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Polymer Vol. 36 No. 13, pp. 2585–2596, 1995
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0032-3861/95/\$10.00+0.00

Simulation model for the modification of polymers via crosslinking and degradation

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(Received 12 July 1994; revised 19 September 1994)

The Monte Carlo sampling technique, in which polymers are sampled randomly from an infinite number of polymer molecules in the reaction system, is used to make computer simulations for the molecular-weight distribution (*MWD*) change during crosslinking and degradation processes. In this method, since one can investigate each polymer molecule directly, very detailed structural information can be easily obtained. This present method is not restricted by the condition of long primary chains with a low degree of crosslinking and degradation, and it is also straightforward to account for the effect of the residence time distribution. When the initial *MWD* is extremely narrow, say $P_w/P_n < 1.1$, a multimodal distribution may be obtained by crosslinking reactions; however, in general, the crosslinking and/or degradation reactions tend to produce a unimodal *MWD* as long as the size and structural dependence of crosslinking and scission reactions is not important. When the expected crosslinking density is not the same for all primary polymer molecules, namely there exists a crosslinking density distribution among the primary polymer molecules, the average crosslinking density at the gel point is smaller than the value of $1/P_{wp}$ that is expected from the Flory–Stockmayer theory, where P_{wp} is the weight-average chain length of the primary polymer molecules.

(Keywords: crosslinking; Monte Carlo method; computer simulation)

INTRODUCTION

The modification of polymers, for example via chain scission, long chain branching, crosslinking and grafting, is an important commercial process aiming at the improvement of the physical and chemical properties of these materials. Crosslinking and degradation of polymer molecules are complex molecular processes, and the theoretical description of such processes[1–9] usually involves difficult mathematical treatment, which has been a strong barrier against the development of industrial processes with higher capabilities for designing and controlling the polymer products. Furthermore, most conventional approaches, in general, provide only the average properties or the moments of the distributions, and the complete distribution functions cannot be obtained. However, in order to fulfil the requirements of these present times to produce higher quality polymers, a consideration of controlling the whole distribution seems inevitable. At present, the analytical techniques available for obtaining the full distribution functions are limited to very special cases, and the numerical solutions for the population balance equations can be complicated and time consuming.

From the point of view of each primary polymer molecule, however, the connection and scission of the primary chains occur stochastically conforming to the appropriate chemical kinetics, and the structure formed should result from such recursive processes. Therefore, once the connection and scission rule among the primary polymer molecules is made clear, the use of Monte Carlo computer simulations can be a powerful method for investigating the whole molecular constitution. On the basis of such an idea, the Monte Carlo sampling technique was recently developed to investigate non-random history-dependent crosslinking[10–13] and branching[14–17] reactions in free-radical polymerizations.

Monte Carlo simulations, except for the sampling method used in this present paper, usually employ a finite reaction system to represent, approximately, an infinite reaction system[18–24], i.e. a very small part is removed from the reaction mixture and the kinetic behaviour of all of the molecules involved in this small volume is simulated. Use of a limited reaction volume makes it possible to conduct percolation type simulations[19–22] which are considered to be equivalent to a non-mean-field theory. However, realistic simulations that must account for the diffusion and mobility during crosslinking and degradation require an excessive amount of calculations, even for an extremely small reaction volume with a limited time interval. At present, percolation type simulations have succeeded in providing only a qualitative description of the complex reaction systems (except for the close vicinity of the gel point where specific system features can be neglected). Furthermore, use of a limited number of monomeric units in a very small reaction volume makes it difficult to obtain distribution functions such as the full *MWD* due to the rather small number of molecules simulated in high polymer systems.

A certain kind of finiteness is required in the computer simulations, since the memory size of a computer is limited. The Monte Carlo sampling technique used in this paper does not require a finite reaction system but instead takes a finite number of polymer molecules from the 'sea' of polymer molecules. By taking a large number of polymer molecules as a sample from the population, the statistical properties can be determined effectively.

In this paper, the Monte Carlo sampling technique is developed for the random crosslinking and degradation reactions of polymer chains under the classical ring-free model[1,2], and the change in the molecular-weight distribution is investigated in detail. Neglect of ring formation may be a drawback in the application to real systems; however, at present the long-range correlations required for the analysis of ring formation are virtually unknown for crosslinked polymer systems. On the other hand, since it is possible to investigate the spatial distribution of the crosslinked polymer chains on the basis of the simulated data obtained in the Monte Carlo sampling technique[13,17,25], it is hoped to overcome such weakness in the context of the present method in the near future. In this paper, we treat rather simple cases; however, since the Monte Carlo sampling technique can account for the effect of the residence time distribution of the primary polymer molecules, as already achieved for crosslinking[10–13] and branching[14–17] reactions, extension of this present method to various reactor types, including extruders, is straightforward.

MODEL DEVELOPMENT

We consider the crosslinking and degradation of polymer chains by the use of the following basic assumptions: (1) crosslinking proceeds without any cycle formation, and (2) crosslinking and scission reactions are mutually independent, and the size and structural dependence of these reactions are neglected. In order to simplify the discussion we further assume that (3) each unit possesses only one crosslinkable functionality and chain scission occurs on the bonding between units, although this assumption is not essential in the present argument. Using these assumptions, the resulting polymer structure is the same whether crosslinking and degradation occur simultaneously or these processes are carried out one-by-one, irrespective of the degree of crosslinking and degradation. This can be understood from the following hypothetical example. Suppose we have a polymer chain with a chain length, $r=6$, as shown in *Figure 1*. Let us assume that the probability of possessing a crosslink point for the ith unit is ρ_i, and the probability of causing main chain scission for the ith bonding is ϕ_i, as shown in *Figure 1*. First, we consider the chemical process in which the scission process (S1) is carried out before the crosslinking process (C2). Suppose that chain scission occurs at the second and the fifth bonding after the S1 process, and that crosslinks are formed at the second and fourth unit due to the C2 process, as shown in the figure. Next, we compare the process in which the crosslinking process (C1) is carried out before the scission process (S2). On the basis of assumption 2 (see above), the probability of possessing a crosslink point for each unit at state A and B is the same; therefore, the structural change during the C1 process shown in the figure is as probable as that of the C2 process. Similarly, the probability of causing chain scission at the second and fifth bonding in the S2 process is the same as that in the S1 process. Consequently, the crosslinking and degradation processes are interchangeable if the above assumptions are valid.

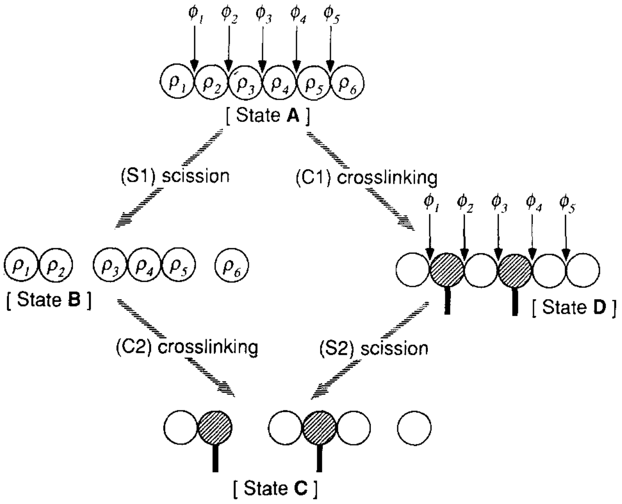

Figure 1 Schematic representation of the crosslinking and degradation reactions considered in this paper. Each circle indicates a unit, with the chain length of the polymer molecule shown in state A consisting of 6 units ($r=6$), while the shaded circles shown in states C and D are crosslinked units. The probability of obtaining the molecular structure shown in state C starting from state A is the same, irrespective of the reaction paths taken, i.e. S1→C2 or C1→S2

Monte Carlo sampling technique

First, we consider a simple case in which the probability of possessing a crosslink point for a unit, ρ, is the same for all units, and the probability of causing chain scission for a bonding, ϕ, is the same for all bondings. Later, we shall investigate the case in which different ρ values exist in the reaction mixture.

