Molecular weight distribution in random crosslinking of polymer–polyfunctional monomer systems

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Abstract

A Monte Carlo sampling algorithm for the simulation of molecular structural evolution in a random crosslinking process of polymer–polyfunctional monomer (PFM) systems is proposed. Combining a simple gel content experiment with this algorithm, various important property changes in a random crosslinking reaction, such as molecular weight distribution, location of gel points, crosslinking density within sol and gel fractions, PFM molecular density within sol and gel fractions, etc., can be fully explored. A virtual polymer–PFM system with a very narrow initial molecular weight distribution and a commercial low density polyethylene–triallyl cyanurate system have been used to demonstrate the application of this algorithm. The implications of the simulated results were also discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular weight distribution; Crosslinking; Polyfunctional monomer

1. Introduction

The modification of polymers using crosslinking and grafting methods is an important commercial process for the purpose of improving the physical and chemical properties of these materials. Usually, the manner in which the molecular structure develops in a process dictates whether this process will be successful or not. In some processes, flow and moldability properties are important. Any premature gelation is undesired and must be avoided. At the final stage of the same process, however, the efficient growth of molecular weight and crosslinking may also be important when a polymer with a very high melt strength and better heat resistance is desired. In a peroxide initiated crosslinking reaction of polymers, peroxides decompose to produce highly reactive free radicals which in turn react with polymer molecules to produce free polymer radicals. These radicals combine randomly with one another to produce crosslinks [1]. In certain circumstances, peroxide crosslinking is not efficient enough to produce the required crosslinking density in polymers [2], and the addition of polyfunctional monomers (PFMs) to promote crosslinking density is an important commercial practice. Recently, reactive modification in polymers during their molding

processes has gained more popularity. In these processes, the reaction rate as well as the molecular weight distribution (MWD) are most important. Polyfunctional monomers have been used to control the reaction rate or the molecular weight distribution effectively. Generally speaking, PFM coagents can be categorized into two types [1]. Type I coagents undergo hydrogen abstraction, producing radicals which lead to chain grafting and crosslinking. They may experience free radical addition, resulting in homopolymerization. These types of coagents promote the crosslinking rate as well as crosslinking efficiency. The other type of coagent, type II, produces more stable radicals and is capable of improving only the crosslinking efficiency. Both types of coagents have been widely applied in various commercial processes.

In order to produce higher quality polymers and to control a process more precisely, a consideration of controlling the entire molecular weight distribution seems inevitable. It is thus very important to find a working model that can be used to predict the molecular structural evolution under different processing conditions. Many theories have been developed to describe the gel/sol partition phenomena in nonlinear polymerization. Recent developments have been a combination of statistical theories with kinetic models to calculate the polymer properties such as MWD and crosslinking density distribution in the reaction path [3–6]. For a random crosslinking process, Saito derived an integrodifferential

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Nomenclature

c	Number of PFM molecules in a polymer chain
$\overline{M}_n$	Number average molecular weight
$\overline{M}_w$	Weight average molecular weight
N_C	Number of PFM molecules in a polymer–PFM system
N_P	Number of polymer segments in a polymer or a polymer–PFM system
N_0, N_1	The number of PFM molecules that have connected to 0, 1, 2, 3 polymers
N_2, N_3	molecules in a polymer–PFM system
p	The probability that any one of the functional groups in a PFM has reacted
$p(n)$	The probability that a primary polymer molecule possesses n tie points
$P_C(n)$	The conditional probability that a tri-functional monomer molecule connected to n polymer molecules when this molecule has connected at least to one polymer molecule
P_0, P_1	The probabilities that a tri-functional monomer molecule has connected to
P_2, P_3	zero, one, two and three polymer molecules, respectively.
r	Polymer chain length (number of structural units)
s	Average number of polymer–PFM tie points for each PFM molecule
u	Number average chain length
w^{gel}	Weight fraction of gel (wt.%)
$W(r)$	Weight fraction distribution function for polymers with chain length r
$W_X(r)$	Fractional MWD for polymers containing X effective tie points
$W_c(r)$	Fractional MWD for polymers containing c PFM molecules
X	Number of effective tie points in a polymer chain
X_C	Number of effective polymer–PFM tie points in a polymer–PFM system
X_P	Number of polymer–polymer tie points in a polymer or a polymer–PFM system
X_T	Number of polymer–PFM tie points in a polymer–PFM system
α	Extent of reaction
$\Gamma(\sigma)$	The Gamma function of σ
ρ	Overall crosslinking density (Number of effective tie points per structural unit)
ρ'	Overall tie point density (Number of tie points per structural unit)
ρ_c	Overall PFM density in a polymer–PFM system (Number of reacted PFM molecules per structural unit)
$\rho_{c,r}$	Average PFM density in a polymer chain (Number of connected PFM molecules per structural unit)
ρ^{gel}	Crosslinking density in the gel
ρ_c^{gel}	PFM density in the gel
$\rho_{c,r}^{sol}\|_{r\to\infty}$	Average PFM density for a polymer of infinite chain length
ρ_r	Average crosslinking density in a polymer chain
$\rho_r^{sol}\|_{r\to\infty}$	Crosslinking density for a polymer of infinite chain length
ρ_r'	Average tie point density in a polymer chain (Number of tie points/unit)
ρ_1	Overall crosslinking density for a polymer without the presence of PFM molecules
ρ_2	Overall crosslinking density for the polymer–PFM system
ρ_2'	Overall tie point density for the polymer–PFM system
σ	$\overline{M}_n/(\overline{M}_w - \overline{M}_n)$
Φ_o^{sol}	The weight fraction of unreacted polymers in the sol (weight of molecules containing zero tie point/weight of all sol molecules)
$\int_{r=0}^{\infty} W_{c=0}(r)$	The weight fraction of polymers to which no PFM molecule has attached

