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Statistical crosslinking of heterochains

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We extend the Flory/Stockmayer gelation theory to systems consisting of N types of polymer chain in which the transition probabilities that a crosslink point on a chain of type i is connected to a chain of type j is explicitly given by p_{ij}. A general formula for the weight-average molecular weight is developed. Gelation is predicted to occur when the largest eigenvalue of the transition matrix $\mathbf{Q}$ defined in the text reaches unity. In addition to the N-component systems, the present theory can be used to elucidate the non-random crosslinking reactions where the expected crosslinking density of the primary chains is different due to the residence time distribution or the history-dependent crosslinking reactions. For the prediction of the full molecular weight distribution, a Monte Carlo simulation method is used to illustrate the resulting distribution profiles. © 1997 Elsevier Science Ltd.

INTRODUCTION

More than 50 years have passed since Flory[1] and Stockmayer[2,3] proposed a comprehensive theory for the random crosslinking of polymer chains. In the meantime, various types of different mathematical languages for polymeric network formation have been proposed[4]. However, a general theory that is capable of applying to a system with N types of different polymer chain has never been developed. In the present paper, we propose a theory for the statistical crosslinking of heterochains in which the chain connection rule is explicitly given by the transition probabilities that a crosslink point on a chain of type i is connected to a chain of type j, p_{ij}. The assumption of ring-free crosslinking reactions used in the Flory–Stockmayer model[1-3] is retained in the present theory.

For binary systems ($N = 2$), Stockmayer[5,6] considered the condensation of polymer chains in which the functional group of type A reacts with type B, whose reaction system consists of $A_1, A_2, \ldots, A_i, \ldots$ moles of the type A chains (the subscripts can be considered as indicating the chain length) and $B_1, B_2, \ldots, B_j \ldots$ moles of the type B chains. Explicitly, his analytical solution corresponds to the cases with $p_{12} = p_{21} = 1$, i.e. the crosslinking reactions occur solely with heterochains. However, consider an imaginary two-stage process in which the crosslinking among the same type of chains is conducted first, and then crosslink different types of chains. In principle, this two-stage process can give the same resulting molecular weight distribution as for any

combination of p_{ij} values, even though it lacks the dynamic picture of gel molecule development. Therefore, although Stockmayer[5,6] did not mention such a two-stage process, it can be considered that Stockmayer gave a general solution for $N = 2$ as an implicit form some 40 years ago. Other mathematical languages[7,8] can be used for this problem, and the effect of the unequal reactivity of functional groups was also considered[9]. Quite recently, Zhu and co-workers[10,11] considered the case where two types of polymer chain are crosslinked via a free-radical polymer grafting with an arbitrary set of p_{11}, p_{22}, p_{12} and p_{21}. In this work, we present a comprehensive theory that enables one to deal with a system with any number of N. A general criterion for the onset of gelation is given.

In practice, the combination of the chemical types of miscible polymer chains in a molten state is limited; however, by employing the solution process[12], a larger number of different types of polymer molecule could be dissolved in common solvents to form a homogeneous mixture. Furthermore, it is worth noting here that the present theory can be applied also for the cases where the chemical type of chain is essentially the same, but the chain connection rule is not the same for all chains, such as due to the residence time distribution. The coexistence of polymer chains with different residence times could lead to the formation of polymer chains with different levels of crosslinking densities, even under the random crosslinking reactions. If we consider the polymer chains with different residence times as different types of chain, the problem reduces to the statistical crosslinking of heterochains.

In the free-radical polymer grafting in which rapidly decomposing peroxides are used, the peroxide molecules diffuse into the polymer matrix and they decompose at the same time, probably even faster. Such localized

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variations in peroxide concentration[13] may also lead to formation of the crosslinking density distribution among primary chains.

The heterochain crosslinking model could be used also for the history-dependent crosslinking reactions, such as free-radical crosslinking copolymerizations of vinyl and divinyl monomers. In such types of reaction, each primary polymer molecule formed at a different time experiences a different history of crosslinking reactions, resulting in formation of a crosslinking density distribution among primary polymer molecules[14-19]. Therefore, if we consider the primary chains formed at different birth times as different types of polymer chain, the free-radical copolymerization could be modelled as the statistical crosslinking of heterochains, with $N \rightarrow \infty$.

Our theory is based on the random sampling technique[17-23] in which polymer molecules are randomly sampled from an infinite number of polymeric species in the reaction mixture. To illustrate the technique, consider the classical example of the random crosslinking of homochains. Let the weight-average chain length of the primary polymer molecules be $\bar{P}_{wp}$ and the crosslinking density be ρ. When $\bar{P}_{wp} \gg 1$, the weight-average chain length (degree of polymerization) for the present case is given by[1-3]

$$\bar{P}_w = \frac{\bar{P}_{wp}}{1 - \rho \bar{P}_{wp}} \qquad (1)$$

We derive equation (1) in the framework of the random sampling technique[22,23]. The weight-average chain length is the expected chain length when a polymer molecule is sampled on a weight basis. The sampling on a weight basis can be made by randomly choosing one unit from all of the units bound to polymer molecules in the reaction mixture. The idea that the weight-average chain length can be obtained by seeking the expected size of a polymer molecule when one unit is chosen randomly, without the full knowledge of the distribution function, is not new at all. The idea itself could, probably, be traced back to the person who first thought of the weight-average of a distribution. In the polymer field, Flory's criterion for the onset of gelation[1] in which gelation occurs when the weight-average chain length goes to infinity stemmed from this idea. Further, the cascade theory proposed by Gordon[7] and the recursive method developed by Macosko and Miller[8] also employ this idea to obtain the weight-average chain length. However, the derivation of equation (1) can be simplified by considering the primary chain as a basic unit for the molecular architecture, as shown below.