In the Monte Carlo sampling technique, one unit is selected randomly from the reaction mixture, and then the size and structure of the polymer molecule that involves this particular unit is determined; therefore, the sampling is made on a weight basis. By taking a large number of polymer molecules, the statistical property of the population (reaction system) is estimated. First, we determine the chain length (degree of polymerization) of the primary polymer molecule that involves the randomly selected unit in the initial polymer distribution. This is equivalent to selecting, on a weight basis, one primary polymer molecule before chain scission. This can simply be done by determining the chain length based on the weight-fraction distribution of the initial polymer distribution, $W(r)$. In general, the chain length r can be determined by using a random number x between 0 and 1 as follows:

$$x=\int_0^r W(r)\,\mathrm{d}r \tag{1}$$

For several types of distribution function, simpler algorithms may be employed to generate random numbers with special distributions. Several examples that use this concept of a sampling technique in generating random numbers are shown in the Appendix.

Since the processes of crosslinking and chain scission are interchangeable, we consider the process in which the chain scission occurs first. Suppose we have selected the nth unit in the primary polymer molecule with chain length r, as shown in *Figure 2*. We call this unit the *base unit*. We have $r_r=(r\text{-}n)$ units on the right-hand side of the base unit, and $r_l=(n\text{-}1)$ units on the left-hand side, where the sibscripts r and l are used to designate the direction, right and left.

Now, let us consider the process of chain scission using *Figure 2*. Suppose chain scission occurs with the probability of chain scission for each bonding being ϕ. Looking from the base unit toward the right-hand side, the probability that chain scission occurs at the (s_r+1)th bonding, thus obtaining s_r units on the right-hand side, is given by the following most probable distribution:

$$N(s_r)=\phi(1-\phi)^{s_r} \tag{2a}$$

$$\cong \phi \exp(-\phi s_r) \qquad (\phi \ll 1) \tag{2b}$$

The chain length s_r can be determined from a random number x between 0 and 1 as follows:

$$s_r=\text{Ceiling}\left[\frac{\ln x}{\ln(1-\phi)}-1\right] \tag{3a}$$

$$\cong \text{Ceiling}\left[\frac{1}{\phi}\ln\left(\frac{1}{x}\right)-1\right] \qquad (\phi \ll 1) \tag{3b}$$

where Ceiling[a] indicates the closest integer greater than or equal to a.

At this stage, a kind of competition of events is considered, namely, if $r_r>s_r$, chain scission really occurs, and the chain length after scission becomes $r_r'=r_s$. On the other hand, if $r_r<s_r$, chain scission is not a *real* event, and $r_r'=r_r$. The chain length after scission on the left-hand side can be determined similarly, and the total chain length after scission is given by $r'=r_r'+r_l'+1$. Now we have therefore determined the chain length of the linear chain after scission containing our initially selected unit; this is called the zeroth generation. The zeroth generation always consists of one linear chain.

Next, we consider the process of random crosslinking for the chain in the zeroth generation. Since the probability of possessing a crosslink point ρ is the same for all units, the probability that the primary polymer molecule with chain length r' possesses n crosslink points is given by the following binomial distribution:

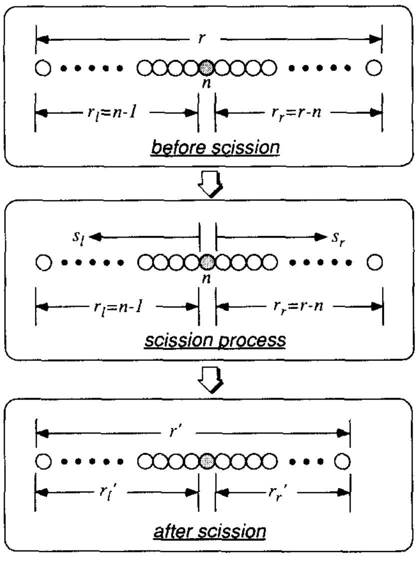

Figure 2 Schematic representation of the process of random scission reactions. The shaded unit, which is called the base unit in the text, is selected randomly, after which the sequence lengths of the units connected to this base unit are then considered

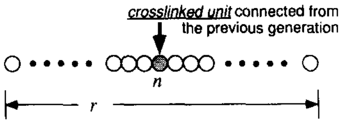

Figure 3 Schematic representation of the primary polymer molecule in the jth generation ($j>0$). The unit which is connected to a primary polymer molecule that belongs to the (j-1)th generation is shown as a shaded circle, and is considered as a base unit for this particular chain

$$p(n)=\binom{r'}{n}\rho^n(1-\rho)^{r'-n} \tag{4}$$

The number of crosslink points on the chain in the zeroth generation is directly equal to the number of chains in the first generation.

The chain length of the primary polymer molecules in the first generation can be again determined from equation (1). When considering the scission and crosslinking process of the primary polymer molecules that belong to the first or later generations, the crosslink unit connected from the previous generation is regarded as the base unit, as shown in *Figure 3*. Then the chain length after the scission process is determined for each primary polymer molecule in the generation by following the procedure described above. The number of crosslink points on the ith chain in the generation under consideration, m_i, is determined from the binomial distribution given in equation (4), namely from $p(m_i)$. For the chains in the first or later generations, one unit is used to connect with the previous generation (as shown in *Figure 3*), so $(r'-1)$ must be used instead of r'. The total number of chains in the $(j+1)$th generation, n_{j+1}, is given by:

$$n_{j+1}=\sum_{i=1}^{n_j} m_i \tag{5}$$

The above processes are repeated until all of the primary polymer molecules fail to be connected to the next generation. By simulating a large number of polymer molecules, such statistical properties as the whole *MWD* can be determined effectively. The simulation algorithm is shown in *Figure 4*.

The concept of the sampling technique is useful, not only to make computer simulations for complex reaction systems, but also to obtain, deductively, the average molecular weights for simpler cases, as shown in the Appendix.

RESULTS AND DISCUSSION

Random crosslinking and degradation of the polymer chains with the Schulz–Zimm distribution

In the present simulation method, one can make simulations for virtually any initial polymer distribution including experimentally determined ones. On the other hand, conventional analytical solutions for the development of the average chain lengths are limited to several simpler types of distribution functions. In order to make comparisons with the conventional methods, we first consider the Schulz–Zimm distribution[26,27], which

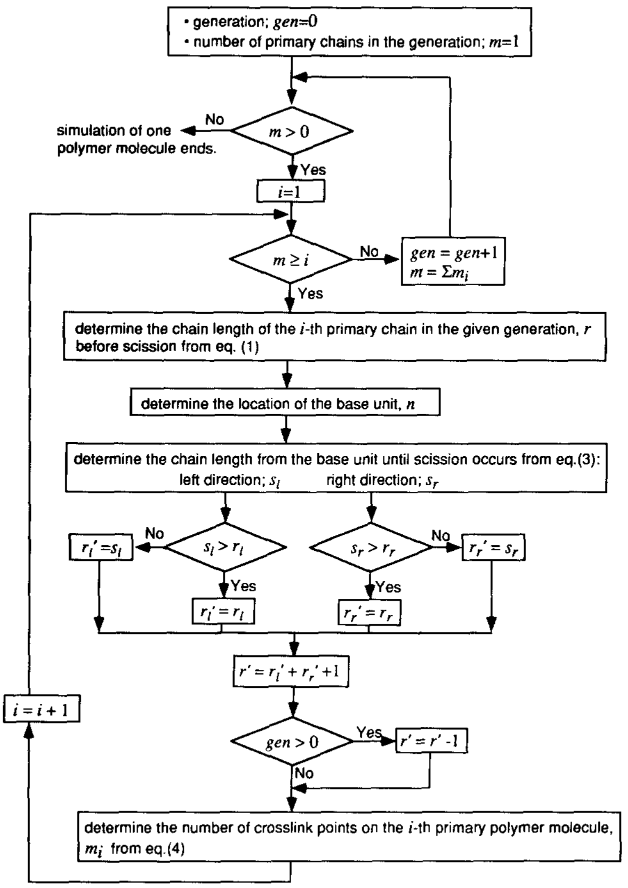

Figure 4 Simulation algorithm for random crosslinking and degradation

is given by the following weight-fraction distribution:

$$W(r)=\frac{\sigma^{\sigma}}{u\Gamma(\sigma)}\left(\frac{r}{u}\right)^{\sigma}\exp\left(-\frac{\sigma r}{u}\right) \tag{6}$$

where u is the number-average chain length ($=P_n$), and σ is a parameter indicating the narrowness of the distribution breadth, namely:

$$\sigma=\frac{P_n}{P_w-P_n}=\frac{P_n}{P_z-P_w}=\cdots\cdots=\frac{P_n}{P_{z+i+1}-P_{z+i}} \tag{7}$$

where P_w, P_z, and P_{z+i} represent the weight-, z- and ($z+i$)-average chain lengths, respectively.

