Scale-Free Power-Law Distribution of Emulsion-Polymerized Nonlinear Polymers: Free-Radical Polymerization with Chain Transfer to Polymer

Hidetaka Tobita[†]

Department of Materials Science and Engineering, University of Fukui, 3-9-1 Bunkyo, Fukui 910-8507, Japan

Received September 12, 2003; Revised Manuscript Received November 17, 2003

ABSTRACT: The power-law distributions in molecular weights are found in the emulsion-polymerized polyethylenes, where the polymer transfer reactions are significant. A simple kinetic model for interval II in emulsion polymerization can describe the polyethylene distribution reasonably well, and this model is used to investigate the molecular weight distribution (MWD) formed in emulsion polymerization that involves chain transfer to polymer. The MWD profiles are dominated by the P_b value, which represents the probability that the chain end is connected, and by increasing P_b, the MWD changes from the exponential to the power-law distribution. A scale-free power-law distribution is formed for $P_b > 0.5$.

Introduction

Recently, there has been increasing interest in the scale-free power-law distribution, which has been found in various fields both in nature and man-made world, such as in the World Wide Web (WWW),[1] the metabolic networks,[2] and the SARS epidemic in Singapore.[3] Various interesting aspects of the scale-free networks are well documented in the popular science books.[4] In the polymer distribution, the high molecular weight tail of the cross-linked polymers right at the gel point is believed to be a power-law distribution.[5] Practically, however, such a polymer mixture right at the gel point is difficult to obtain. In this article, it is shown that the scale-free power-law distribution can be obtained in nonlinear emulsion polymerization.

The molecular weight distribution (MWDs) of the branched[6−9] and cross-linked[10−13] polymers formed in emulsion polymerization are sometimes much different from those in corresponding bulk polymerization. In nonlinear polymer formation, assembly of a large number of linear primary chains may lead to form huge polymer molecules, but the molecular weight of the largest polymer formed in emulsion polymerization cannot exceed the molecular weight of the polymer particle. In general, the MWD of polymers in emulsion polymerization is dependent on the particle size distribution (PSD). Suppose that all primary chains in each polymer particle are connected to form a single polymer molecule, the MWD is equivalent to the PSD, and a strong order imposed by the PSD is reflected in the MWD. On the other hand, because the primary chains follow a random distribution that is most simply represented by the most probable distribution, the MWD conforms to the exponential distribution without branching/cross-linking. The scale-free power-law distributions are often found between the order and disorder, and a weak governance of particle size on the MWD may lead to such types of distribution.

In addition, in terms of the molecular weights of polymers, the models developed for nonlinear emulsion polymerization[8,10] are essentially equivalent to the model proposed in ref 1 to reproduce a scale-free power-law distribution. In ref 1, it was shown that the scale-free networks are formed as a consequence of two generic mechanisms: (i) networks expand continuously by the addition of new vertexes, and (ii) new vertexes attach preferentially to sites that are already well connected. Consider an emulsion polymerization that involves chain transfer to polymer, as an example. New primary chains are formed consecutively in a polymer particle, and a larger polymer molecule consisting of a larger number of primary chains has a better chance of being connected to a newly formed primary chain because it possesses a larger number of functional groups. The growth and preferential attachment of primary chains are important characteristics of nonlinear emulsion polymerization.

In this article, first the MWDs of the emulsion-polymerized polyethylene reported in the literature are investigated, and it is shown that a power-law distribution applies to the MWDs for the important range of molecular weights. Then, a very simple kinetic model that can represent the polyethylene MWD reasonably well is discussed. This model is used to clarify the necessary conditions to form scale-free power-law MWDs.

MWD of Emulsion-Polymerized Polyethylene

Two MWDs reported in ref 7 are used for the present investigation. Both types of polyethylene are produced in a batch emulsion polymerization. A cationic surfactant was used for case 1 and an anionic surfactant for case 2. It is known that the polymer transfer reactions are significant in free-radical ethylene polymerization.