Suppose we have randomly selected one monomeric unit, as shown in *Figure 1*. Because the selection is made on a weight basis, the primary chain that involves this particular unit follows the weight fraction distribution of the primary polymer molecules, and the expected chain length is $\bar{P}_{wp}$. Let this primary polymer molecule be the zeroth generation (gen. 0 shown in *Figure 1*). The expected number of crosslink points on this primary chain is $\rho \bar{P}_{wp}$. From the point of view of the connected primary polymer molecules in the first generation, any unit within the chain can be connected with equal probability, which means that the primary chains that belong to the first generation are also selected on a weight basis. Therefore, the expected weight (number of monomeric units) of the primary chains that belong to the first generation is $\rho(\bar{P}_{wp})^2$.
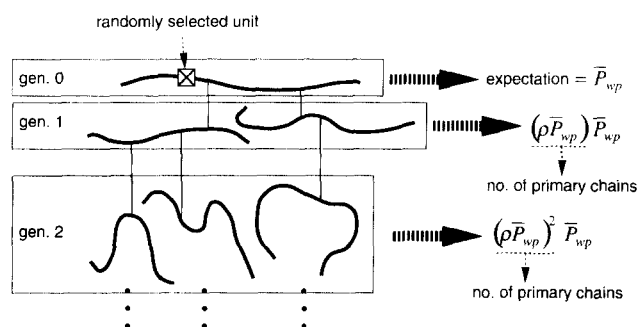

Figure 1 Schematic drawing for the derivation of the weight-average chain length of the crosslinked polymer system
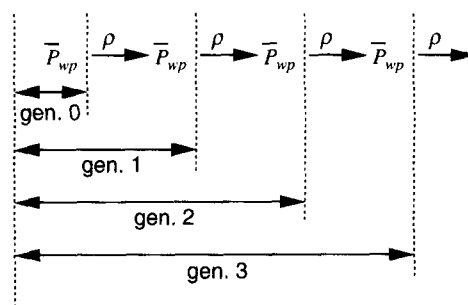

Figure 2 Diagram that shows the calculation method of the expected weight of polymer chains that belong to each generation for the random crosslinking of homochains

Similarly, the expected number of crosslink points connected to the second generation is given by $(\rho \bar{P}_{wp})^2$. Note that, strictly speaking, the expected number of crosslink points is $\rho^2 \bar{P}_{wp}(\bar{P}_{wp} - 1)$, because one unit on each primary chain in the first generation is used to connect with the zeroth generation[22,23]. With this strict treatment, one obtains the exact solution for the present problem; $\bar{P}_w = \bar{P}_{wp}(1 + \rho)/\{1 - \rho(\bar{P}_{wp} - 1)\}$. However, in the present article, we assume that $\bar{P}_{wp} \gg 1$, and use $\bar{P}_{wp}$ instead of $(\bar{P}_{wp} - 1)$, including the derivation for the N-component systems.

Therefore, the expected weight of the primary chains that belong to the second generation is given by $\rho^2(\bar{P}_{wp})^3$. *Figure 2* shows the diagram for calculating the expected weight of each generation. In the figure, the product of the quantities contained within the line with arrows at both ends ($\leftrightarrow$) indicates the expected weight of the polymers that belong to the given generation, which shows that the expected weight of primary chains that belong to the nth generation is given by $\bar{P}_{wp}(\rho \bar{P}_{wp})^n$. Therefore, the total expected weight, which is the weight-average chain length, is given by the following infinite series:

$$\bar{P}_w = \bar{P}_{wp} \sum_{n=0}^{\infty} (\rho \bar{P}_{wp})^n = \frac{\bar{P}_{wp}}{1 - \rho \bar{P}_{wp}} \qquad (2)$$

The result obtained is exactly the same as equation (1). The same type of argument was used by Gordon and Ross-Murphy[24] to derive the weight-average chain length of a random f-functional polycondensate. We extend the present method to the systems with N types of polymer chain. Further, we calculate the full molecular weight distribution profiles by combining the present technique with the Monte Carlo method.

WEIGHT AVERAGE MOLECULAR WEIGHT

Consider a polymer mixture that consists of N types of chain whose weight fractions are w_i $(i = 1, 2, \ldots, N)$ and weight-average chain lengths are $\bar{P}_{wp,i}$. Let the transition probability that a crosslink point on a chain of type i is connected to a chain of type j be p_{ij}, and the crosslinking density of chains of type i be ρ_i. The following relationships hold for the fractions:

$$\sum_{i=1}^{N} w_i = 1 \tag{3}$$

$$\sum_{j=1}^{N} p_{ij} = 1 \tag{4}$$

The average crosslinking density of the whole system is given by

$$\rho = \sum_{i=1}^{N} w_i \rho_i \tag{5}$$

The weight-average chain length of the whole primary polymer molecules, $\bar{P}_{wp}$ is given by

$$\bar{P}_{wp} = \sum_{i=1}^{N} w_i \bar{P}_{wp,i} \tag{6}$$

Because the total number of connections from the chains of type i to the chains of type j must be equal to the connection from j to i, the following relationship between the type i and j chains holds:

$$w_i \rho_i p_{ij} = w_j \rho_j p_{ji} \tag{7}$$

For simplicity, we elucidate the technique by using a binary system first. Suppose the primary chain we have randomly selected on a weight basis is type 1. The probability of making such a selection is w_1. By referring to *Figure 3*, we can derive the weight-average chain length in a straightforward manner. The expected chain length of this primary chain is $\bar{P}_{wp,1}$. The expected number of crosslink points on this chain is $\bar{P}_{wp,1}\rho_1$. Within these crosslink points, $\bar{P}_{wp,1}\rho_1 p_{11}$ of them are connected to chains of type 1, while $\bar{P}_{wp,1}\rho_1 p_{12}$ crosslink points are connected to chains of type 2. The expected sizes of each connected chain are $\bar{P}_{wp,1}$ and $\bar{P}_{wp,2}$, respectively. By
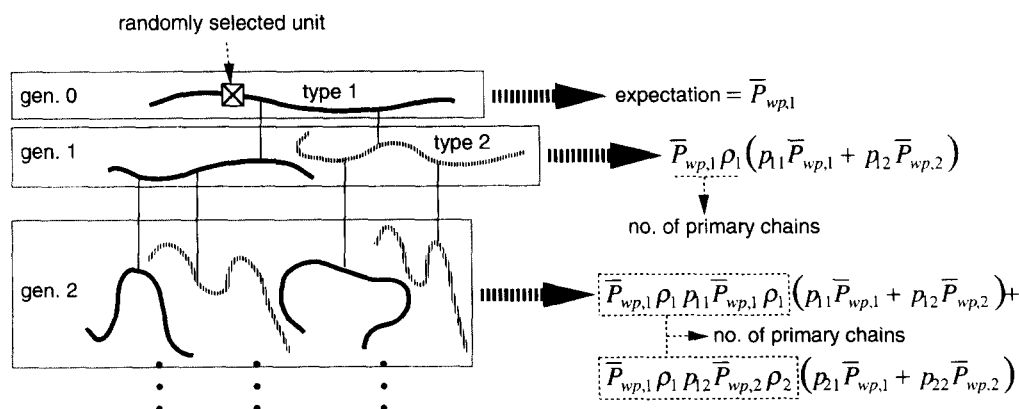
Figure 4 Diagram for calculating the expected weight of each generation for the statistical crosslinking of a binary system, given that the initially selected unit belongs to a polymer chain of type 1