On the basis of the integro-differential equation developed by Saito[4,5], which describes the *MWD* development during random crosslinking and degradation, Inikuti obtained the weight-average chain length for the random crosslinking (ρ) and scission (ϕ) of the polymer chains that initially possess the Schulz–Zimm distribution as follows[6]:

$$\frac{u}{P_w}=\frac{(u\phi)^2}{2\left[u\phi-1+\left(1+\frac{u\phi}{\sigma}\right)^{-\sigma}\right]}-u\rho \tag{8}$$

Note that there is a typographical error in ref. 6, and that these authors used the density of crosslinkages, instead of the probability of possessing a crosslink point for a unit (ρ), to represent the degree of crosslinking. Actually, the value of ρ used in this paper is the same as the crosslinking density defined by Flory[1]. Since two crosslinked units are produced for each crosslinkage, ρ is twice as large as the density of crosslinkages.

On the other hand, on the basis of the theory of branching processes, Demjanenko and Dusek[8] derived the following equation for the weight-average chain length:

$$P_w=\frac{\left\{u[1-(1-\phi)^2]-2(1-\phi)+2(1-\phi)\left(\frac{\sigma}{\sigma-u\ln(1-\phi)}\right)^{\sigma}\right\}(1+\rho)}{u\phi^2-2\rho(1-\phi)\left\{u\phi-1+\left(\frac{\sigma}{\sigma-u\ln(1-\phi)}\right)^{\sigma}\right\}} \tag{9}$$

The reason for the disagreement between equations (8) and (9) is as follows. In the development of equation (8), very large chain lengths for the primary polymer molecules are assumed and the rate of scission is assumed to be proportional to r rather than $(r-1)$, while $(r-1)$ is used for equation (9).

The number-average chain length can be derived from the stoichiometric argument as long as cyclizations are neglected:

$$P_n=\frac{u}{1+(u-1)\phi-u\rho/2} \tag{10}$$

In this work, we have used the calculation conditions shown in *Table 1*. In each series, the crosslinking density level (ρ) is kept constant and the scission density (ϕ) is changed. The series S employs a very narrow initial polymer molecular-weight distribution whose polydispersity index is given by $P_w/P_n=1.005$. The series M has the most probable distribution, while the series B uses a broad initial distribution with $P_w/P_n=10.1$. *Figure 5* shows the calculated average chain lengths from equations (8)–(10), as well as the present simulated results. Simulations are made for 5000 polymer molecules for each condition. Both simulated and calculated results show that the *MWD* becomes narrower as the degree of chain scission increases.

The difference between equations (8) and (9) becomes significant for the narrower initial distributions. Since the number-average chain length of the initial polymer molecules ($u=200$) is the same for each series, the fraction of larger chain lengths (in which the difference between r and $(r-1)$ is not significant) is smaller for the narrower distributions. The present simulation results give better agreement with equation (9), which accounts for the finite chain lengths of the initial polymer molecules.

Figure 6 shows the weight fraction distribution formed under the various reaction conditions. For the cases without chain scission ($\phi=0$), the weight fraction distributions are calculated from the analytical solution

Table 1 Calculation conditions investigated in this work

Series	Parameters for the initial distribution u	σ	Crosslinking density ρ
S	200	200	1×10^{-2}
M	200	1	5×10^{-3}
B	200	0.11	1×10^{-3}

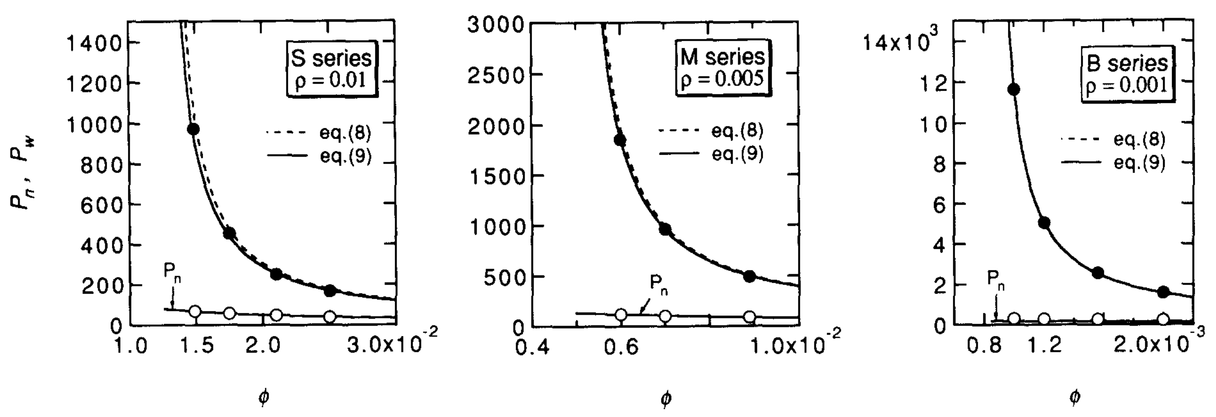

Figure 5 Calculated number (P_n)- and weight (P_w)-average chain lengths; for each type of initial distribution, the crosslinking density ρ is kept constant while the scission density ϕ is changed. The keys show the simulation results obtained from this present work

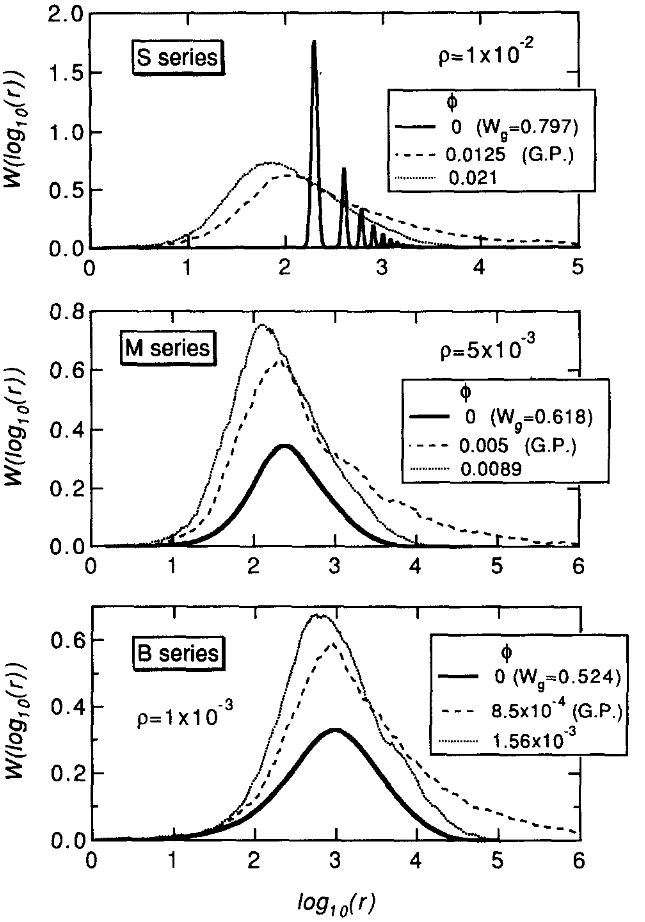

Figure 6 Weight fraction distributions formed under the various conditions indicated; for each type of initial distribution, the crosslinking density ρ is kept constant while the scission density ϕ is changed. When $\phi = 0$, gel molecules exist with a weight fraction W_g; the broken curves show the distribution at the gel point (indicated by G.P.)

developed earlier[28,29]. In each series, a finite amount of gel (indicated by W_g) exists for the cases with $\phi = 0$. Since the crosslinking and scission processes are interchangeable, each series can be considered as being a process of degradation of crosslinked polymers, including gel molecules (formed under the ring-free model[1,2]), as well as simultaneous crosslinking and scission. One might argue that the degradation of gels cannot be handled based on the present simulation method, since a gel molecule is expected to possess a large number of rings. However, at least gels formed under the classical ring-free model can be simulated based on the following reasoning.