The upper panels of Figures 1 and 2 show the reported MWDs. The independent variable for these MWDs is the logarithm of molecular weight, log M, as usually employed in a GPC analysis. The MWD is bimodal, when represented as the weight fraction distribution, $W(\log M)$.

The lower panels of Figures 1 and 2 represent the log−log plot of the number fraction distribution, $N(M)$; i.e., the relationship between log $N(M)$ and log M is shown. The number fraction distribution conforms to the power-law distribution, given by eq 1 for the largest part of the molecular weights.

$$N(M) \propto M^{-\gamma} \tag{1}$$

[†] E-mail: tobita@matse.fukui-u.ac.jp.

10.1021/ma035357c CCC: $27.50

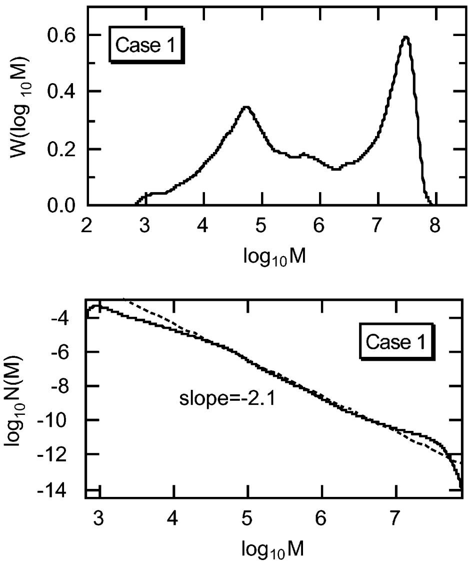


Figure 1. MWD of the emulsion-polymerized polyethylene reported in ref 7.

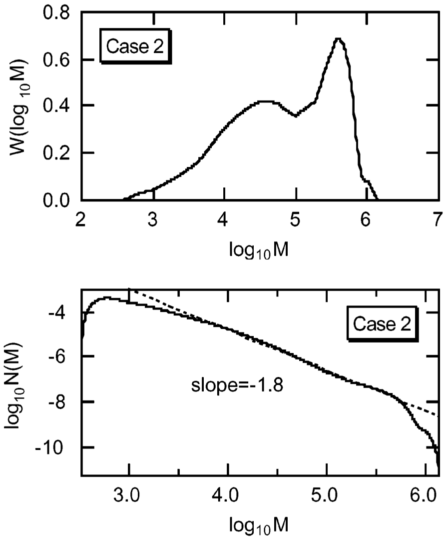


Figure 2. MWD of the emulsion-polymerized polyethylene reported in ref 7.

When the number fraction distribution follows the power-law distribution, the weight fraction distribution is given by

$$W(M) \propto M^{-(\gamma-1)} \tag{2}$$

The applicability of eq 2 to these two MWDs was also confirmed.

Note that the power law always displays a characteristic cutoff because of the finite size of the system. In general, the observed distribution is a straight line on a log–log plot, over some limited range. Further, note that a strict power-law distribution should not show a bimodal distribution when plotted as *W*(log *M*). However, the power-law relationship holds for the molecular weight range approximately between two peaks of *W*(log *M*), as shown in Figures 1 and 2.

As clarified earlier,[9,10] the high molecular weight, narrow distribution component in *W*(log *M*) basically consists of the largest polymer molecule in each polymer particle, and the bimodal MWDs are formed because of the limited space effects; i.e., the polymerization locus is confined in a very small particle. For the emulsion cross-linking copolymerization of styrene and divinylbenzene, it was shown experimentally[13] that bimodal MWDs are formed by setting the number of divinylbenzene units per chain ca. 5. It was further shown that the location of the high molecular weight peak can be controlled mainly by the particle size, while that for the low molecular weight peak is controlled by the chain length of primary chains.

The higher molecular weight peak shows an order imposed by the particle size. The lower molecular weight peak represents the randomness in size of primary chains, which is the exponential type. A power-law distribution holds between the order and disorder, which is the region approximately between two peaks of *W*(log *M*).