repeating the similar procedure as shown in *Figure 3*, the expected weight of a polymer molecule, given that the type 1 chain is selected initially, $\bar{P}_{w,1}$ is given by

$$\bar{P}_{w,1} = \bar{P}_{wp,1} + \bar{P}_{wp,1}\rho_1(p_{11}\bar{P}_{wp,1} + p_{12}\bar{P}_{wp,2})$$
$$+ \bar{P}_{wp,1}\rho_1\{p_{11}\bar{P}_{wp,1}\rho_1(p_{11}\bar{P}_{wp,1} + p_{12}\bar{P}_{wp,2})$$
$$+ p_{12}\bar{P}_{wp,2}\rho_2(p_{21}\bar{P}_{wp,1} + p_{22}\bar{P}_{wp,2})\} + \cdots \tag{8}$$

Figure 4 shows the diagram for the present calculation. In the figure, the sum of the products along the arrows within a given generation gives the expected weight of the polymer chains that belong to the generation.

When the initially selected unit belongs to a chain of type 2, a similar diagram can be prepared in a straightforward manner. The expected weight of a polymer molecule, given

Figure 3 Schematic drawing for the derivation of the weight-average chain length for the statistical crosslinking of chains of types 1 and 2, given that the initially selected unit belongs to a polymer chain of type 1
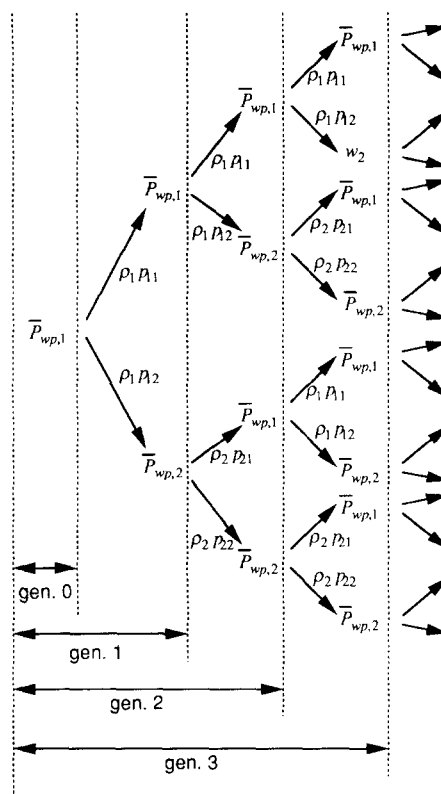
that the type 2 chain is selected initially, $\bar{P}_{w,2}$ is given by

$$
\begin{aligned}
\bar{P}_{w,2} = {} & \bar{P}_{wp,2} + \bar{P}_{wp,2}\rho_2(p_{21}\bar{P}_{wp,1} + p_{22}\bar{P}_{wp,2}) \\
& + \bar{P}_{wp,2}\rho_2\{p_{21}\bar{P}_{wp,1}\rho_1(p_{11}\bar{P}_{wp,1} + p_{12}\bar{P}_{wp,2}) \\
& + p_{22}\bar{P}_{wp,2}\rho_2(p_{21}\bar{P}_{wp,1} + p_{22}\bar{P}_{wp,2})\} + \cdots
\end{aligned}
\tag{9}
$$

In brief, the expected number of primary chains in the nth generation connected from the chains of type i is given by the product of ρ_i and the weight of type i chains in the $(n-1)$th generation. The expected weight of polymer connected from such a crosslink point is given by $\Sigma_{j=1}^2 p_{ij}\bar{P}_{wp,j}$. Therefore, the total weight of the primary chains that belong to the nth generation can be given by first-order Markov chain statistics.

The total expected weight, which is the weight-average chain length of the whole raction mixture, $\bar{P}_w$ is given by

$$
\bar{P}_w = w_1\bar{P}_{w,1} + w_2\bar{P}_{w,2} = \sum_{n=0}^{\infty}\mathbf{W_pQ}^n\mathbf{1}
\tag{10}
$$

where

$$
\mathbf{W_p} = (w_1\bar{P}_{wp,1}, w_2\bar{P}_{wp,2})
\tag{11}
$$

$$
\mathbf{Q} = \begin{pmatrix} q_{11} & q_{12} \\ q_{21} & q_{22} \end{pmatrix} = \begin{pmatrix} \rho_1 p_{11}\bar{P}_{wp,1} & \rho_1 p_{12}\bar{P}_{wp,2} \\ \rho_2 p_{21}\bar{P}_{wp,1} & \rho_2 p_{22}\bar{P}_{wp,2} \end{pmatrix}
\tag{12}
$$

$$
\mathbf{1} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}
\tag{13}
$$

When the molecular weights of a monomeric unit in chains of type 1 and 2 are different, the weight-average chain length $\bar{P}_w$ cannot be connected with the weight-average molecular weight $\bar{M}_w$ directly. In the present method, we can account for such differences by changing the expected number of monomeric units in each generation to the molecular weights in a straightforward manner. For example, the expected molecular weights of a polymer molecule, given that the type 1 chain is selected initially, $\bar{M}_{w,1}$ is given by