If the mass action law is valid and the spatial correlation is neglected, the probability of ring formation within sol polymer molecules is zero, since the concentration of functional groups on its own polymer molecule, i.e. the weight fraction of one sol polymer molecule, is zero. This is the so-called ring-free model. (Note, however, that a very small number of rings may be formed in huge sol polymer molecules in the close vicinity of the gel point, since a gel is an infinitely large molecule and huge macromolecules would be present just before the gel point is reached[30]). On the other hand, as the weight fraction of a gel molecule possesses a non-zero value in the postgelation period, ring formation is permitted within the gel fraction even under the classical ring-free model. Note, however, that the size of the rings formed within the gel fraction in the context of the ring-free model must be infinitely large, because the probability of ring formation within finite parts of the gel must be zero. Therefore the degradation of the gel formed under the ring-free model can be handled within the framework of the present simulations.

When the initial *MWD* is very narrow (S series), a multimodal distribution is formed in random crosslinking; however, random chain scission makes each peak broader and, as a consequence, a unimodal distribution is obtained. *Figure 7* shows a comparison of the *MWD* formed with and without degradation at the same weight-average chain length levels (P_w) and a dramatic effect of chain scission is displayed. *Figures 8* and *9* show the same results for the series M and B, respectively. The number-average chain length (P_n) is smaller for the cases with degradation, due to the formation of smaller primary chains that constitute crosslinked polymers, so the polydispersity index (P_w/P_n) is larger for the cases that involve chain scission.

Crosslinking and degradation of bimodal distributions

Next we consider random crosslinking and degradation of polymer molecules with a bimodal distribution, and clarify some of the important features of the present reaction system. The *MWD* is the probability density

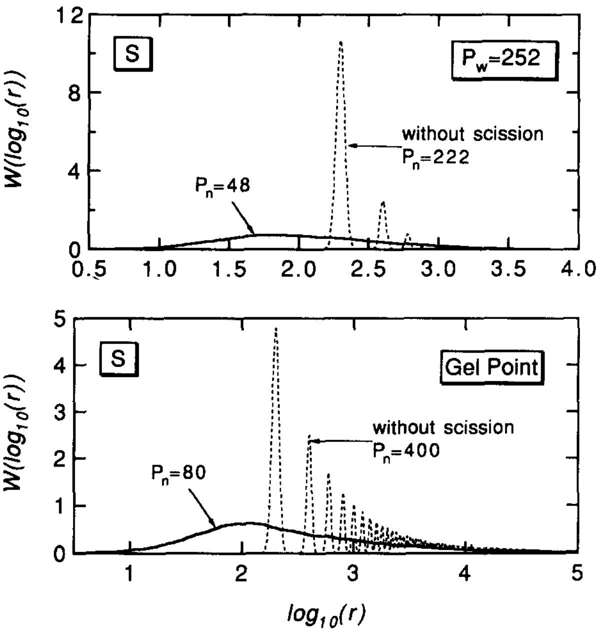

Figure 7 Comparison of the weight fraction distributions in the S series with and without degradation reactions; the weight-average chain lengths are the same for both types of curves

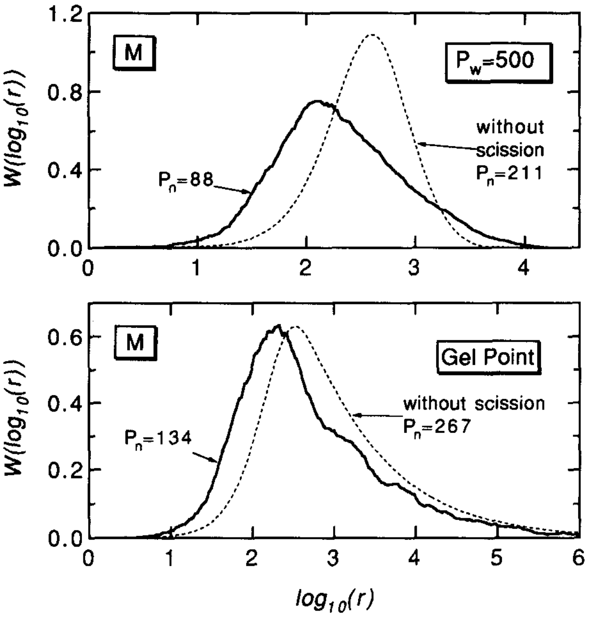

Figure 8 Comparison of the weight fraction distributions in the M series with and without degradation reactions, at the same weight-average chain length levels

distribution; therefore, it is the area that possesses a clear physical meaning as probability, and not the shape of the *MWD*. However, the shape is quite appealing for those human eyes possessing excellent image analysis ability. It is well known that the distribution shape is completely different depending on whether it is given on a weight or a number basis. Here, we discuss only the weight fraction distribution, which is usually more important in determining various physical properties of polymer systems.

We employed a binomial distribution by blending the two most probable distributions with different average chain lengths, namely:

$$W(r)=g\frac{r}{(u_1)^2}\exp\left(-\frac{r}{u_1}\right)+(1-g)\frac{r}{(u_2)^2}\exp\left(-\frac{r}{u_2}\right) \tag{11}$$

Figure 10 shows the distribution with $u_1=200$, $u_2=2000$, and the weight fraction of polymers with distribution 1, $g=0.5$. The distribution shape looks completely different for the two cases in which the independent variable is the chain length r and the logarithm of chain length $\log_{10}(r)$. The weight-based chain length distribution given as a function of the logarithm of chain length, $W(\log_{10} r)$,

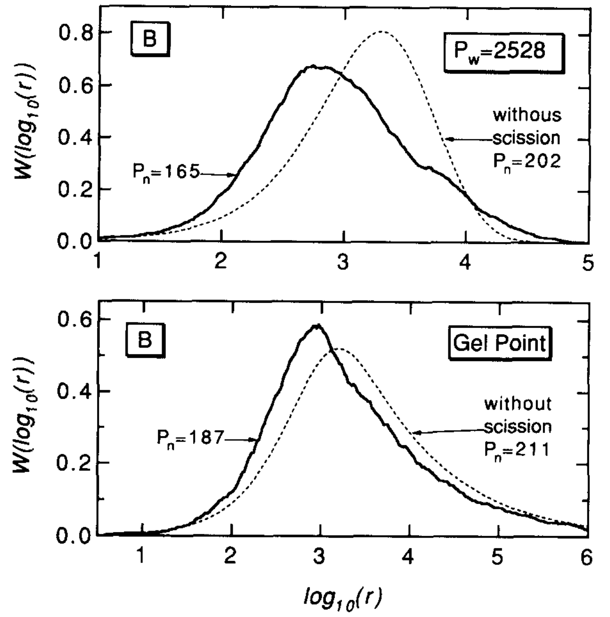

Figure 9 Comparison of the weight fraction distributions in the B series with and without degradation reactions, at the same weight-average chain length levels

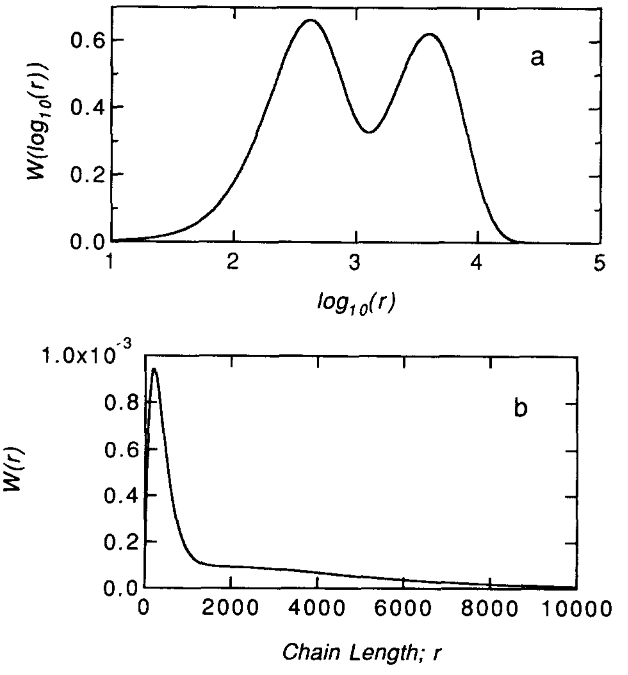

Figure 10 Weight fraction distribution of the initial polymer distribution with $u_1=200$, $u_2=2000$ and $g=0.5$ in equation (11): (a) $W(\log_{10} r)$; (b) $W(r)$

is important due to the formal relationship with the elution curves in gel permeation chromatography (g.p.c.) measurements. When discussing the modality of the *MWD*, $W(\log_{10} r)$ is usually more convenient to use than $W(r)$, since the modality is more pronounced in $W(\log_{10} r)$, i.e. if the second peak cannot be observed in $W(\log_{10} r)$, it is generally impossible to find such a peak in $W(r)$. We use $W(\log_{10} r)$ for expressing the *MWD* throughout this present paper.

