar{\Phi}^{=}(x) \tag{28}$$

The fraction of terminal double bonds within all units bound to the accumulated polymer, $\bar{\Phi}^{=}$ is given by

$$\bar{\Phi}^{=}(x) = \frac{1}{x}\int_0^x \Phi^{=}(\theta,x)\,\mathrm{d}\theta \tag{29}$$

where $\Phi^{=}(\theta,x)$ is the fraction of the terminal double bonds within the monomeric units bound to the primary chains born at $x = \theta$, when the conversion at the present time is x. The fundamental equation for $\Phi^{=}(\theta,x)$ is given by[8]

$$\frac{\partial\Phi^{=}(\theta,x)}{\partial x} = -K\frac{\Phi^{=}(\theta,x)}{1-x} \tag{30}$$

Right at the birth time of the primary chains, all terminal double bonds on these chains are alive; therefore, the initial condition for eq 30 is given by

$$\Phi^{=}(\theta,\theta) = \frac{v_{\mathrm{fm}}(\theta)}{v_{\mathrm{p}}(\theta)} = C_{\mathrm{fm}}f_2 \tag{31}$$

If C_{fm} and K do not change during polymerization, the analytical solution of $\Phi^{=}(\theta,\psi)$ is given by

$$\Phi^{=}(\theta,\psi) = C_{\mathrm{fm}}f_2(\theta)\left(\frac{1-\psi}{1-\theta}\right)^K \tag{32}$$

Total Branching Density of the Primary Chains Formed at $x = \theta$. The total branching density of the primary polymer molecule, which is the sum of branching densities formed by both CTP and TDBP, $\rho_{\mathrm{T}}(\theta,\psi)$, is given by

$$\rho_{\mathrm{T}}(\theta,\psi) = \rho^*(\theta) + \rho(\theta,\psi) \tag{33}$$

Therefore, one can estimate the expected branching density of the primary polymer molecules as a function of the birth conversion, θ, at any given present conversion level.

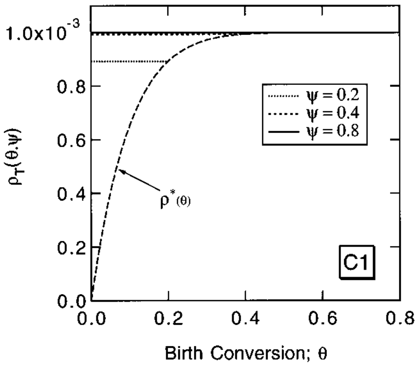

Figure 4. Expected branching density of the primary polymer molecule born at $x = \theta$, when the present conversion levels are $\psi = 0.2$, 0.4, and 0.8, under condition C1.

Copolymerizations with the Same Type of Double Bonds

When the chemical structure of the double bond of a CTM is the same as the comonomer, M_1, the kinetic parameters may be given by eqs 10−12, i.e., $r_1 = r_2 = 1$, $K = 1$, and $C_{\mathrm{fm}} = C_{\mathrm{fp}}$. Here, we consider such special cases.

Because $r_1 = r_2 = 1$, $F_2 = f_2$. By substituting this relationship into eq 23, one obtains

$$f_2 = f_2^0(1-x)^{C_{\mathrm{fm}}} \tag{34}$$

where f_2^0 is the initial mole fraction of CTM. Equation 34 shows that the mole fraction of M_2, f_2, decreases with the progress of polymerization, because M_2 disappears by two routes, i.e., propagation and chain transfer to monomer.

By substituting eq 34 into eq 27, the branching density formed by CTP, $\rho(\theta,\psi)$, is given by

$$\rho(\theta,\psi) = f_2^0\{(1-\theta)^{C_{\mathrm{fm}}} - (1-\psi)^{C_{\mathrm{fp}}}\} \tag{35}$$