Simple Model System

It was shown that the MWDs given in Figures 1 and 2 agree reasonably well with a Monte Carlo (MC) simulation model proposed in ref 9. However, the model used there accounts for various complex kinetic events, including the entry and exit of radicals and the formation of polyradicals. To clarify the mechanisms and conditions to form a scale-free power-law distribution, a more simplified model[14,15] is used in this article.

Basically, the following reaction conditions are assumed. (1) The simple "zero-one" system[16] in which a newly entered radical to a polymer particle containing one polymer radical is terminated instantaneously applies, (2) the system is in interval II[16] where monomer is supplied continuously from monomer droplets to replace that which has reacted and the polymer/monomer ratio in the polymer particle is kept constant, and (3) all polymer particles contain the same number of primary chains, *n*. These assumptions are reasonable, at least, to clarify the important characteristics of nonlinear polymer formation in emulsion polymerization.

With the above assumptions, the primary polymer molecules follow the most probable distribution, whose number fraction distribution is given by

$$N(r) = \tau \exp(-\tau r) \tag{3}$$

$$\tau = C_P + C_{fm} + C_{fCTA}\frac{[CTA]_p}{[M]_p} + \frac{1}{k_p[M]_p\bar{t}_e} \tag{4}$$

$$C_P = C_{fp}\frac{x_c}{1 - x_c} \tag{5}$$

where C_{fm}, C_{fCTA}, and C_{fp} are the chain transfer constants to monomer, chain transfer agent (CTA) and polymer, respectively. $[M]_p$ and $[CTA]_p$ are the concentrations of monomer and CTA in the polymer particle, respectively. The parameter k_p is the propagation rate constant, $\bar{t}_e$ is the average time interval between radical entry, and x_c represents the weight fraction of polymer in the polymer particle, which is usually equal to the monomer conversion at which monomer droplets disappear.

The probability that a newly formed primary chain has started growing from a radical center on a backbone chain, i.e., the probability that the primary chain end is connected to a backbone chain, P_b, is given by

$$P_b = C_P/\tau \tag{6}$$

In the present simplified model, constant values of τ and P_b are assumed. In the MC simulation, the primary chains following the most probable distribution given by eq 3 are generated one by one in a polymer particle. Every time a new primary chain is generated, it is connected to a polymer molecule in the particle with probability P_b. The connected polymer is chosen on a weight basis; i.e., the probability is proportional to the molecular weight of polymer. The simulation continues until the number of primary chains in a particle reaches a given value of n. A certain number of particles are investigated in order to obtain sufficient number of polymer molecules for the statistical analysis.

Some of the important characteristics of the present simplified model that had already been clarified prior to the present investigation are discussed below.

Weight-Average Chain Length. The weight-average chain length, $\bar{P}_w$, at the time when the number of primary chain in a polymer particle is n, is given by the following recursion formula[14]

$$\bar{P}_w(n+1) = \frac{n}{n+1}\left(1 + \frac{2P_b}{n+1}\right)\bar{P}_w(n) + \frac{\bar{P}_{wp}}{n+1} \tag{7}$$

where $\bar{P}_{wp}$ is the weight-average chain length of primary chains, $\bar{P}_{wp} = 2/\tau$. Obviously, $\bar{P}_w(1) = \bar{P}_{wp}$.

From eq 7, the limiting value of $\bar{P}_w$ for $n \to \infty$, $\bar{P}_w(\infty)$ is given by[15]

$$\bar{P}_w(\infty) = \frac{\bar{P}_{wp}}{1 - 2P_b} \tag{8}$$

Equations 7 and 8 show that $\bar{P}_w$ reaches a stationary value for $P_b < 0.5$, which means that the effects of particle size disappears, at least for large n values. On the other hand, for $P_b > 0.5$, $\bar{P}_w$ increases continuously during polymerization and is affected by the particle size. The $\bar{P}_w$ development changes drastically at $P_b = 0.5$.