Figure 11 shows the *MWD*s formed under the various conditions indicated. The *MWD* curves are depicted based on the simulation of 10^4 polymer molecules for each condition. It is clearly shown that most reactions occur only for those polymer molecules that belong to the peak with longer chain lengths. This is due to the fact that larger molecules have a better chance of being subject to both crosslinking and degradation, since the reaction rates for both reactions are proportional to the degree of polymerization, as long as the size and structure dependent kinetics are neglected.

Another important point worth noting here is that both crosslinking and degradation tend to produce unimodal distributions, i.e. bimodal distributions are not stable in random reactions. Here, let us consider the modality of the *MWD* formed in crosslinking reactions. As shown in *Figures 6* and *7*, a multimodal distribution may be formed when the initial *MWD* is extremely narrow. However, even the second peak does not appear if the polydispersity index (P_w/P_n) of the initial distribution is larger than 1.2, as discussed elsewhere[28]. Therefore, the formation of multimodal distributions due to the superposition of *MWD*s with different numbers of crosslinks is rather limited to special cases with extremely narrow initial distributions. This is due to the fact that the fractional *MWD* containing k crosslinkages overlaps significantly with different k values when broader initial distributions are used [29]. (Note that the *MWD* of crosslinked polymer molecules formed during polymeric network formation is the sum of the fractional *MWD*s containing 0, 1, 2, 3, etc. crosslinkages.) Furthermore, as shown in *Figure 11*, even when a bimodal distribution is formed for some reason, the distribution is not stable toward random crosslinking reactions. Therefore, it is reasonable to conclude that bimodal distributions cannot be formed in crosslinking reactions in which the *MWD* of the primary polymer molecules is not narrow enough, as long as the size and structure dependence is neglected. On the other hand, bimodal distributions have been observed experimentally for free-radical crosslinking copolymerizations[31] (in which the polydispersity index of the primary polymer molecules must be larger than 1.5). Some people speculate that bimodal distributions may be obtained due to the superposition of various fractional distributions, and recently Teymour and Campbell[32] proposed a modified method of moments in which bimodal distributions are derived. This is clearly wrong, i.e. their results simply arise from the inappropriate approximations they used to solve the moment equations. (Note that the use of the Schulz–Zimm distribution for each fraction (called the 'generation' in ref. 32), as well as the closure rule for their moment equations, has *never* been justified theoretically.) It would be necessary to consider the size and structure dependent kinetics, including cyclizations, in order to rationalize the bimodal distributions obtained in non-linear polymerizations.

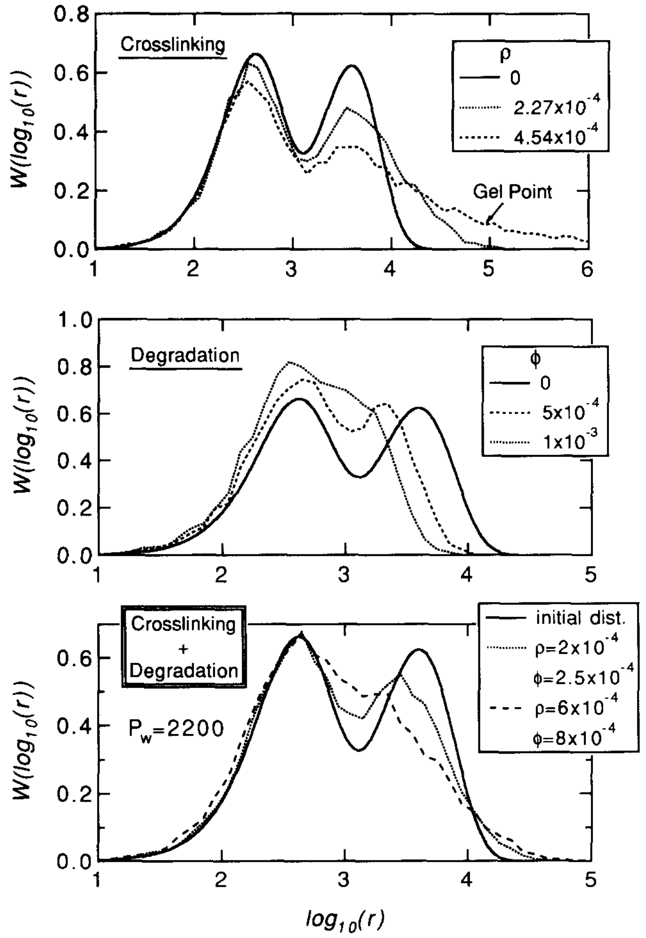

Figure 11 Weight fraction distributions formed under various reaction conditions starting from the bimodal distribution (solid curve). In the bottom figure, where both crosslinking and degradation occur, the weight-average chain length is kept constant ($P_w = 2200$) for all cases

Figure 12 shows an example of the fractional *MWD*s containing k crosslinkages, as well as the complete *MWD*. The *MWD*s with $k=0$ and 1 possess two peaks, but unimodal distributions, however, are obtained for larger k values. For random crosslinking of polymer chains with an initial Schulz–Zimm distribution, the following equations are obtained for the number- ($P_{n,k}$) and weight- ($P_{w,k}$) average chain lengths that contain k crosslinkages[29]:

$$P_{n,k} = \frac{[k(\sigma+2)+\sigma]u}{\sigma+\rho u} \tag{12}$$

$$P_{w,k} = \frac{[k(\sigma+2)+\sigma+1]u}{\sigma+\rho u} \tag{13}$$

$$P_{w,k}/P_{n,k} = \frac{k(\sigma+2)+\sigma+1}{k(\sigma+2)+\sigma} \xrightarrow[k\to\infty]{} 1 \tag{14}$$

As shown in *Figure 12*, $P_{w,k}/P_{n,k}$ does approach unity as k increases, even when the initial distribution is bimodal, and is thus significantly different from the Schulz–Zimm distribution. The linear relationship of $P_{n,k}$ and $P_{w,k}$ as a function of k also holds approximately for the initial bimodal distribution. (Strictly, however, the linear regression line shows a negative intercept for $P_{n,k}$, probably due to the highly distorted *MWD*s for $k=0$

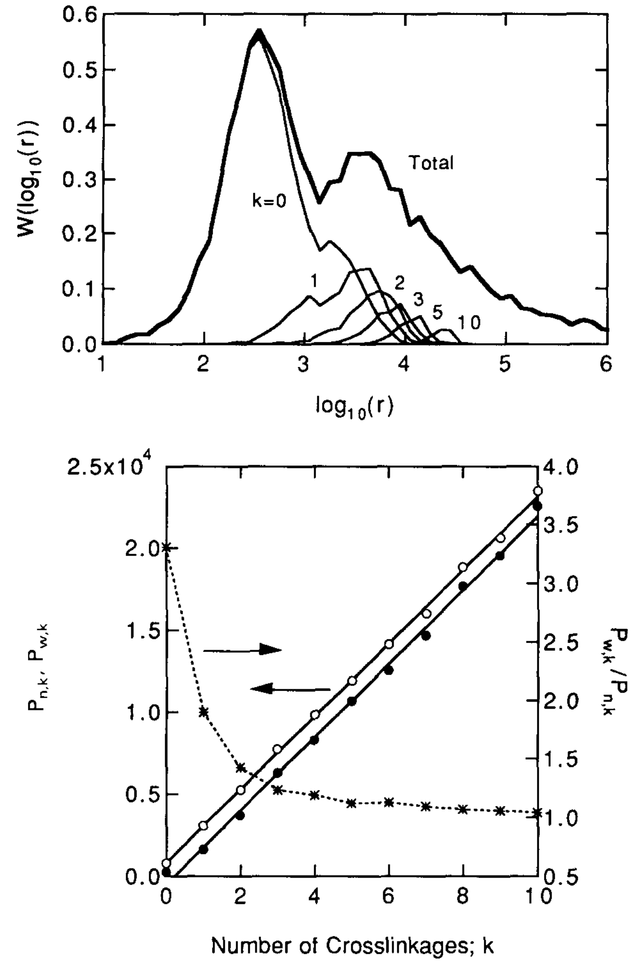

Figure 12 Weight fraction distributions for the system containing k crosslinkages and the average chain lengths of each fractional chain length distribution formed at the gel point with $\rho = 4.54 \times 10^{-4}$, starting from the bimodal distribution shown in *Figure 10*

and 1.) Similar relationships have been observed for free-radical polymerizations with long-chain branching[17], and this type of behaviour may be a general feature of non-linear polymerizations as long as any size or structure dependence is neglected.