$$
\begin{aligned}
\bar{M}_{w,1} = {} & \bar{P}_{wp,1}M_1 + \bar{P}_{wp,1}\rho_1(p_{11}\bar{P}_{wp,1}M_1 + p_{12}\bar{P}_{wp,2}M_2) \\
& + \bar{P}_{wp,1}\rho_1\{p_{11}\bar{P}_{wp,1}\rho_1(p_{11}\bar{P}_{wp,1}M_1 + p_{12}\bar{P}_{wp,2}M_2) \\
& + p_{12}\bar{P}_{wp,2}\rho_2(p_{21}\bar{P}_{wp,1}M_1 + p_{22}\bar{P}_{wp,2}M_2)\} + \cdots
\end{aligned}
\tag{14}
$$

where M_1 and M_2 are the molecular weights of the monomeric unit of chains of types 1 and 2, respectively.

Therefore, the weight-average molecular weight, $\bar{M}_w$, is given in a matrix form as follows:

$$
\bar{M}_w = w_1\bar{M}_{w,1} + w_2\bar{M}_{w,2} = \sum_{n=0}^{\infty}\mathbf{W_pQ}^n\mathbf{M1}
\tag{15}
$$

where $\mathbf{M}$ is a diagonal matrix defined by

$$
\mathbf{M} = \begin{pmatrix} M_1 & 0 \\ 0 & M_2 \end{pmatrix}
\tag{16}
$$

For a system with N types of chain, the expected weight (number of monomeric units) of primary chains that belong to the nth generation can be calculated similarly with that for a binary system: (1) the expected number of primary chains in the nth generation

connected from the chains of type i is given by the product of ρ_i and the total number of monomeric units of type i chains in the $(n-1)$th generation, and (2) the expected weight of polymer connected from such a crosslink point is given by $\Sigma_{j=1}^N p_{ij}\bar{P}_{wp,j}$. The product of the quantity in items (1) and (2) gives the expected weight of the primary chains in the nth generation connected from the chains of type i. The total expected weight of primary chains in the nth generation is given by summing up for all i values. Therefore, by using the row vector, $\mathbf{W_p} = (w_i\bar{P}_{wp,i})$, the square matrix, $\mathbf{Q} = (q_{ij}) = (\rho_i p_{ij}\bar{P}_{wp,j})$, and the column vector, $\mathbf{1} = (1)$, the weight-average chain length for an N-component system is given by:

$$
\bar{P}_w = \sum_{n=0}^{\infty}\mathbf{W_pQ}^n\mathbf{1}
\tag{17}
$$

Similarly, the weight-average molecular weight is given by

$$
\bar{M}_w = \sum_{n=0}^{\infty}\mathbf{W_pQ}^n\mathbf{M1}
\tag{18}
$$

where $\mathbf{M}$ is the diagonal matrix whose elements are $m_{ii} = M_i$.

Equation (17) or (18) shows that the weight-average chain length diverges to infinity when the largest eigenvalue of $\mathbf{Q}$ reaches unity. Obviously, for a single-component system, equation (17) reduces to the Flory–Stockmayer equation given by equation (1), and the gelation is predicted to occur at $\rho\bar{P}_{wp} = 1$.

As a special case, if $\rho_i\bar{P}_{wp,j}$ becomes unity for all pairs of i and j values at the same time, the transition matrix becomes stochastic whose largest eigenvalue of $\mathbf{Q}$ is unity. Therefore, under this special condition, gelation occurs when $\rho_i\bar{P}_{wp,j} = 1$ irrespective of any chain connection rule, p_{ij}. Such conditions may be considered a 'universal' gelation point.

On the other hand, when the probability that a crosslink point on a chain of type i connects with a chain of type j is equal to the weight fraction of chains j, w_j, the discrimination of the types of the chains becomes just nominal, and the problem reduces to the random crosslinking of a single type of chain, i.e. the Flory–Stockmayer theory should be valid for this special case. This situation $(p_{ij} = w_j)$ can be rationalized by using equation (17) as follows. On the basis of equation (7), $\rho_i = \rho_j$ for the present case. In other words, the expected crosslinking density is the same for all types of chain. The elements of the transition matrix $\mathbf{Q}$ for this case is given by

$$
q_{ij} = \rho w_j\bar{P}_{wp,j} \qquad \text{(for } p_{ij} = w_j)
\tag{19}
$$

Therefore, the maximum eigenvalue of $\mathbf{Q}$ is given by

$$
\lambda_{\max} = \rho\sum_{j=1}^N w_j\bar{P}_{wp,j} = \rho\bar{P}_{wp} \qquad \text{(for } p_{ij} = w_j)
\tag{20}
$$

Equation (20) shows that gelation occurs when $\rho\bar{P}_{wp} = 1$, which agrees with the Flory–Stockmayer theory[1-3].

Binary systems (N = 2)

Here, we show the solution for binary systems, which would be of practical interest in polymer modifications.
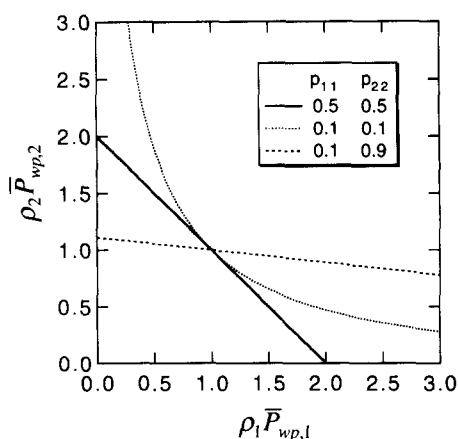
Figure 5 Gel point for the binary systems. When the system reaches the point on the curve, gelation is predicted to occur, where $\rho_1 \bar{P}_{wp,1}$ and $\rho_2 \bar{P}_{wp,2}$ mean the number of crosslink points per primary chain on the weight-average basis for chains of types 1 and 2, respectively