MWD Profiles. The MWD profiles represented by $W(\log M)$ are bimodal[15] for $P_b > 0.5$. The high molecular weight, narrow distribution component moves to larger molecular weight as polymerization proceeds and the particle size becomes larger.

MC Simulation Results

Before conducting a systematic study for the formation of scale-free power-law distributions, the MWD of polyethylene shown in Figure 1 is simulated. The kinetic parameters taken from various literature for free-radical polymerization of ethylene are summarized in Table 1 of ref 9. Using those values, one obtains $\tau = 5.35 \times 10^{-3}$ and $P_b = 0.813$ for case 1. It is assumed that the molecular weight of a polymer particle is 1.4×10^8 g/mol; that is, $n = 26\,750$. To obtain statistically valid MWDs, about 10^5 polymer molecules were generated. Figure 3 shows the simulated MWD. It is confirmed that the present simplified model can describe the MWD of polyethylene reasonably well, although complicated kinetics, such as the entry and exit of radicals and the chain scission reactions are neglected.

Next, a set of MC simulations are conducted for $\tau = 0.001$, i.e., the number-average chain length of primary chains is $\bar{P}_{np} = 1000$. The P_b value was changed to investigate the MWDs formed. Approximately 10^5 polymer molecules were generated for each reaction condition.

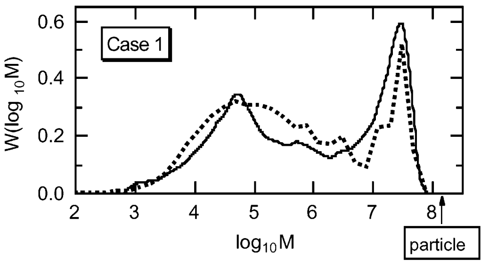


Figure 3. MWD of the emulsion-polymerized polyethylene. The dotted curve shows the MC simulation results of the present simplified model, while the solid curve is the experimental result reported in ref 7. The particle size assumed is indicated by an arrow.

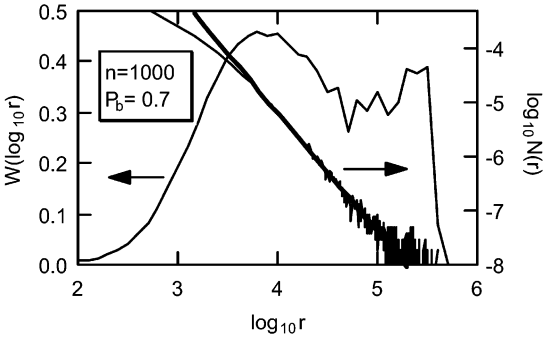


Figure 4. Simulated MWD with $P_b = 0.7$, showing that the distribution is a power law.

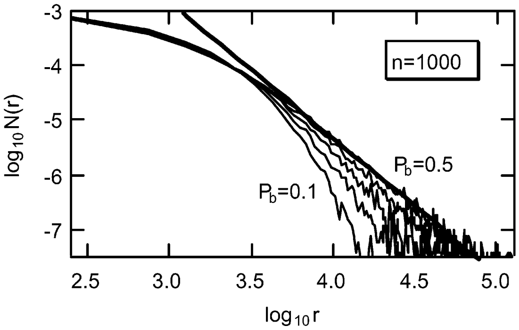


Figure 5. Log–log plot of the number fraction distribution for $P_b = 0.1$, 0.2, 0.3, 0.4, and 0.5.

Figure 4 shows the MWD formed for $P_b = 0.7$ when the number of primary chains in a particle, $n = 1000$. In the figure, r represents the chain length (degree of polymerization). Note that the dried particle size represented by the number of monomeric units, r is given by $n\bar{P}_{np}$, and therefore, $\log r = 6$ in the present calculation condition. In terms of $W(\log r)$, the MWD is bimodal. On the other hand, however, the log–log plot of the number fraction distribution, $N(r)$ shows a clear straight line between these two peaks of $W(\log r)$. The present emulsion polymerization model yields a power-law distribution.