For random chain scission reactions, it is well known that the *MWD* approaches the most probable distribution as the degree of scission increases, irrespective of the initial *MWD*s that are used[4,5]. In order to rationalize this phenomenon, let us suppose that most chains experience chain scission reactions and $\phi \gg \rho$ (i.e. most polymer molecules are linear); the probability then for a unit to be connected to another unit is $p \approx (1-\phi)$ and is the same for all units. Therefore, the chain length distribution is given by the following most probable distribution:

$$W(r)=r\phi^2(1-\phi)^{r-1} \qquad (1/u \ll \phi) \qquad (15)$$

Equation (15) shows the limiting distribution for random degradation. As a special case, when the linear polymer molecules with the most probable distribution are subject to random scission reactions, the problem can be restated that we have randomly cut a circular polymer chain with chain length N to obtain $N_p+\phi(N-N_p)$ linear polymer chains, where N_p is the total number of chains before chain scission. (Obviously, the number-average chain length before scission is $u=N/N_p$.) The overall probability for a unit to be connected with another unit, p, is given by:

$$p=\frac{N-[N_p+\phi(N-N_p)]}{N} \qquad (16)$$

Therefore, in this special case the *MWD* is always the most probable distribution, irrespective of the degree of chain scission, and is given by:

$$W(r)=r\left(\frac{1-\phi}{u}+\phi\right)^2\left[1-\left(\frac{1-\phi}{u}+\phi\right)\right]^{r-1} \qquad (17)$$

The number- and weight-average chain lengths are given by:

$$P_n=\frac{1}{1-p}=\frac{u}{1+(u-1)\phi} \qquad (18)$$

and

$$P_w=2P_n-1=\frac{2u}{1+(u-1)\phi}-1 \qquad (19)$$

(In deriving equation (19), the use of equation (A5) given in the Appendix facilitates the treatment greatly.)

On the other hand, Guaita *et al.*[24] considered the cases in which the possibility of chain scission is not random by application of the Monte Carlo method, i.e. the chain scissions are preferred near the centres of the chains or near the chain ends, using linear polymers. It is straightforward to include such types of location dependence of scission points in the context of the present simulation method.

Crosslinking of polymer mixtures containing different levels of crosslinking density

Finally, we consider the case where the crosslinking density is not the same for all primary polymer molecules. For a kinetically controlled crosslinking copolymerization such as the free-radical copolymerization of vinyl/divinyl monomers, the crosslinking density is different depending on the 'birth' time of each primary polymer molecule[10–12]. In such cases, a small but clear deviation from the Flory–Stockmayer theory of the gel point is observed, i.e. the gel point occurs at earlier conversions than that expected from the Flory–Stockmayer theory. The objective of the investigation in this section is at least twofold: (1) to rationalize the effect of the existence of the crosslinking density distribution on the polymeric network formation, and (2) to provide some fundamental ideas in order to extend the present simulation method to the continuous flow reactors in which the primary polymer molecules with various levels of crosslinking density may be formed due to the residence time distribution.

In order to simplify the discussion, we consider a rather simple example, as follows: (stage 1) we crosslink polymer chains with a level of crosslinking density ρ_1, then linear polymer molecules with a weight fraction g are blended, and (stage 2) we crosslink the polymer mixture with a crosslinking density ρ. This type of process, known as the intermediate feeding method[33], was proposed earlier as a method of controlling the *MWD*. In this case, the weight fraction $(1-g)$ of primary polymer molecules possess the crosslinking density, $\rho_1+(1-\rho_1)\rho \approx \rho_1+\rho$

(called P1 chains), while the weight fraction, g, of the primary polymer molecules possess the crosslinking density ρ (called P2 chains). We used the most probable distribution of the primary polymer molecules with $u = 200$ and $\rho_1 = 2 \times 10^{-3}$ for the crosslinking density level for stage 1, while the weight fraction (g) of the added polymer molecules at stage 2 is 0.5. The *MWD*s, before and after blending of the linear polymer molecules, are shown in *Figure 13*. Only the relative peak height for $k = 0$ is increased significantly by the blending process.

The present problem can be handled easily by modifying the simulation algorithm, as shown in *Figure 14*. The gel point was determined by following the method proposed earlier[10–12,14], namely, (1) the polymer molecule that continues to grow more than 100 generations is considered to be a gel molecule, (2) the weight fraction of gel is determined by simulating 100 polymer molecules, and (3) the 95% confidence intervals of the weight fraction of the gel are calculated from five sets of item (2). *Figure 15* shows the calculated weight fractions of the gel with their 95% confidence intervals. The onset of gelation is considered to occur between $\rho = 8 \times 10^{-4}$ and 8.5×10^{-4}, since the weight fraction of the gels fails to include zero within the 95% confidence intervals.

In the present example, the gel point can be determined exactly from the Flory–Stockmayer theory by using the weight-average chain length at the start of stage 2 (after blending), i.e. $P_{\rm w0}$, and the crosslinking density ρ as the average crosslinking density. The crosslinking density at the gel point can be calculated as follows:

$$P_{\rm w0} = \frac{1}{2}\left(\frac{2u}{1 - 2u\rho_1} + 2u\right) = 1200 \qquad (20)$$

$$\rho_{\rm gp} = 1/P_{\rm w0} = 8.33 \times 10^{-4} \qquad (21)$$

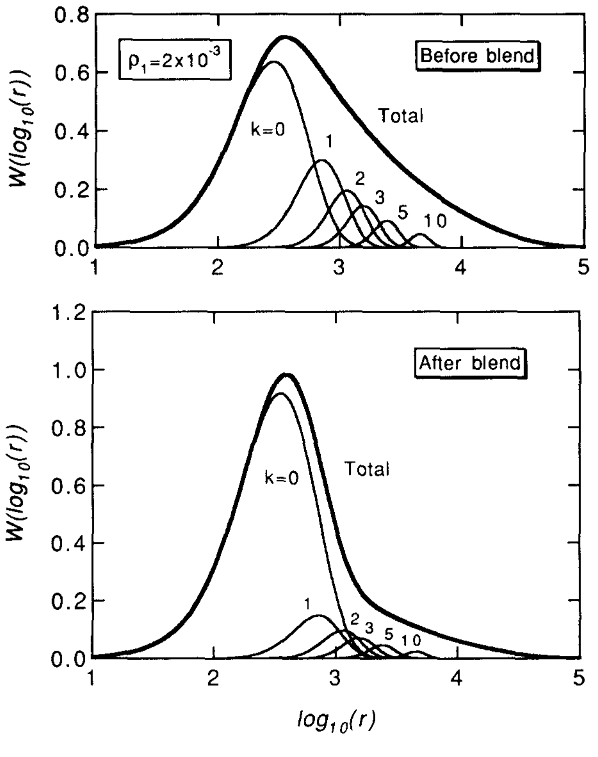

Figure 13 Weight fraction distributions for the system containing k crosslinkages, before and after blending of linear polymer molecules