equation based on statistical considerations and population balance to predict the molecular structural evolution [7]. Kimura obtained analytical series solutions to Saito's equation for various types of initial polymer distributions [8]. It was recognized later that a correction is required in Kimura's solution for the initial Schulz–Zimm's distribution [9,10]. Tobita rederived the series solution and verified with a computer simulation based on a Monte Carlo sampling technique [10,11]. When an initiator, e.g. dicumyl peroxide, was used to modify a polyolefin, the kinetics of the molecular structural evolution was determined essentially by the decomposition kinetics of the initiator. Suwanda and Balke combined gel content experiments, chemical kinetics, and molecular theories to study the effect of initiators on the molecular weight distribution of polyethylene at low initiator dosage [12,13]. If a high initiator dosage is used, the molecular weight may increase in such a way that the polymers system finally gels. Combining

Saito–Kimura–Tobita's scheme along with experimental crosslinking kinetics, Tai successfully explored the structural evolution in a peroxide-initiated low density polyethylene (LDPE) random crosslinking process [2,14].

The area of quantitative evaluation in the development of a polymer network in a random crosslinking process of a polymer–PFM system remains unexplored. It will be very difficult to derive a simple equation to calculate the molecular weight distribution analytically. On the other hand, the use of Monte Carlo computer simulations is a powerful method for investigating the entire molecular constitution. Detailed structural information such as the full molecular weight distribution profile, the distribution of the crosslink points among various polymer molecules, the sol–gel fraction, and the spatial distribution of the crosslinked polymer chains can all be revealed. The applications of Monte Carlo simulations to the properties of dense polymer networks range from rather rigid model systems, where the crosslinks cannot move, to highly complicated, fully mobile randomly crosslinked polymer melts [15–18]. Most Monte Carlo simulations use a limited reaction volume to conduct non-mean field percolation type calculations. They failed to provide a quantitative description of the complex reaction systems. Recently, Tobita developed several Monte Carlo sampling techniques to investigate history-dependent crosslinking, branching reactions in free-radical polymerization, and random crosslinking and degradation reactions of polymer chains [10,11,19–21]. Tobita's approach used a large number of polymer molecules as samples from the population, enabling one to determine the statistical properties effectively. In this report, we adapted this approach to develop a Monte Carlo simulation algorithm. Based on this algorithm, the structural evolution in the random crosslinking of polymer chains with the presence of PFM molecules can be simulated. We demonstrate that a multimodal distribution is obtained for a very narrow imaginary initial MWD. We also demonstrate how the proposed algorithm can be applied to explore the molecular evolution in a commercial LDPE-triallyl cyanurate crosslinking process with the help of gel content measurements. Since the Monte Carlo sampling technique can account for the effect of residence time distribution of the reacting species, extension of this present method to various reactor types is straightforward if the parameters for the related reaction kinetics are available. The results of this research will be helpful in gaining insights into the processing structure–property relationships of various reactive polymer processes.