On the other hand, from eqs 29, 32, and 34, one obtains

$$\bar{\Phi}^{=}(x) = f_2^0\{(1-x)/x\}\{1-(1-x)^{C_{\mathrm{fm}}}\} \tag{36}$$

By substituting eq 36 into eq 28, the branching density formed via TDBP, $\rho^*(\theta)$ is given by

$$\rho^*(\theta) = f_2^0\{1-(1-\theta)^{C_{\mathrm{fm}}}\} \tag{37}$$

The total branching density, $\rho_{\mathrm{T}}(\theta,\psi)$ is therefore given by

$$\rho_{\mathrm{T}}(\theta,\psi) = f_2^0\{1-(1-\psi)^{C_{\mathrm{fp}}}\} \tag{38}$$

Equation 38 shows that $\rho_{\mathrm{T}}(\theta,\psi)$ is independent of the birth conversion, θ, which means that the expected total branching density is the same for all primary polymer molecules at any stage of polymerization. In other words, the probability of possessing a branch point is the same for all units bound to polymer chains.

Figures 4 and 5 show some of the calculated branching density distribution profiles. The y-axis shows the expected branching density of the primary polymer molecules formed at $x = \theta$ that is given by the value

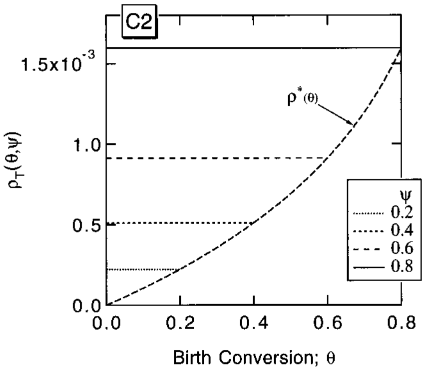

Figure 5. Expected branching density of the primary polymer molecule born at $x = \theta$, when the present conversion levels are $\psi = 0.2$, 0.4, 0.6, and 0.8, under condition C2.

Table 2. Calculation Conditions

	C1	C2	C3	C4
f_2^0	0.001	0.1	0.001	0.1
r_1	1	1	0.8	0.8
r_2	1	1	0.8	0.8
C_{fm}	10	0.01	10	0.01
C_{fp}	10	0.01	8	0.008
K	1	1	0.8	0.8

shown in the x-axis. The branching density distribution profiles are calculated for various present conversion levels, ψ. The calculation conditions are shown in Table 2. The expected branching density is the same for all primary chains irrespective of the magnitude of the chain transfer constants, at any present conversion level.

For free-radical copolymerization of vinyl and divinyl monomers in a batch reactor, the expected cross-linking density becomes the same for all primary chains[22-24] only under Flory's simplifying assumptions:[25] i.e., (1) the reactivities of all types of double bonds are equal, (2) all double bonds react independently, and (3) there are no cyclization reactions. Under Flory's simplifying assumptions, the instantaneous cross-linking density, which corresponds to $\rho^*(\theta)$ in the present reaction system, becomes a straight line. On the other hand, it is interesting to note that $\rho^*(\theta)$ can be curved to form a flat $\rho_T(\theta,\psi)$ profile, as shown in Figures 4 and 5. The smaller or larger $\rho^*(\theta)$ value compared with the diagonal line is exactly canceled out by a larger or smaller $\rho(\theta,\psi)$ value. If one uses a semibatch operation, in principle, it is possible to obtain a flat cross-linking density profile with a curved instantaneous cross-linking density development profile.[26] However, a flat cross-linking density profile is accomplished only at a certain time even under a semibatch operation, while a flat $\rho_T(\theta,\psi)$ profile with a curved $\rho^*(\theta)$ can be obtained at any stage of polymerization in the present reaction system.

In real systems, however, the reactivity ratios may not be exactly unity, and the reactivity of the functional groups located on polymeric species may decrease compared with those on the corresponding monomeric species. Figures 6 and 7 show the calculated branching density distribution profile change under conditions C3 and C4, listed in Table 2. The conditions C3 and C4 are the slightly modified conditions of C1 and C2, respectively. The expected $\rho_T(\theta,\psi)$ values do not deviate significantly from the flat profiles, which shows that we may be able to obtain branched polymers whose branching density is approximately the same for all primary polymer molecules experimentally.