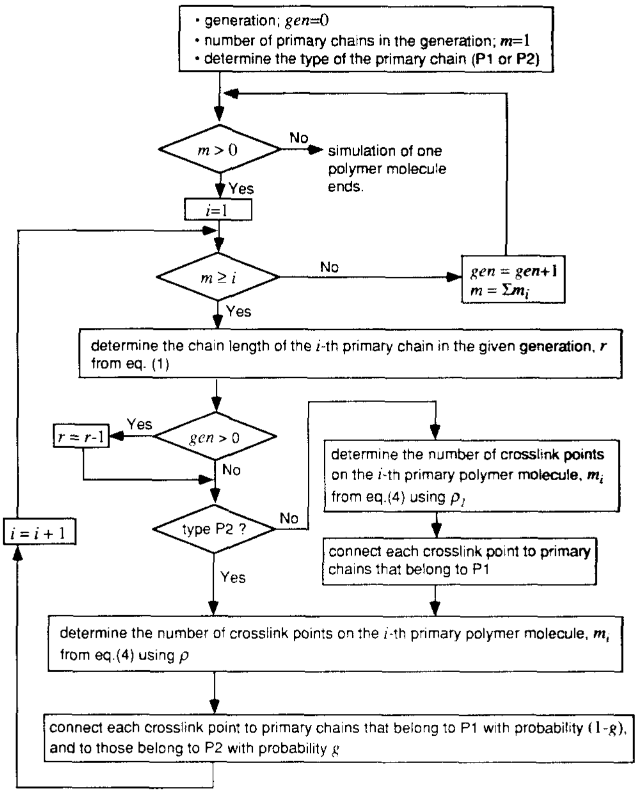

Figure 14 Simulation algorithm for the intermediate feeding method

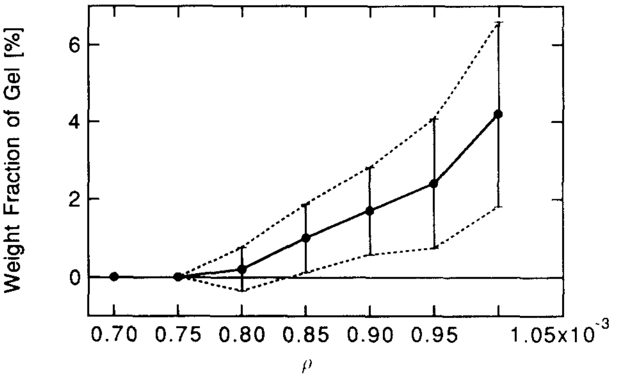

Figure 15 Simulated weight fractions of gel and the corresponding 95% confidence intervals (broken lines)

The crosslinking density obtained in this way, $\rho_{\rm gp}$, agrees well with the simulation result. The present example, therefore, can be handled well by the Flory–Stockmayer theory since the crosslinking density is the same with respect to the polymer molecules that exist at the start of the stage 2 (i.e. the crosslinks formed at stage 1 are not counted). However, for general distributions of the crosslink points among the primary polymer molecules in which the residence time distribution of the primary polymer molecules must be properly accounted for, at present one needs to resort to the simulation method developed earlier[10–17]. Now we consider two stages of the crosslinking reactions as a whole. The average crosslinking density of all polymer molecules at the gel point is:

$$\bar{\rho}_{\rm gp} = (1 - g)(\rho_1 + \rho_{\rm gp}) + g\rho_{\rm gp} = 1.83 \times 10^{-3} \qquad (22)$$

On the other hand, if the crosslinking density distribution does not exist, i.e. the expected crosslinking density is the same for all primary polymer molecules, the Flory–Stockmayer theory gives the crosslinking density at the gel point as follows:

$$\bar{\rho}_{gp}=1/P_{wp}=2.5\times10^{-3} \tag{23}$$

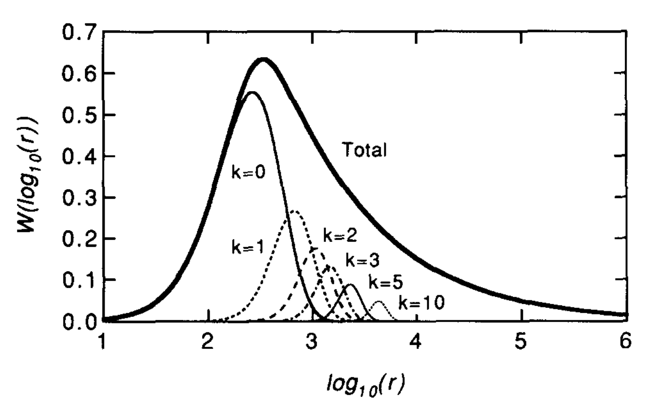

Figure 16 Weight fraction distributions for the system containing *k* crosslinkages formed without the existence of any crosslinking density distribution, at the gel point, i.e. the expected crosslinking density is the same for all of the primary polymer molecules

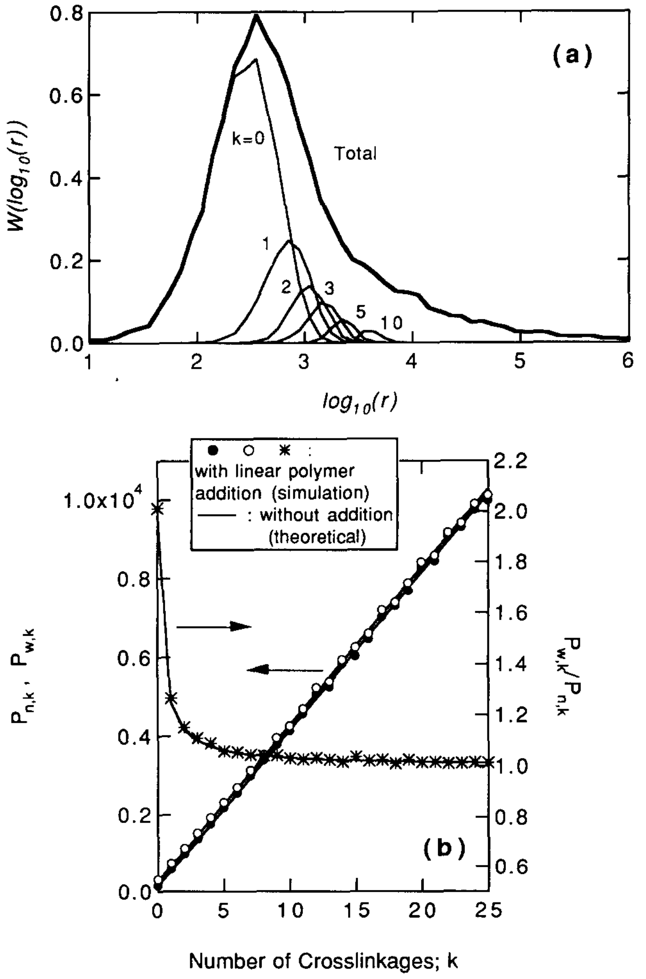

Figure 17 Weight fraction distributions for the system containing *k* crosslinkages (a) and the average chain lengths of each fractional chain length distribution formed at the gel point (b) when linear polymer molecules are added at the second stage, as described in the text. The solid lines shown in (b) are calculated by assuming the expected crosslinking density is the same for all of the primary polymer molecules i.e. the identical case to that shown in *Figure 16*

This present example clearly shows that the existence of a crosslinking density distribution among the primary polymer molecules makes the average crosslinking density level smaller at the gel point, which verifies the earlier observations for free-radical crosslinking copolymerizations[10–12]. When the crosslinking density is not the same for all primary polymer molecules, those molecules with the larger crosslinking densities improve the chain connectivity substantially and contribute significantly to the formation of large polymer molecules.

Figure 16 shows the *MWD*s at the gel point when the expected crosslinking density is the same for all chains (without the intermediate addition of any linear polymer), while *Figure 17a* shows the *MWD*s at the gel point as produced in the present example (with intermediate polymer addition). The height of the peak is larger in *Figure 17a*, due to the existence of a larger amount of linear polymer ($k=0$). *Figure 17b* shows the number- and weight-average chain lengths for each peak, with the lines being calculated from equations (12)–(14) using $u=200$ and $\rho=2.5\times10^{-3}$. These calculated lines agree satisfactorily with the simulated results, and the addition of linear polymer at stage 2 has a negligible effect on the average molecular weights for polymer molecules with *k* crosslinkages, even though the relative amounts of polymer molecules in each fraction are changed.

CONCLUSIONS

The Monte Carlo sampling technique is used to investigate modifications of the *MWD* via crosslinking and degradation reactions, and is shown to be a useful technique to obtain simulations of complex reactions which aim at the development of novel processes for obtaining polymers with tailored *MWD*s and structures. By introducing the scission density distribution, which can be defined in a similar way to that of the crosslinking and branching density distributions developed earlier[10–17], it is straightforward to extend the present technique to account for the effect of the residence time distribution of the primary polymer molecules, which might be important in commercial reactors. Furthermore, the present technique can be applied irrespective of the reactor type that is being used. The concept of the sampling technique is useful for obtaining the full *MWD* functions, including detailed structural information, and in addition the averages may be determined for simpler cases by deduction.