Figure 5 shows the log–log plot of the number fraction distribution for $P_b = 0.1$–0.5. Obviously, $P_b = 0$ yields an exponential distribution given by eq 3, and the distribution changes from the exponential to the power-law distribution by increasing the P_b value. At $P_b = 0.5$, a wide range of linear relationship is observed.

As the polymerization proceeds, the average molecular weight increases continuously for $P_b > 0.5$ as represented by eq 7, and therefore, the MWD plotted

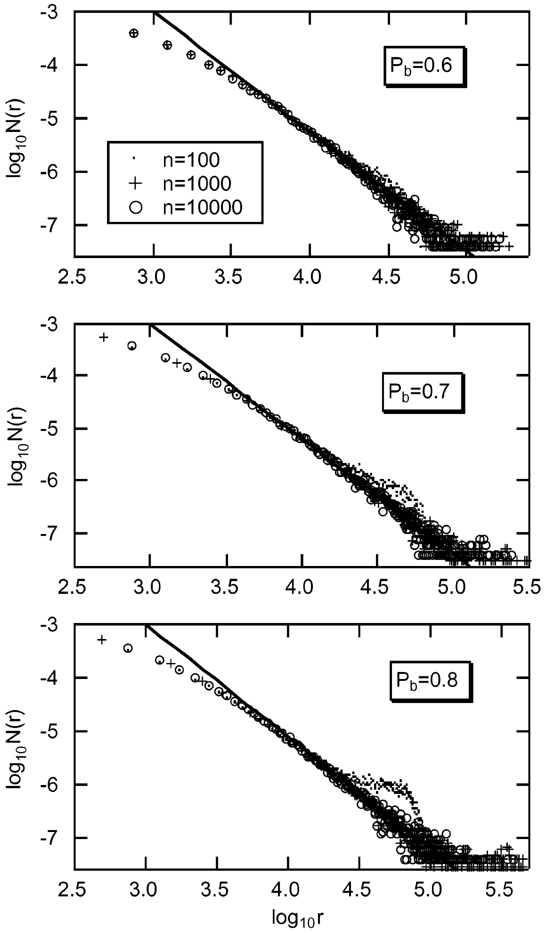


Figure 6. MWD development for $P_b = 0.6$, 0.7, and 0.8, showing that the distribution is a scale-free power law.

as $W(\log r)$ changes with n.[15] On the other hand, however, Figure 6 shows that the distribution is scale-free and is independent of time, i.e., the power-law distribution holds how large the particles may grow. The cutoff limit increases as polymerization proceeds but the distribution follows the same power-law line. It is clearly shown that the present emulsion polymerization model leads to a scale-free power-law distribution.

Distribution of Branch Points

In this section, I consider how branching points are distributed among primary chains. In the present simplified model, the expected branching density of the *i*th primary chain within the polymer particles consisting of n ($i \le n$) primary chains, $\rho(i,n)$ is given by[14]

$$\rho(i,n) = C_P[\psi(n) - \psi(i)](9) \tag{9}$$

where $\psi(z)$ is the digamma function defined by $\psi(z) = \mathrm{d}(\ln\Gamma(z))/\mathrm{d}z$.

When both n and i are much larger than unity, eq 9 reduces to

$$\rho(i,n) = C_P \ln(n/i) \tag{10a}$$

To consider ρ as a continuous function, the integer i is changed to real number x

$$\rho(x,n) = C_P \ln(n/x) \tag{10b}$$

The weight fraction of primary chains whose branching density is smaller than ρ, $F(\rho)$, is given by

$$F(\rho) = (n - x)/n \tag{11a}$$

or

$$F(\rho') = (n - x)/n \tag{11b}$$

where $\rho' = \rho/C_P$.

From eqs 10b and 11b, one obtains the probability density distribution function, $f(\rho')$ ($=\mathrm{d}F(\rho')/\mathrm{d}\rho'$), as follows:

$$f(\rho') = \exp(-\rho') \tag{12}$$

Equation 12 shows that the distribution of branch points among primary chains is the exponential distribution.