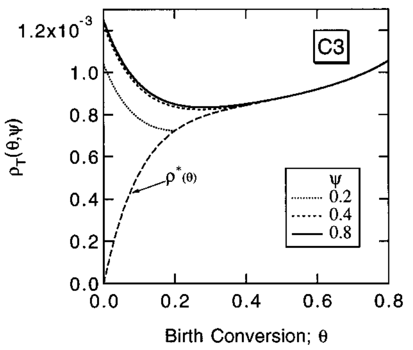

Figure 6. Expected branching density of the primary polymer molecule born at $x = \theta$, under condition C3.

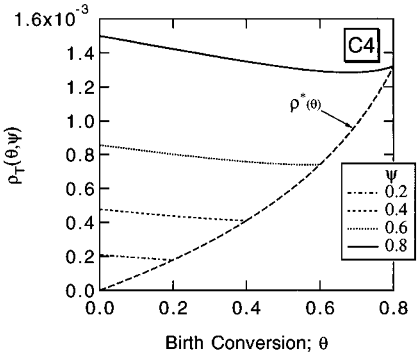

Figure 7. Expected branching density of the primary polymer molecule born at $x = \theta$, under condition C4.

Is the Formed Branched Structure Homogeneous?

Suppose we have obtained a polymer system in which the probability of possessing a branch point is the same for all units in polymers. Does this mean that we have obtained homogeneously branched polymers?

Before answering this question, we have to clarify what the homogeneously branched polymers are. Here, we define the homogeneously branched polymers as the polymers that are obtained by connecting all primary chains randomly. Figure 8 shows an example of a homogeneously branched polymer whose primary chains conform to the most probable distribution. The simulation method to generate a polymer molecule as shown in Figure 8 can be found elsewhere.[9,16] We consider that the homogeneously branched polymers consist of only T-shaped junctions, without forming the H-shaped junctions. The H-shaped junctions that can be formed by combination termination should be considered cross-linking, not branching, because the H-shaped junctions enable the system to cause gelation.[15,27] When one considers the branching density of each primary polymer molecule, bimolecular termination modes do not play a role, because primary chains are those obtained when all branch points are cut. However, we assume $k_{tc} = 0$ in the present discussion for the homogeneity of the branched structure to distinguish the global structural differences. An example of homogeneously branched polymers, where primary chains with the most probable distribution are connected randomly, was considered by Zimm and Stockmayer[28] as early as 1949 to obtain the theoretical description of the radius of gyration for branched polymers.

In order to form a homogeneously branched polymer system, (1) the probability of possessing a branch point is the same for all units and (2) the connection among primary chains must be random. Item 2 states that

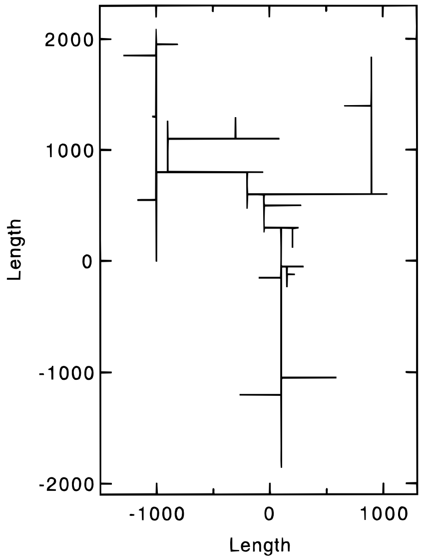

Figure 8. Example of a homogeneously branched polymer that is formed by randomly connecting primary chains with the most probable distribution. The number-average chain length of the primary chains of the whole reaction system is 500, and the branching density of the whole reaction system is 0.001.

when one branch point is selected, this branch point must be connected to any primary chain with equal probability. The reason for requiring item 2 can be rationalized by considering the following thought experiment. Suppose we have two different homogeneously branched polymer systems (X and Y), whose branching densities are the same for both systems, but the primary chain length distributions are different. When we mix these two types of polymers, item 1 is satisfied; however, the whole polymer system cannot be considered homogeneous because chains of X are not connected with chains of Y. The formed molecular weight distribution would be significantly different from that formed when all chains are connected randomly. Item 2 is required except when the primary chain length distributions of X and Y are the same.