For a binary system, the largest eigenvalue is given by

$$\lambda_{max} = \frac{1}{2} \left\{ \rho_1 \bar{P}_{wp,1} p_{11} + \rho_2 \bar{P}_{wp,2} p_{22} \right.$$

$$\left. + \sqrt{\left(\rho_1 \bar{P}_{wp,1} p_{11} - \rho_2 \bar{P}_{wp,2} p_{22} \right)^2 + 4 \rho_1 \rho_2 \bar{P}_{wp,1} \bar{P}_{wp,2} p_{12} p_{21}} \right\}$$

$$(21)$$

Equation (21) shows that λ_{max} is determined only by $\rho_1 \bar{P}_{wp,1}$, $\rho_2 \bar{P}_{wp,2}$, and the transition probabilities, p_{ij}. The values of $\rho_1 \bar{P}_{wp,2}$ and $\rho_2 \bar{P}_{wp,1}$ are not involved. Furthermore, under conditions $\rho_1 \bar{P}_{wp,1} = \rho_2 \bar{P}_{wp,2} = 1$ the value of λ_{max} is always unity irrespective of the chain connection rule, p_{ij} values.

Figure 5 shows the combination of $(\rho_1 \bar{P}_{wp,1}, \rho_2 \bar{P}_{wp,2})$ in which gelation occurs for the binary systems. The point $(\rho_1 \bar{P}_{wp,1}, \rho_2 \bar{P}_{wp,2}) = (1,1)$ shows the 'universal' gelation point in which gelation occurs irrespective of the p_{ij} values. When $p_{11} = p_{22} = 0.1$, the crosslinking reactions tend to occur between different types of chain. In such a case, if $\rho_1 \bar{P}_{wp,1}$ becomes smaller, the value of $\rho_2 \bar{P}_{wp,2}$ at the gel point must become significantly larger to compensate for a smaller $\rho_1 \bar{P}_{wp,1}$ value.

When $p_{11} = 0.1$ and $p_{22} = 0.9$, the chains of type 2 tend to play a dominant role to form crosslinked polymers, and the value of $\rho_2 \bar{P}_{wp,2}$ needs to be close to unity at the gel point.

From equation (17), a general solution of the weight-average chain length for a binary system is given by:

$$\bar{P}_w = \frac{\bar{P}_{wp} + w_1 \bar{P}_{wp,1}(q_{12} - q_{22}) + w_2 \bar{P}_{wp,2}(q_{21} - q_{11})}{(1 - q_{11})(1 - q_{22}) - q_{12} q_{21}}$$

$$(22)$$

Incidentally, when crosslinking occurs only with different types of chain as originally considered by Stockmayer[5,6], i.e. $p_{12} = p_{21} = 1$, equation (22) reduces to

$$\bar{P}_w^{hetero} = \frac{w_1 \bar{P}_{wp,1} + w_2 \bar{P}_{wp,2} + (w_1 \rho_1 + w_2 \rho_2) \bar{P}_{wp,1} \bar{P}_{wp,2}}{1 - \rho_1 \rho_2 \bar{P}_{wp,1} \bar{P}_{wp,2}}$$

$$(23)$$

In this case, from equations (3) and (7), it is straightforward to show that $w_1 = \rho_2/(\rho_1 + \rho_2)$ and $w_2 =$

$\rho_1/(\rho_1 + \rho_2)$, and equation (23) can be further modified to

$$\bar{P}_w^{hetero} = \left(\frac{1}{\rho_1 + \rho_2} \right) \frac{\rho_2 \bar{P}_{wp,1} + \rho_1 \bar{P}_{wp,2} + 2 \rho_1 \rho_2 \bar{P}_{wp,1} \bar{P}_{wp,2}}{1 - \rho_1 \rho_2 \bar{P}_{wp,1} \bar{P}_{wp,2}}$$

$$(24)$$

Equation (24) agrees with the solution obtained by Stockmayer[6] with $\bar{P}_{wp,1}$, $\bar{P}_{wp,2} \gg 1$.

Free-radical polymer grafting

We consider the polymer grafting of two different polymer chains via free-radical mechanisms. This problem was investigated earlier[10,11] by using the method of moments. Let the fraction of radical generation rate on chains of type i be g_i (i.e. the radical generation rate on type i chains is given by $g_i \nu_R$, where ν_R is the radical generation rate on all types of chains), and the bimolecular termination constant between polymer radicals of the types i and j be k_{ij}. Note that $k_{12} = k_{21}$, because both termination rate constants describe the same type of termination reactions. We introduce the following reactivity ratios[10]:

$$r_1 = k_{11}/k_{12} \tag{25}$$

$$r_2 = k_{22}/k_{12} \tag{26}$$

The transition probabilities for the present case are given by

$$p_{11} = \frac{r_1 \phi_1^\bullet}{r_1 \phi_1^\bullet + \phi_2^\bullet} \tag{27}$$

$$p_{12} = \frac{\phi_2^\bullet}{r_1 \phi_1^\bullet + \phi_2^\bullet} \tag{28}$$

$$p_{22} = \frac{r_2 \phi_2^\bullet}{r_2 \phi_2^\bullet + \phi_1^\bullet} \tag{29}$$

$$p_{21} = \frac{\phi_1^\bullet}{r_2 \phi_2^\bullet + \phi_1^\bullet} \tag{30}$$

where $\phi_1^\bullet$ and $\phi_2^\bullet$ are the mole fractions of the polymer radicals of types 1 and 2, respectively.

By application of the stationary-state hypothesis for the concentration of polymer radicals, one obtains:

$$\frac{\phi_1^\bullet}{\phi_2^\bullet} = \frac{(g_1 - g_2) + \xi}{2 r_1 g_2} \tag{31}$$

where

$$\xi = \sqrt{(g_1 - g_2)^2 + 4 r_1 r_2 g_1 g_2} \tag{32}$$

Therefore, equations (27)–(30) reduce to

$$p_{11} = \frac{1 + \xi - 2 g_2}{1 + \xi} \tag{33}$$

$$p_{12} = \frac{2 g_2}{1 + \xi} \tag{34}$$

$$p_{22} = \frac{2 r_1 r_2 g_2}{2 r_1 r_2 g_2 + 1 + \xi - 2 g_2} \tag{35}$$

$$p_{21} = \frac{1 + \xi - 2 g_2}{2 r_1 r_2 g_2 + 1 + \xi - 2 g_2} \tag{36}$$

It is worth noting here that all transition probabilities involve the reactivity ratios, r_1 and r_2, as the product form, r_1r_2, not separately. In other words, the chain connection rule is determined only by the magnitude of r_1r_2. Because $\mathbf{W_p}$ has no relation with the reactivity ratios, the weight-average chain length is governed only by the product, r_1r_2, not by the individual terms of r_1 and r_2, as originally reported[10].