2. Experimental

2.1. Materials

The LPDE resin used in this study was NA 112-27, supplied by USI Far East Corporation. It has a melt index of 3 g/10 min and a density of 0.921 g/cm^3. Its weight average molecular weight $\overline{M}_w$ is 216,000 g/mol and its number average molecular weight $\overline{M}_n$ is 36,000 g/mol. The organic peroxide used was dicumyl peroxide (DCP) with an assay higher than 99% supplied by Coin Chemicals Corporation. Triallyl-cyanurate (TAC), which served as a crosslinking coagent, was supplied by Aldrich Chemicals Inc. It was stored in a −40°C refrigerator. All materials were used as received.

2.2. Sample preparation and analysis

The LDPE-TAC compounds were prepared using a Brabender Plasti-Corder PL2000 at 120°C at a mixing speed of 30 rpm. Roller blade type rotors were chosen for mixing the three components. The amounts of DCP and TAC added to the compounds were the same, each at a weight fraction of 1%. LDPE pellets were first placed into the mixing chamber and were allowed to melt for 1 min, followed by TAC for another minute. After complete mixing of the compounds, DCP was added and mixing was maintained for one more minute. The torque readings were watched closely to avoid any scorch of the compound. The compounds were quickly taken out of the mixing chamber and pressed into a thin sheet using a compression molding machine at a temperature of 120°C. These sheet specimens were then placed in a vacuum oven and heated isothermally at a temperature of 200°C for more than 2 h to ensure the full DCP conversion. The gel contents were then measured using the reflux extraction method. A sample of about 0.3 g was placed in a pouch made of 120 mesh stainless steel cloth and immersed in boiling xylene for 12 h. The amount of remaining gel was calculated according to ASTM D2765 [22]. Crosslinking densities ρ were then calculated using the following equations [11,23]:

$$w^{gel} = 1 - \left(\frac{\sigma}{\sigma + \rho u w^{gel}} \right)^{\sigma+1} \tag{1}$$

where w^{gel} is the experimental weight fraction of gel, u is the number average chain length, and σ is a measure of the distribution breadth and is defined as:

$$\sigma = \frac{1}{(\overline{M}_w/\overline{M}_n) - 1} = \frac{\overline{M}_n}{\overline{M}_w - \overline{M}_n} \tag{2}$$

3. Algorithm development

The Monte Carlo sampling technique has been very effective in simulating the random crosslinking process of homopolymers [10,11]. Here we applied this technique to simulate the random crosslinking process among polymers and polyfunctional monomers. Suppose that there are long chain polymer molecules and tri-functional monomer molecules in the system initially, and the crosslinkages are

introduced randomly among these molecules. The basic assumptions are:

1. Crosslinking proceeds without any cycle formation.
2. Only two types of linkages exist: the one formed by the combination of two polyradicals and the one formed by the combination between a polyradical and a PFM molecule. Since the concentration of PFM molecules is generally quite low, it is plausible to assume that there are no PFM-PFM linkages.
3. All functional groups on the PFM are equally reactive; the principle of equal reactivity is assumed to hold throughout the crosslinking reaction so that the reactivity of a given functional group is independent of the size or structure of the molecule to which it is attached [24,25].

Once the connection rule among the primary polymer molecules and the PFM molecules was made clear, the Monte Carlo computer simulation could be implemented to investigate the entire molecular constitution. To begin with, one unit was selected randomly from all primary polymer molecules exist in the reaction system. The size of the polymer molecule to which this particular unit belongs was determined by the Monte Carlo method. This molecule was designated as the zeroth generation polymer molecule. For the initial polymer distribution, one of the most employed MWD is the Schulz–Zimm (a Gamma-type) distribution, whose weight fraction distribution is given by:

$$W(r) = \frac{\sigma^{\sigma}}{u\Gamma(\sigma)} \left(\frac{r}{u}\right)^{\sigma} \exp\left(-\frac{\sigma r}{u}\right) \qquad (3)$$

where r is the chain length and $\Gamma(\sigma)$ is the Gamma function of σ. The chain length of this selected primary polymer molecule was determined using Eq. (3). After choosing the zeroth generation polymer molecule, we then proceeded to determine the number of tie points that it possessed. The probability for each structural unit of all primary polymer molecules to possess a tie point is the same and is equal to the overall tie point density. A tie point is defined here as either a polymer–polymer tribranching point or a polymer–PFM junction point. The combination of two polyradicals forms a 4-branch crosslink with a C–C bridge. Two tie points are created and two units are crosslinked. When a polyradical combines with a PFM molecule, a single tie point but no crosslink is formed. A 4-branch crosslink forms if this particular PFM reacts with one more polyradical; there are two tie points and two crosslinked units. A 6-branch crosslink forms if this particular PFM reacts with two more polyradicals, i.e., all three functional groups have reacted; there are three tie points and three crosslinked units. The number of tie points, n, on a primary polymer molecule of chain length r can be determined from a binomial distribution