The present reaction system fulfills item 1, provided the reactivity of all types of double bonds are equal and $C_{\rm fm} = C_{\rm fp}$. If the primary chain length drift during polymerization does not occur, such reaction systems can provide homogeneously branched polymer systems. However, in general, the primary chain length drift occurs in a batch free-radical polymerization. Therefore, the homogeneously branched polymer system can be formed only when a given primary chain is connected to the primary chains formed at different conversions with equal probability.

Connection via CTP. Consider a branched polymer molecule shown in Figure 9 formed only by CTP. This polymer molecule consists of three primary chains, A, B, and C, whose birth conversions are $\theta_{\rm A}$, $\theta_{\rm B}$, and $\theta_{\rm C}$, respectively. Because branch chains are formed on the backbone polymer chains that were formed earlier, the relationship $\theta_{\rm B} < \theta_{\rm A} < \theta_{\rm C}$ holds.

By looking from chain A, chain B was connected at conversion, $x = \theta_{\rm A}$. At $x = \theta_{\rm A}$, the chain end of A could be connected at any chain transfer functional group. Therefore, the probability that the birth conversion of the connected primary chain was born in the conversion interval, $0 < x < \theta_{\rm B}$, $P_i(\theta_{\rm B}|\theta_{\rm A})$, is given by

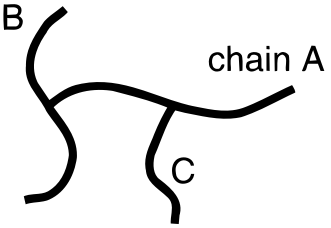

Figure 9. Schematic example of a branched polymer formed by CTP. The birth conversion of the primary chains A, B, and C are $\theta_{\rm A}$, $\theta_{\rm B}$, and $\theta_{\rm C}$, respectively. The conversion at the present time is ψ.

$$P_i(\theta_{\rm B}|\theta_{\rm A}) = \frac{\int_0^{\theta_{\rm B}} \{F_2(x) - \rho(x,\theta_{\rm A})\}\, {\rm d}x}{\int_0^{\theta_{\rm A}} \{F_2(x) - \rho(x,\theta_{\rm A})\}\, {\rm d}x} \tag{39}$$

Suppose the conditions given by eqs 10–12 are applicable. In such cases, by substituting eqs 34 and 35 into eq 39, one obtains

$$P_i(\theta_{\rm B}|\theta_{\rm A}) = \theta_{\rm B}/\theta_{\rm A} \tag{40}$$

Equation 40 shows the connected chain, B, is chosen randomly from the primary chains whose birth conversion is between 0 and $\theta_{\rm A}$.

Next, consider the connection rule from chain A to C. This connection was formed some time after $x = \theta_{\rm A}$, i.e., in the conversion interval from $\theta_{\rm A}$ to the present conversion, ψ. Therefore, the probability that a branch point on primary chain A is connected to a branch chain formed in the conversion interval $\theta_{\rm A} < x < \theta_{\rm C}$, $P_{\rm a}(\theta_{\rm C}|\theta_{\rm A})$ is given by

$$P_{\rm a}(\theta_{\rm C}|\theta_{\rm A}) = \frac{\rho(\theta_{\rm A},\theta_{\rm C})}{\rho(\theta_{\rm A},\psi)} \tag{41}$$

When conditions given by eqs 10–12 are valid, eq 41 reduces to

$$P_{\rm a}(\theta_{\rm C}|\theta_{\rm A}) = \frac{(1-\theta_{\rm A})^{C_{\rm fp}} - (1-\theta_{\rm C})^{C_{\rm fp}}}{(1-\theta_{\rm A})^{C_{\rm fp}} - (1-\psi)^{C_{\rm fp}}} \tag{42}$$

Equation 42 shows that chain C can be chosen randomly from the birth conversion $\theta_{\rm A} < x < \psi$, only when $C_{\rm fp} = 1$.