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APPENDIX

In general, equation (1) in the text can be used to obtain random numbers with special distributions. However, such processes may require a large amount of calculations. Here, we propose some simpler methods to generate distributions that are useful in polymer science. First, let us consider the most probable distribution, whose number fraction ($N(r)$) and weight fraction ($W(r)$) distributions are given by the following:

$$N(r)=\frac{1}{u}\exp\left(-\frac{r}{u}\right) \qquad \text{(A1)}$$

$$W(r)=\frac{r}{u^2}\exp\left(-\frac{r}{u}\right) \qquad \text{(A2)}$$

where u is the number-average chain length. The most probable distribution is obtained if the probability of connecting the next unit is the same for all units; this is equal to $(1-(1/u))$. Such a type of distribution is observed in the instantaneous chain length distribution (formed within a very small time interval) for linear free-radical polymerizations without termination by combination, and in linear step-growth polymerizations at high conversions. Note that the number fraction distribution is obtained if one samples the polymer molecules by selecting each chain end randomly, while the weight fraction distribution can be obtained if one takes polymer molecules by selecting randomly, one by one, a unit bound into the polymer chains.

Generation of a random number following equation (A1) can simply be done by using a homogeneous random number x (between 0 and 1) based on equation (A3), which can be obtained from equation (1) in the text:

$$r=u\ln(1/x) \qquad \text{(A3)}$$

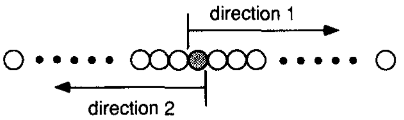

Figure A1 A polymer molecule that involves a randomly selected unit (shown as a shadowed circle). The probability of bond formation between the units is the same for all units in this polymer molecule, and therefore the chain length distribution in both directions 1 and 2 follows the number fraction distribution given by equation (A1)

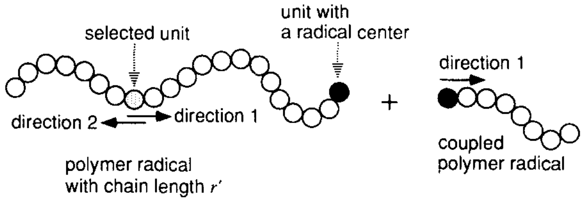

Figure A2 Schematic representation of the process of bimolecular termination by combination in free-radical polymerizations; the distribution of the dead polymer molecules follows equation (A6)

Several useful weight fraction distributions can be obtained from equation (A3) based on the concept of the sampling technique. Let us first consider the weight fraction distribution given by equation (A2). When one unit is selected randomly, as shown in *Figure A1*, the chain length distribution in the direction 1 is given by equation (A1). Similarly, the chain length distribution in the direction 2 from the selected unit is also given by equation (A1). Therefore, the random number that obeys equation (A2) can be obtained from two homogeneous random numbers (x_1 and x_2) between 0 and 1:

$$r=u\ln(1/x_1)+u\ln(1/x_2)-1 \qquad \text{(A4)}$$

Incidentally, on the basis of the present concept shown in *Figure A1*, the weight-average chain length for the most probable distribution is given simply by:

$$\begin{aligned} P_w &= 2P_n-1=2u-1 \\ &\approx 2u \qquad (u \gg 1) \end{aligned} \qquad \text{(A5)}$$

Next, let us consider the instantaneous weight fraction distribution formed in linear free-radical polymerizations with chain termination occurring solely by combination[34]:

$$W(r)=\left(\frac{\beta^3}{2}\right)r^2\exp(-\beta r) \qquad \text{(A6)}$$

where $\beta=R_{tc}/R_p$, R_p is the polymerization rate, and R_{tc} is the rate for bimolecular termination by combination. Equation (A6) can also be obtained by setting $\sigma=2$ in the Schulz–Zimm distribution shown in equation (6) in the text.

Even when the dead polymer distribution follows equation (A6), the polymer radical distribution follows the most probable distribution given by equations (A1) and (A2) with $u=1/\beta$[34]. When one polymer radical, just before bimolecular termination, is selected randomly on a weight basis, as shown in *Figure A2*, the chain length of this polymer radical, r', follows the weight fraction distribution given by:

$$W(r')=r'\beta^2\exp(-\beta r') \qquad \text{(A7)}$$

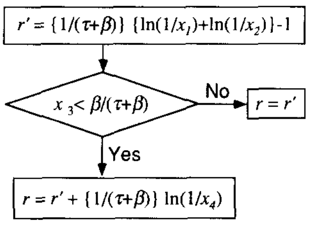

Figure A3 Simulation algorithm for the instantaneous weight fraction distribution formed in free-radical polymerizations

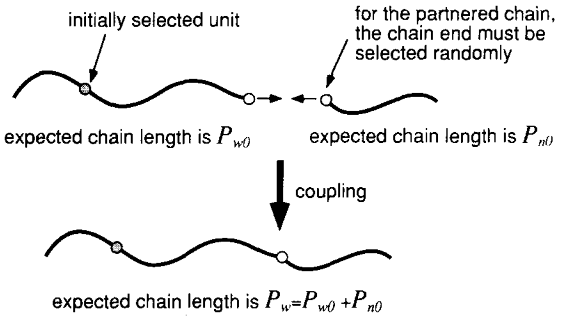

Figure A4 Schematic representation of the coupling of linear polymer molecules at their chain ends

whose distribution can be generated from the following:

$$r' = (1/\beta)\ln(1/x_1) + (1/\beta)\ln(1/x_2) - 1 \qquad \text{(A8)}$$

When this polymer is coupled with another polymer radical, the partnered polymer radical must be selected on a number basis, since only chain ends with active centres are selected randomly. Therefore, the distribution of the dead polymer molecules can be obtained from the following equations by using three random numbers:

$$r = (1/\beta)[\ln(1/x_1) + \ln(1/x_2) + \ln(1/x_3)] - 1 \qquad \text{(A9)}$$

Finally, a general expression for the instantaneous weight fraction distribution in linear free-radical polymerizations is given by the following[34]:

$$W(r) = (\tau+\beta)[\tau + (\beta/2)(\tau+\beta)(r-1)]r\exp[-(\tau+\beta)r] \qquad \text{(A10)}$$

where $\tau = (R_f + R_{td})/R_p$, R_f is the rate of chain transfer, and R_{td} is the rate of bimolecular termination by disproportionation. A similar argument to that shown above leads to the algorithm shown in *Figure A3* for producing random numbers that follow equation (A10).

This present argument, based on the sampling technique, is useful not only for generating random numbers with special distributions, but also for considering average molecular weights. For example, let us consider the case where linear polymer molecules are coupled to each other at the chain ends, as in the case of bimolecular termination by combination. For this problem, Guaita *et al.*[24] developed the following equation for the *MWD* found after coupling, based on the population balance equations:

$$\frac{P_w}{P_n} = \frac{1}{2}\left(1 + \frac{P_{w0}}{P_{n0}}\right) \qquad \text{(A11)}$$

where P_n and P_w are, respectively, the number- and weight-average chain lengths after coupling, while P_{n0} and P_{w0} are the corresponding parameters before coupling.

It is straightforward to derive equation (A11) without using any difficult mathematical operations. First of all, since the coupling process halves the number of polymer molecules, $P_n = 2P_{n0}$. As shown in *Figure A4*, since the partner in the coupling process must be selected on a number basis, then $P_w = P_{w0} + P_{n0}$. The ratio of these two equations gives equation (A11). (This is why the instantaneous *MWD* formed via bimolecular termination by combination in free-radical polymerizations ($P_{w0}/P_{n0} = 2$) gives $P_w/P_n = 1.5$.) In general, if f chains are connected at the chain ends, a similar argument leads to the following:

$$\frac{P_w}{P_n} = \frac{1}{f}\left(f - 1 + \frac{P_{w0}}{P_{n0}}\right) \qquad \text{(A12)}$$

If a tetrafunctional chain transfer agent is used and the chain transfer reaction dominates the polymer chain formation with the chain transfer constant $C = 1$ ($f = 4$ and $P_{w0}/P_{n0} = 2$ in this case), $P_w/P_n = 1.25$, as shown recently[35]. The relationship $P_w/P_n = 1 + 1/f$ for multichain polymers in condensation reactions ($P_{w0}/P_{n0} = 2$) was developed a long time ago[36], based on a consideration of the full *MWD* function.