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

where ρ' is defined as the fraction of units that either bear tribranching polymer–polymer tie points or polymer–PFM tie points.

The next thing was to determine the type of each tie point. Assuming that the overall tie point density for the polymer with an initiator alone is ρ_1 and the overall tie point density of the polymer with the presence of a PFM coagent is ρ'_2. Notice that, in the absence of PFM molecules, the overall tie point density is equal to the crosslinking density. With the presence of PFM molecules, the system consists of polymer–polymer crosslink points, polymer–PFM–polymer crosslink points and pedant polymer–PFM tie points. Those tie points which contribute to the crosslinking density in a polymer–PFM system (all tie points excluding those pedant polymer–PFM tie points) are call effective tie points in this article. The increase in tie point density is due to the creation of polymer–PFM tie points. The fractions of polymer–polymer and polymer–PFM tie points are ρ_1/ρ'_2 and $1 - (\rho_1/\rho'_2)$, respectively. If a polymer–polymer tie point is selected, the chain length of the connected primary molecules (next generation) can again be determined from Eq. (3). If, instead, a polymer–PFM tie point is selected, then the number of polymer molecules connected to this PFM molecule must be determined. The average number of polymer–PFM tie points on each PFM molecule, s, can be obtained experimentally. Let P_0, P_1, P_2 and P_3 be the probabilities that a tri-functional monomer molecule has connected to zero, one, two or three polymer molecules, respectively. It follows:

$$0 \times P_0 + 1 \times P_1 + 2 \times P_2 + 3 \times P_3 = s \qquad (5)$$

Since the probability that any one of the functional groups in a PFM has reacted, p, is the same for all functional groups, the probability, P_0, P_1, P_2, P_3 is given by a binomial distribution:

$$P_j = \binom{3}{j} p^j (1 - p)^{3-j} \qquad (6)$$

By using Eq. (5), p, and thus P_0, P_1, P_2 and P_3 can be solved easily. The equation required to calculate the probabilities for the PFM molecule on the selected polymer–PFM tie point to be connected to one, two or three polymer molecules is

$$P_C(n) = \binom{2}{n-1} p^{n-1} (1 - p)^{3-n} \qquad (7)$$

where n can be either 1, 2 or 3. If there are more than one polymer molecules connected to this PFM molecule, the chain length of the connected primary molecules (next generation) can again be determined from Eq. (3). These procedures are reiterated until all primary polymer molecules fail to be connected to the next generation. The simulation algorithm is depicted in Fig. 1. Noted that the above algorithm is not restricted to treating the MWD problem of polymer–trifunctional monomer systems. It can be easily
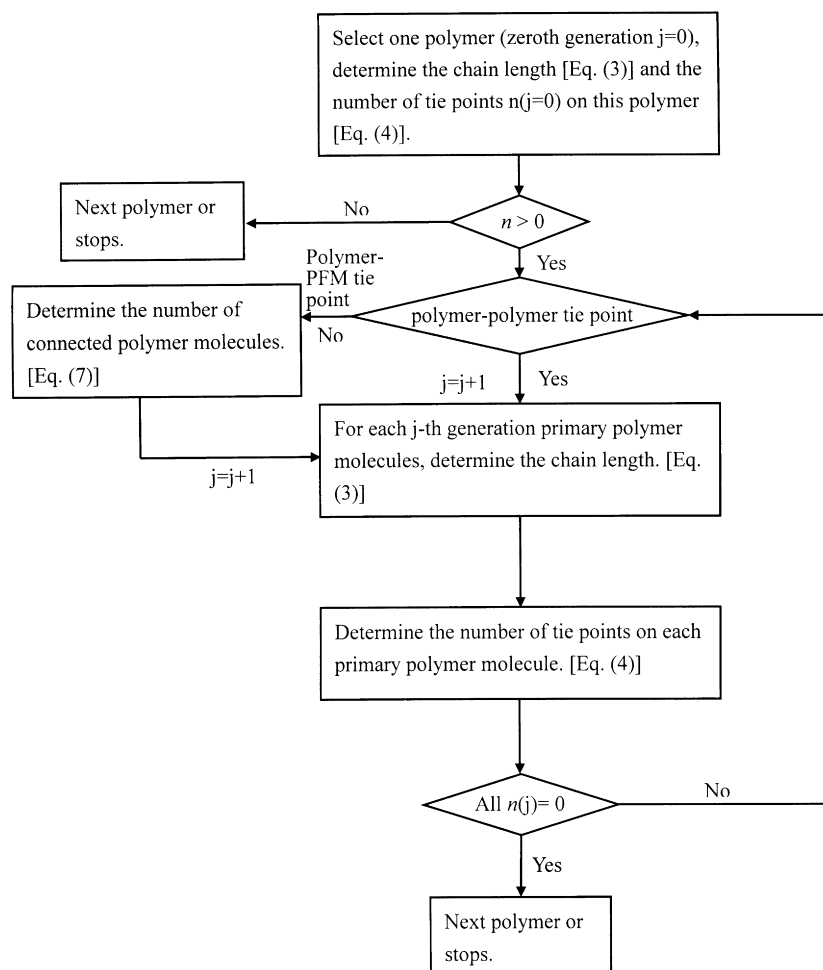
Fig. 1. The algorithm for the random crosslinking in polymer–PFM systems based on the Monte Carlo sampling technique.