The number of branch points on a primary chain follows the exponential distribution and not the power law. The exponential distribution is often associated with the randomness; however, one needs to note that the distribution given by eq 12 does not result from a complete randomness. The primary chains formed earlier have a larger expected branching density than those formed later.

On the other hand, however, it is interesting to note that in terms of the primary chains, both distributions of molecular weights and branch points are the exponential, although the assembly of such primary chains results in forming the MWD that follows a scale-free power-law distribution. A power-law distribution emerges from the exponential distributions.

MWD of Branched Polymers Formed in Homogeneous Media

Finally, I consider if the limitation of reaction volume is essential to form a scale-free power-law distribution. As a most simple example, the MWD of randomly branched polymers formed in an infinitely large space is considered. In the present context, the randomly branched polymers are those formed by connecting one of two chain ends of primary chains randomly. The expected branching density is the same for all primary chains.

When the MWD of primary chains follows the most probable distribution, the number fraction distribution of the randomly branched polymers is given by[17]

$$N(r) = \frac{I_1(2r\sqrt{\rho/\bar{P}_{\mathrm{np}}})}{r\sqrt{\rho\bar{P}_{\mathrm{np}}}}\exp\left[-\left(\frac{\rho\bar{P}_{\mathrm{np}} + 1}{\bar{P}_{\mathrm{np}}}\right)r\right] \tag{13}$$

where I_1 is the modified Bessel function of the first kind and of the first order. $\bar{P}_{\mathrm{np}}$ is the number-average chain length of the primary chains.

Figure 7 shows the MWD represented as $W(\log r)$ and the log−log plot of $N(r)$. It is clearly shown that the distribution is not a power law. The present example shows the importance of the particle size that imposes a weak order to the formed MWD. A random connection of chains does not form a power-law distribution, except right at the gel point.[5]

Then, is it impossible to obtain a scale-free power-law distribution using homogeneous polymerization where the reaction space is infinitely large? I think it possible by giving the system another type of weak order.

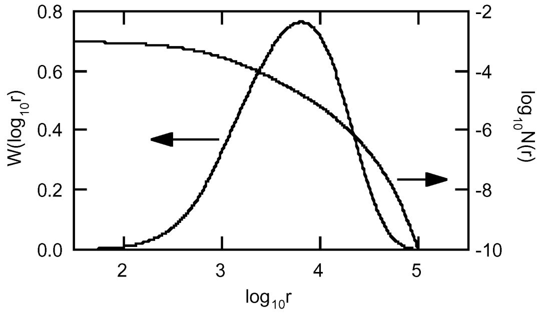


Figure 7. MWD of homogeneously branched polymer with $\bar{P}_{np}$=1000 and $\rho = 0.0005$, showing that the distribution is not a power law.

The present emulsion polymerization model represents a variable-volume system with constant composition. As correctly pointed out by Hamielec et al,[18] this reaction system is equivalent to an ideally mixed continuous stirred tank reactor (CSTR) where polymer/monomer ratio is kept constant. Therefore, another method to obtain a scale-free power-law distribution would be to use a CSTR. (Note that in this case there is no size limit for the polymer to grow.) After reaching a constant polymer/monomer ratio,[19] the distribution becomes scale-free for $P_b > 0.5$. I have already confirmed this; however, the details of this topic will be reported separately.

The scale-free power-law distribution could be obtained by imposing appropriate chain connection rule also for polymerization in homogeneous media.

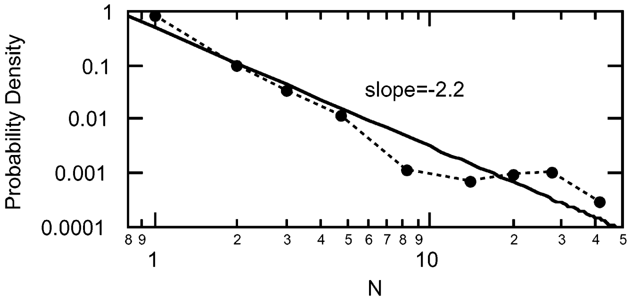
Conclusions

The power-law distributions in molecular weights were found in the emulsion-polymerized polyethylenes, where the polymer transfer reactions are significant. The power-law relationship holds for the molecular weight range between two peaks of $W(\log M)$. The higher molecular weight peak shows the order imposed by the particle size, while the lower molecular weight peak represents the randomness in size of primary chains. The power-law distribution emerges between the order and disorder.