By substituting equations (33)–(36) into the general solution for the binary system, equation (22), one obtains the analytical solution for the present case. As a special case, when $r_1r_2 = 1$, $\bar{P}_w$ is given by

$$\bar{P}_w = \frac{\bar{P}_w - \rho(w_2 g_1 - w_1 g_2)^2 \bar{P}_{wp,1} \bar{P}_{wp,2}/(w_1 w_2)}{1 - \rho(g_1^2 \bar{P}_{wp,1}/w_1 + g_2^2 \bar{P}_{wp,2}/w_2)}$$

$$\text{(for } r_1 r_2 = 1) \quad (37)$$

Equation (37) agrees with the earlier derivation by using the method of moments[10], and it reduces to equation (1) when $g_1 = w_1$, i.e. the radicals are generated equally for all units irrespective of the chain types.

The validity of all analytical equations derived in refs. 10 and 11 has been reconfirmed by the present general solution given by equation (22).

Systems with crosslinking density distribution

As mentioned in the Introduction, the solution for the present model equations (17) and (18), could be applied for the cases where the chemical type of chain is essentially the same but the chain connection rule is not the same for all chains, such as due to the residence time distribution or the history-dependent crosslinking reactions. For example, in a random crosslinking reaction, if the residence time distribution is significant, some polymer chains would possess larger crosslinking density than the others. In the reactive extrusion of polymers by using peroxides, a similar situation could be caused if the rapidly decomposing peroxide molecules cannot be mixed into the polymer melt within a very short time[13], even when the variance of the residence time distribution is small. As the simplest model for such a process, consider a random crosslinking reaction operated under the following two-stage process: (1) we crosslink polymer chains up to a level of crosslinking density, ρ_α, then additional linear polymer chains, which are identical with the initial material for stage 1, are blended with the weight fraction w_2, and (2) we introduce additional crosslinking density, ρ_β, to the whole reaction system. This type of process is not simply a model for the systems with the residence time distribution, but it was actually used to control the molecular weight distribution (MWD) of the product polymers[25,26].

In the present case, $\rho_1 = \rho_\alpha + \rho_\beta$, $\rho_2 = \rho_\beta$ and $\bar{P}_{wp,1} = \bar{P}_{wp,2} = \bar{P}_{wp}$. Further, the transition probabilities, p_{ij}, are given by

$$p_{11} = \frac{\rho_\alpha + w_1\rho_\beta}{\rho_\alpha + \rho_\beta} \quad (38)$$

$$p_{12} = \frac{w_2\rho_\beta}{\rho_\alpha + \rho_\beta} \quad (39)$$

$$p_{21} = w_1 \quad (40)$$

$$p_{22} = w_2 \quad (41)$$

Therefore, the transition matrix $\mathbf{Q}$ is given by

$$\mathbf{Q} = \bar{P}_{wp}\begin{pmatrix} \rho_\alpha + w_1\rho_\beta & w_2\rho_\beta \\ w_1\rho_\beta & w_2\rho_\beta \end{pmatrix} \quad (42)$$

From equation (22), $\bar{P}_w$ is given by

$$\frac{\bar{P}_w}{\bar{P}_{wp}} = \frac{1 - w_2\rho_\alpha\bar{P}_{wp}}{1 - (\rho_\alpha + \rho_\beta)\bar{P}_{wp} + w_2\rho_\alpha\rho_\beta\bar{P}_{wp}^2} \quad (43)$$

On the other hand, suppose we do not know the existence of the residence time distribution. In such a situation, we would use equation (1). Because the average crosslinking density of the whole reaction mixture is $\rho = w_1\rho_\alpha + \rho_\beta$, we would estimate the weight-average chain length, $\bar{P}_w^{est}$ as follows:

$$\frac{\bar{P}_w^{est}}{\bar{P}_{wp}} = \frac{1}{1 - (w_1\rho_\alpha + \rho_\beta)\bar{P}_{wp}} \quad (44)$$

The ratio $\bar{P}_w^{est}/\bar{P}_w$ is, therefore, given by

$$\frac{\bar{P}_w^{est}}{\bar{P}_w} = \frac{1 - (\rho_\alpha + \rho_\beta)\bar{P}_{wp} + w_2\rho_\alpha\rho_\beta\bar{P}_{wp}^2}{1 - (\rho_\alpha + \rho_\beta)\bar{P}_{wp} + w_2\rho_\alpha\rho_\beta\bar{P}_{wp}^2 + w_1w_2\rho_\alpha^2\bar{P}_{wp}^2} < 1 \quad (45)$$

Equation (45) shows that if we apply the Flory–Stockmayer equation to the present reaction system with non-random distribution of crosslink points, we would underestimate the weight-average chain length for a given (average) crosslinking density value, or we would overestimate the average crosslinking density level based on the measurement of $\bar{P}_w$ values.

The same argument holds also for free-radical copolymerization of vinyl/divinyl monomers. In this case, the expected crosslinking density of the primary chains are different, depending on the birth time[14-19]. (Note that the first-shell substitution effect[27] and the reactivity ratios of comonomers are fully accounted for in the mathematical model for the crosslinking density distribution[15-19].) The onset of gelation for such systems must be assessed from the point of view of the largest eigenvalue of the transition matrix, $\mathbf{Q}$, not by the value of $\rho\bar{P}_{wp}$. Obviously, however, one needs to realize that other non-ideal effects such as cyclization reactions as well as the size and structural dependence of crosslinking reactions, which seem to have a formidable role in the context of a mean-field theory, are expected to be significant in non-linear free-radical polymerizations[28,29].