adapted to treat more general conditions, where arbitrary PFM molecules with any specific functional groups are used, as long as all of the parameters needed in the simulation can be obtained.

4. Results and discussion

4.1. MWD for a polymer with a narrow initial distribution

The first condition we examined involved a polymer whose initial MWD was very sharp with a polydispersity index $\overline{M}_w/\overline{M}_n = 1.005$. The initial MWD can be described by Eq. (3), with $\sigma = 200$ and $u = 200$. The equivalent chain length of the trifunctional monomer molecule was 20. The crosslinking densities for the homopolymer and for the polymer–PFM systems are both equal to 5×10^{-3}. The fraction of polymer–PFM crosslink points is 0.1; the average number of polymer–PFM tie points on each PFM molecule s is equal to 1. The calculated value of the probability that any one of the function groups has reacted, p, is 1/3. Fig. 2 shows the comparison of MWD between polymers with and
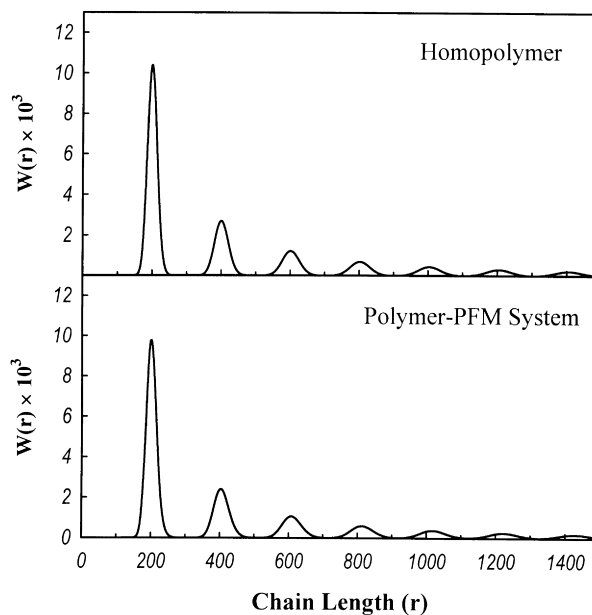