A simple kinetic model for interval II in emulsion polymerization that can describe the polyethylene distribution reasonably well was used to investigate the MWD formed in emulsion polymerization that involves chain transfer to polymer. It was found that the scale-free power-law distribution is formed when the probability of chain connection, $P_b > 0.5$, for which the effects of limited reaction space cannot be neglected throughout the polymerization. On the basis of the present investigation, the power-law distribution seems to appear with a weak governance of order to an essentially random system.

References and Notes

(1) Barabasi, A.-L.; Albert, R. *Science* **1999**, *286*, 509−12.
(2) Jeong, H.; Tombor, B.; Albert, R.; Oltvai, Z. N.; Barabasi, A.-L. *Nature* **2000**, *407*, 651−654.
(3) The probability density function (PDF, the number fraction distribution) of the number of persons infected by the same virus, N (that is larger by one than the number of persons infected by an individual patient) appears to follow the power-law distribution as shown below. The data points are plotted at the middle points of each column of the histogram. This distribution can be reproduced reasonably well by the model developed in ref 1 with $m_0 = m = 1$. More details can be obtained from the author upon request.



(4) (a) Barabasi, A.-L. *Linked: The New Science of Networks*; Perseus Press: Cambridge, MA, 2002. (b) Watts, D. J. *Six Degrees*; Norton, New York, 2003.
(5) Stauffer, D.; Conoglio, A.; Adam, M. *Adv. Polym. Sci.* **1982**, *44*, 103−158.
(6) Senrui, S.; Suwa, T.; Takehisa, M. *J. Polym. Sci., Polym. Chem.* **1974**, *12*, 93−103.
(7) Starkweather, H. W., Jr.; Han, M. C. *J. Polym. Sci., Polym. Chem.* **1992**, *30*, 2709−13.
(8) Tobita, H. *Polymer* **1994**, *35*, 3023−3031.
(9) Tobita, H. *J. Polym. Sci., Polym. Chem.* **2002**, *40*, 3426−3433.
(10) Tobita, H.; Yamamoto, K. *Macromolecules* **1994**, *27*, 3389−3396.
(11) Matsumoto, A.; Mori, Y.; Takahashi, S.; Aota, H. *Netsukokaseijushi* **1995**, *16*, 131−143.
(12) Tobita, H.; Kumagai, M.; Aoyagi., N. *Polymer* **2000**, *41*, 481−487.
(13) Tobita, H.; Aoyagi, N.; Takamura, S. *Polymer* **2001**, *42*, 7583−7587.
(14) Tobita, H. *J. Polym. Sci., Polym. Phys.* **1997**, *35*, 1515−1532.
(15) Tobita, H. Bimodal Molecular Weight Distribution Formed in Emulsion Polymerization with Long-Chain Branching. *Polym. React. Eng.*, in press.
(16) Gilbert, R. G. *Emulsion Polymerization*; Academic Press: London, 1995.
(17) Tobita, H. *Macromolecules* **1996**, *29*, 3010−3021.
(18) Friis, N.; Goosney, D.; Write, J. D.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1974**, *18*, 1247−1259.
(19) When free-radical polymerization that involves chain transfer to polymer is conducted in an ideally mixed CSTR, the concentration and the number-average MW will reach a steady state but the weight-average MW may keep on increasing unlimitedly, as implied by eq 8. Continuous increase of the weight-average MW in a CSTR is discussed in: Tobita, H. *J. Polym. Sci., Polym. Phys.* **1998**, *36*, 2015−2018. The MWD will be scale-free under an idealized condition.

MA035357C