Connection via TDBP. Consider a branched polymer molecule shown in Figure 10 formed only by TDBP. This polymer molecule consists of three primary chains, A, D, and E, whose birth conversions are $\theta_{\rm A}$, $\theta_{\rm D}$, and $\theta_{\rm E}$, respectively. In TDBP, branch chains are formed on the backbone polymer chains during the formation of the backbone polymer, so the relationship $\theta_{\rm E} < \theta_{\rm A} < \theta_{\rm D}$ holds.

By looking from chain A, chain D was connected some time after $x = \theta_{\rm A}$ by consuming the terminal double bond on chain A, i.e., in the conversion interval from $\theta_{\rm A}$ to the present conversion, ψ. Therefore, the probability that the branch chain A is connected to a backbone chain formed in the conversion interval $\theta_{\rm A} < x < \theta_{\rm D}$, $P_{\rm a}^*(\theta_{\rm D}|\theta_{\rm A})$, is given by

$$P_{\rm a}^*(\theta_{\rm D}|\theta_{\rm A}) = \frac{1 - \Phi^{=}(\theta_{\rm A},\theta_{\rm D})/\Phi^{=}(\theta_{\rm A},\theta_{\rm A})}{1 - \Phi^{=}(\theta_{\rm A},\psi)/\Phi^{=}(\theta_{\rm A},\theta_{\rm A})} \tag{43}$$

Suppose conditions given by eqs 10–12 are valid. By using eqs 31, 32, and 34, eq 43 reduces to

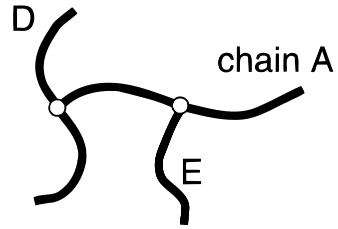

Figure 10. Schematic example of a branched polymer formed by TDBP. The birth conversion of the primary chains A, D, and E are θ_A, θ_D, and θ_E, respectively. The conversion at the present time is ψ.

$$P_a^*(\theta_D|\theta_A) = \frac{\theta_D - \theta_A}{\psi - \theta_A} \tag{44}$$

Equation 44 shows the birth conversion of the connected chain, D, is chosen randomly from θ_A to ψ.

Next, consider the statistics of chain connection from chain A to E. At $x = \theta_A$, the backbone chain A could be connected to any terminal double bond that exists at $x = \theta_A$. Therefore, the probability that a branch point of A is connected to a primary chain whose birth conversion is between 0 and θ_E, $P_i^*(\theta_E|\theta_A)$, is given by

$$P_i^*(\theta_E|\theta_A) = \frac{\int_0^{\theta_E} \Phi^{=}(x,\theta_A)\,dx}{\int_0^{\theta_A} \Phi^{=}(x,\theta_A)\,dx} \tag{45}$$

If conditions given by eqs 10–12 are applicable, from eqs 32 and 34, one obtains

$$P_i^*(\theta_E|\theta_A) = \frac{1 - (1 - \theta_E)^{C_{fm}}}{1 - (1 - \theta_A)^{C_{fm}}} \tag{46}$$

Equation 46 shows that chain E is considered to be chosen randomly from the birth conversion $0 < x < \theta_A$, only when $C_{fm} = 1$.

Conditions To Produce Homogeneously Branched Polymers. On the basis of eqs 40, 42, 44, and 46, in order to produce homogeneously branched polymers in the present reaction scheme, one needs the following relationship in addition to eqs 10 and 11:

$$C_{fm} = C_{fp} = 1 \tag{47}$$

The branching density distribution development under this ideal condition is shown in Figure 11. In this case, $\rho^*(\theta)$ becomes a straight line. The formed branched structure is homogeneous at any stage of polymerization.

The present theoretical investigation results show that by using a series of CTMs whose chain transfer constants are different, one may be able to investigate the difference of the chain connection statistics with keeping the branching density of the primary polymer molecules the same. Such investigations would promise to reveal the effect of the detailed structural differences on the physical properties of branched polymer systems.