MWD

In this section, we consider more detailed statistical properties, i.e. the full MWD profiles. The analytical solution for the full MWD might be obtained for simpler cases by using the concept of the random sampling technique[20-23]. However, for more realistic cases, one may need to resort to the Monte Carlo simulation technique. In the context of the random sampling technique, it is rather straightforward to construct a Monte Carlo simulation algorithm[17-23] for any type of chain connection rule. With the Monte Carlo simulations, it is straightforward to account for the change in the transition probabilities, p_{ij}, with the progress of crosslinking reactions.

Suppose we have randomly selected one unit, as shown in *Figure 1*. With probability, w_i, we would choose a

chain of type i. Therefore, we can determine the type of the selected chain by generating an equidistributed random number between 0 and 1 in Monte Carlo simulation. Because the selection is conducted on a weight basis, the chain length of the primary polymer molecule that contains this particular unit conforms to the weight fraction distribution of the primary polymer molecules of type i, $W_{p,i}(r)$. By generating a random number that follows $W_{p,i}(r)$, we can determine the chain length of the initially selected primary chain.

Because the crosslinking density of chains of type i is ρ_i, the number of crosslink points on this primary polymer molecule can be determined from the following binomial distribution, i.e. the probability that the primary chain of type i with chain length r possesses m crosslink points is given by

$$P(m) = \binom{r}{m} \rho_i^m (1 - \rho_i)^{r-m} \qquad (46)$$

Each crosslink point is connected to a chain of type j with the probability, p_{ij}. Therefore, we can determine the types of the connected chains in the next generation. From the point of view of the connected chains, any unit within the chain can be connected with equal probability; therefore, the chain lengths of the primary chains follow the weight fraction distribution of the primary chains, $W_{p,j}(r)$.

By continuing the above procedures until no more primary chains are connected, we can determine the size and structure of one polymer molecule. By generating a large number of polymer molecules in this way, we can effectively determine the full MWD, as well as more detailed statistical properties, such as the radii of gyration and the fractal dimension of the formed polymer molecules[30–32].

Illustrative calculations

The present Monte Carlo simulation can be applied for a system with any N-value. However, for simplicity, we show illustrative calculation results with $N = 2$, where both chain length distributions follow the most probable distribution:

$$W_{p,i}(r) = \{r/(\bar{P}_{np,i})^2\} \exp(-r/\bar{P}_{np,i}) \qquad (47)$$

where $\bar{P}_{np,i}$ is the number-average chain length of type i chains, which is equal to $\bar{P}_{np,i} = \bar{P}_{wp,i}/2$ for the most probable distribution.

As mentioned in the Introduction, Stockmayer[5,6] considered the condensation of polymer chains in which $A_1, A_2, \ldots, A_i, \ldots$ moles of the type A chains react with $B_1, B_2, \ldots, B_j, \ldots$ moles of the type B chains.
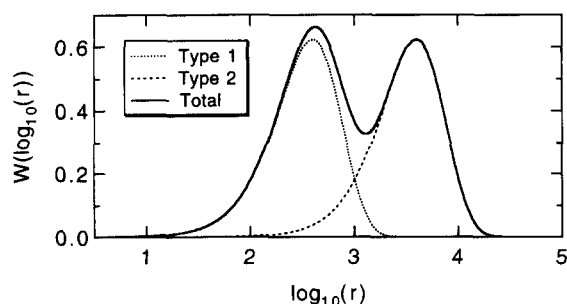

Figure 6 Primary chain length distribution used for the simulation
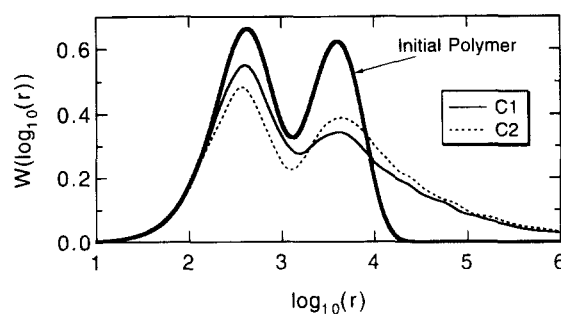

Figure 7 Weight fraction distribution at the gel point. The bold curve shows the initial distribution with $\bar{P}_{wp,1} = 400$, $\bar{P}_{wp,2} = 4000$ and $w_1 = 0.5$. C1: $p_{11} = p_{22} = 0.5$; C2: $p_{11} = p_{22} = 0.1$
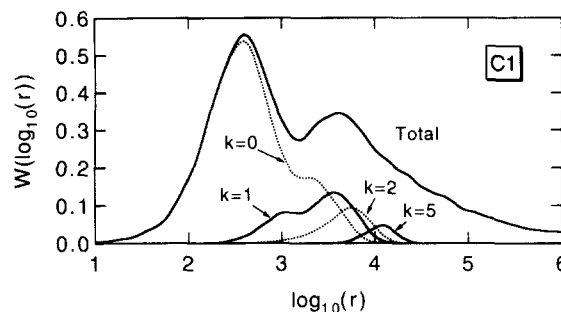

Figure 8 Fractional weight-based distribution containing k crosslinkages as well as the whole weight fraction distribution at the gel point under condition C1

He obtained an analytical solution, $N\{m_i, n_j\}$ that represents the number of moles of species consisting of $m_1, m_2, \ldots, m_i, \ldots$ chains of the type A combined with $n_1, n_2, \ldots, n_j, \ldots$ chains of the type B. Note that, in order to obtain the number of polymer molecules with chain length r, one needs to consider all of the possible combinations to form polymer molecules with chain length r. His equation is useful for obtaining the average molecular weights through the use of appropriate generating functions; however, it is not practical to use his $N\{m_i, n_j\}$ function to calculate the full MWD profiles directly, especially for primary chains with a broad MWD. As far as the authors know, this is the first attempt to show full MWD profiles even with $N = 2$ where both types of chain are polydisperse and $\bar{P}_{wp,1}, \bar{P}_{wp,2} \gg 1$.