Fig. 2. Molecular weight distributions at a crosslinking density of $\rho = 5 \times 10^{-3}$ for a homopolymer and for a polymer–PFM system, both with a initial $\overline{M}_w/\overline{M}_n = 1.005$.
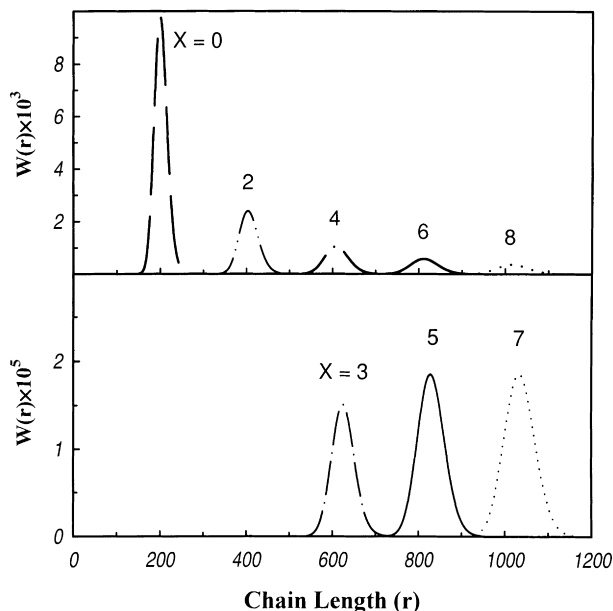
Fig. 3. Fractional molecular weight distributions in a polymer–PFM system (initial $\overline{M}_w/\overline{M}_n = 1.005$) for polymers containing 0, 2, 3, 4, 5, 6, 7, and 8 effective tie points.

Fig. 4. Fractional molecular weight distributions in a polymer–PFM system (initial $\overline{M}_w/\overline{M}_n = 1.005$) for polymers containing 0, 1, 2, 3 and 4 PFM molecules.

without the presence of PFM molecules at the same cross-linking density. It shows the existence of a multimodal distribution in both systems. Let us use X to denote the number of effective tie points in a polymer chain. For the system of polymers without PFM molecules, each peak corresponds to the fractional MWD containing $0, 1, 2, 3, \cdots$ crosslinkages ($X = 0, 2, 4, 6, \cdots$). The acme of each peak is located at chain lengths of the multiples of 200, which manifests that each peak corresponds to the combination of $1, 2, 3, 4, \cdots$ primary polymers. With the introduction of trifunctional monomer molecules, the positions of each peak shifted. The shift in the peak position is, of course, due to the increase in molecular weight through the incorporation of PFM molecules. The value of the molecular weight distribution density function, $W(r)$, for each peak for the polymer–PFM system was lower than the value for each corresponding peak for the system without PFM molecules. Or more exactly, the area under the homopolymer distribution peaks is greater than that under the polymer–PFM peaks. This was due to the higher gel fraction in the polymer–PFM system, of which the gel point is at a crosslinking density of 4.91×10^{-3} (see Table 2). In comparison, the gel point of the homopolymer system is at 4.98×10^{-3}. The introduction of PFM molecules also makes the distribution peaks broader, and the higher the molecular weight, the broader the peak.

The MWD for the polymers is a summation of the fractional distributions for the polymers with $X = 0, 2, 3, 4, \cdots$. Fig. 3 shows the fractional MWD for polymers with $X = 0, 2, 3, 4, 5, 6, 7$ and 8. It is clear that the first two peaks are exactly the first two peaks in the overall MWD for the polymer–PFM system in Fig. 2; while the third MWD
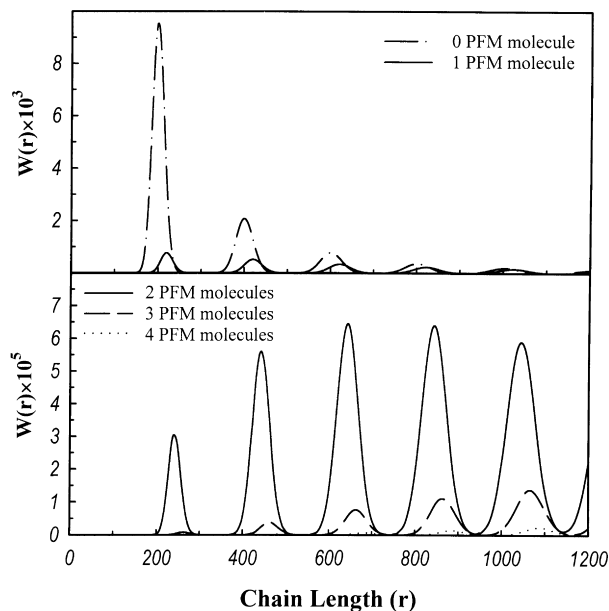
peak in Fig. 2 is a summation of the fractional distributions for $X = 3$ and $X = 4$. $X = 3$ distribution peak corresponds to the polymer fraction containing exactly one tri-connected PFM molecule. Actually, all $X = 3$, $X = 5$, and $X = 7$ distribution peaks correspond to the polymer fractions containing exactly one tri-connected PFM molecule. Because the fraction of polymer–PFM crosslink points is only 10% of the total crosslink points, the fraction of the polymers containing tri-connected PFM molecules is very low. The values for the fractional MWD for $X = 3, 5, 7$ are significantly lower than those for $X = 0, 2, 4, 5$ and 8. It is also worth mentioning that the fractional distribution with $X = 6$ should also consisted one more peak around $r = 1000$, which is the fractional distribution for polymer containing exactly two tri-connected PFM molecules. The fraction is too small to be recognized. For polymers with a high number of X, the distribution becomes much more complex, but with a vanishing fraction. In summary, we can easily identify each peak in the overall MWD as polymer fractions containing $1, 2, 3, \ldots$ primary polymers. But it becomes more difficult when it comes to identify each peak in terms of the number of crosslink points a polymer molecule contains for the polymer–PFM system.