Conclusions

A theoretical investigation was conducted for the distribution of branch points in a batch free-radical copolymerization with chain transfer monomer. The fundamental equations to estimate the branching density of primary chains as a function of the birth conversion, as well as those for chain connection statistics have been developed. It was found that if the reactivities of all types of double bonds can be considered equal and the reactivity of chain transfer functional groups does not change even after being incorporated into polymer chains (i.e., under conditions $r_1 = r_2 = 1$, $K = 1$, and $C_{fm} = C_{fp}$), the expected branching density becomes the same for all primary chains, irrespective of the magnitude of chain transfer constants. On the other hand, however, the primary chains are not connected randomly except under $C_{fm} = C_{fp} = 1$. Therefore, to produce homogeneously branched polymers by using the present reaction in a batch polymerization, one needs a special chain transfer monomer that satisfies $C_{fm} = C_{fp} = 1$ in addition to the conditions with equal reactivity of double bonds.

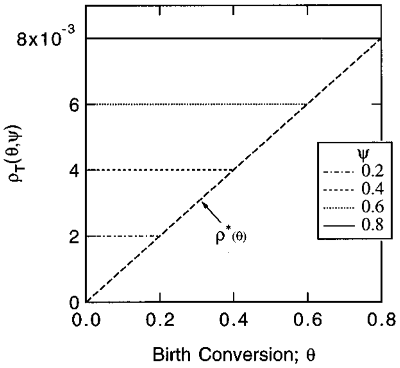

Figure 11. Calculated branching density distribution profile at various present conversion levels under the "ideal" condition where homogeneously branched polymer molecules are formed. The initial mole fraction of CTM is $f_2^0 = 0.01$.

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Glossary of Principal Symbols

C_{fm}	monomer chain transfer constant ($=k_{fm}/k_p$)
C_{fp}	polymer chain transfer constant ($=k_{fp}/k_p$)
F_2	instantaneous mole faction of CTM bound to polymer chains by propagation reactions
f_1, f_2	mole fraction of M_1 and M_2, respectively
f_2^0	initial mole fraction of M_2
K	terminal double bond reactivity ($=k^*/k_p$)
k_{fm}, k_{fp}, k_{fT}	pseudokinetic rate constants for chain transfer reactions to monomer, polymer, and chain transfer agents, respectively
k_p, k^*	pseudokinetic rate constants for propagation and terminal double bond polymerization reactions, respectively
k_{tc}, k_{td}	pseudokinetic rate constants for bimolecular termination by combination and disproportionation, respectively
M_1	monomer whose chain transfer constant is much smaller than for the chain transfer monomer
M_2	chain transfer monomer (CTM)
[M]	total monomer concentration ($=[M_1] + [M_2]$)
Q_1	first-order moment of polymer molecules ($= \sum_{r=1}^{\infty}[P_r]$), which is equal to $[M]_0 V_0 x/V$, where the subscript 0 is used to designate the initial values
$[R^\bullet]$	total radical concentration
r_1, r_2	reactivity ratios, $r_1 = k_{p,11}/k_{p,12}$ and $r_2 = k_{p,22}/k_{p,21}$

V	reactor volume
v_{fm}, v_{fp}, v_{fT}	rates of chain transfer reactions to monomer, polymer, and chain transfer agents, respectively
v_{p}, v^*	propagation (polymerization) rate and the rate of terminal double-bond polymerization, respectively
x	conversion

Greek Letters

$\Phi^{=}(\theta,\psi)$	fraction of terminal double bonds within the units bound to polymer chains at $x = \theta$, when the present conversion is $x = \psi$
$\bar{\Phi}^{=}(x)$	accumulated fraction of terminal double bonds within all units bound to polymer chains at conversion x (see eq 29)
θ	conversion at which the given primary polymer molecule was born (birth conversion)
$\rho(\theta,\psi)$	expected branching density of the primary polymer molecules born at $x = \theta$ formed by CTP, when the present conversion is $x = \psi$
$\rho^*(\theta)$	expected branching density of the primary chains born at $x = \theta$ formed by TDBP
$\rho_{\mathrm{T}}(\theta,\psi)$	expected branching density of the primary polymer molecules born at $x = \theta$, when the present conversion is $x = \psi$ $(=\rho^*(\theta) + \rho(\theta,\psi))$
ψ	conversion at the present time (present conversion)

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