We consider the cases where the weight-average chain lengths for types 1 and 2 are $\bar{P}_{wp,1} = 400$ and $\bar{P}_{wp,2} = 4000$, respectively, and the weight fraction of chains of type 1 is $w_1 = 0.5$. The primary chain length distribution is shown graphically in *Figure 6*. Here, we consider two types of connection rule: under condition C1, $p_{11} = p_{22} = 0.5$, and under condition C2, $p_{11} = p_{22} = 0.1$. Because $w_1 = w_2 = 0.5$ in the present example, the crosslinking behaviour under condition C1 reduces to the case with a single type of chain, i.e. random crosslinking of polymer chains in which the Flory–Stockmayer theory[1–3] is applicable. Under condition C2, the crosslinking with the other type of chain is significant.

From equations (7) and (21), gelation is predicted to occur at $\rho_1 = \rho_2 = 4.545 \times 10^{-4}$ under condition C1, while the gel point for C2 is $\rho_1 = \rho_2 = 7.286 \times 10^{-4}$. A larger crosslinking density is required under condition C2, because a larger number of smaller chains (type 1 chains) are incorporated into the gel molecule due to a
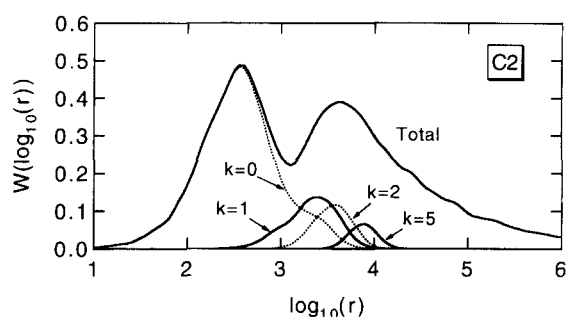
Figure 9 Fractional weight-based distribution containing k cross-linkages as well as the whole weight fraction distribution at the gel point under condition C2

greater tendency of crosslinking between heterochains. *Figure 7* shows the simulated weight fraction distribution at the gel point. The total of 4×10^4 polymer molecules are generated in the simulation for each condition. A larger number of type 1 chains (smaller chains) are used for crosslinking reactions under condition C2 than under C1.

The MWD of the crosslinked polymer molecules is the sum of the fractional MWDs containing $0, 1, 2, \ldots$ crosslinkages. When the polymer molecules are fractionated by the number of crosslinkages, one obtains the fractional MWD as shown in *Figures 8* and *9*. *Figure 8* shows the case under condition C1 at the gel point, while *Figure 9* shows that for C2. In the figures, the k values indicate the number of crosslinkages in a polymer molecule. Even at the gel point, a large amount of linear polymer molecules ($k = 0$) still remains for both cases. It is shown that the peak location of the fractional MWD at the same k value is smaller for C2, i.e. a larger number of crosslinkages is required to form larger-sized polymer molecules under condition C2 because of a significant amount of heterochain crosslinking. The MWD profiles formed can vary significantly depending on the chain connection rule, even at the same weight-average molecular weight levels.

CONCLUSIONS

We have proposed a general theory for the statistical crosslinking of heterochains. The weight averages of the chain length and molecular weight distributions are given by $\bar{P}_w = \Sigma_{n=0}^{\infty} \mathbf{W_p} \mathbf{Q}^n \mathbf{1}$ and $\bar{M}_w = \Sigma_{n=0}^{\infty} \mathbf{W_p} \mathbf{Q}^n \mathbf{M1}$, respectively. The gel point can be determined only from the transition matrix, $\mathbf{Q}$, i.e. gelation is predicted to occur when the largest eigenvalue of $\mathbf{Q}$ reaches unity. The present theory clearly shows that the Flory–Stockmayer theory cannot be used for non-random crosslinking reactions. The onset of gelation for such reaction systems must be assessed on the basis of the largest eigenvalue of $\mathbf{Q}$, not the value of $\rho\bar{P}_{wp}$.

For the cases of free-radical polymer grafting with two types of chain, the transition probabilities are given only by the product of the reactivity ratios; therefore, the weight-average chain length development is dominated by the product of $r_1 r_2$, not the individual terms of r_1 and r_2. The equations obtained for $\bar{P}_w$ confirmed the validity of the earlier results[10,11] derived by using the method of moments.

To obtain more detailed structural information such as the full MWD, it is straightforward to set up a Monte Carlo simulation algorithm on the basis of the random sampling technique.

GLOSSARY OF SYMBOLS

g_i	Fraction of the radical generation rate on chains of type i
k	Number of crosslinkages in a polymer molecule
k_{ij}	Bimolecular termination rate constant between radicals of type i and j
M_i	Molecular weight of the monomeric unit of type i chain
$\bar{M}_w$	Weight-average molecular weight
$\bar{P}_w$	Weight-average chain length
$\bar{P}_{wp}$	Weight-average chain length of all primary chains
$\bar{P}_{wp,i}$	Weight-average chain length of the chains of type i
p_{ij}	Transition probability that a crosslink point on a chain of type i crosslinks a chain of type j
q_{ij}	Elements of the transition matrix, $\mathbf{Q} = (q_{ij}) = (\rho_i p_{ij} \bar{P}_{wp,j})$
r	Chain length (degree of polymerization)
r_1, r_2	Reactivity ratios for the bimolecular termination reactions, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{12}$
$W(r)$	Weight fraction distribution
$W_{p,i}(r)$	Weight fraction distribution of the primary chains of type i
w_i	Weight fraction of polymer chains with type i

Bold letters

$\mathbf{1}$	Column vector whose elements are all unity
$\mathbf{M}$	Diagonal matrix whose elements are $m_{ii} = M_i$
$\mathbf{Q}$	Transition matrix whose elements are given by $q_{ij} = \rho_i p_{ij} \bar{P}_{wp,j}$
$\mathbf{W_p}$	Row vector whose elements are $w_i \bar{P}_{wp,i}$

Greek letters

ρ	Average cross-linking density of the whole reaction mixture
ρ_i	Cross-linking density of chains of type i
$\phi_i^{\bullet}$	Number fraction of the polymer radicals of type i

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