One can also consider the MWD for the polymers as a summation of the fractional distributions for the polymers containing $0, 1, 2, 3, 4, \ldots$ PFM molecules, as portrayed in Fig. 4. For the fractional distribution for the polymers containing zero PFM molecule, the acmes are located at multiples of 200. Each peak decreases in size with increasing chain length. It is possible for a polymer with a high molecular weight to contain no PFM molecule. However, the higher the molecular weight, the less probable that no
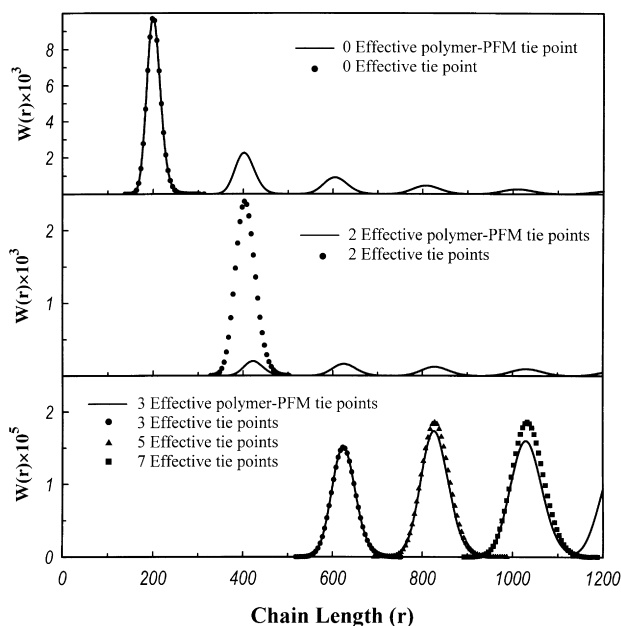
Fig. 5. Cross-comparison between fractional distribution pairs containing 0, 2, 3, 5, 7 effective tie points and 0, 2, 3 effective polymer–PFM tie points (initial $\overline{M}_w/\overline{M}_n = 1.005$).

polymer–PFM tie point exists in the polymer. The distribution peaks for polymers containing one PFM molecule center, accordingly, at the multiples of 200 plus the equivalent chain length of a single PFM molecule. It is also interesting to note that the fractional distributions become more uniform for the polymer molecules that contain more PFM molecules.

The simulation enabled us to examine the constitution of each fractional distribution. Fig. 5 is the cross-comparison between the distributions for polymers containing various numbers of effective tie points, X, and effective polymer–PFM tie points. In Fig. 5, we see that the fractional distribution for $X = 0$ is equal to the first distribution peak for polymers containing zero effective polymer–PFM tie point. By comparing the fractional MWD containing zero effective polymer–PFM tie point with the overall MWD in Fig. 2, we also see the most of the sol molecules do not contain any effective polymer–PFM tie point. For the next distribution pairs for the polymers with $X = 2$ and for the polymers containing two effective polymer–PEM tie points, the fraction of the latter is much smaller but its distribution peaks are of similar size and span over a long chain length. It

is also interesting to see that the fractional distribution peaks for polymers containing three effective polymer–PFM tie points almost coincide with the summation of the fractional distributions for polymers with $X = 3, 5, 7, \dots$ The deviation becomes greater as X increases. The fractional distribution for polymers with $X = 3$ is exactly equal to the first peak in the distribution for three effective polymer–PFM tie points, which is for the polymers containing one tri-connected PFM molecule and containing no other effective tie point. The fractional distribution for polymers with $X = 5$ is nearly equal to the second distribution peak for the polymers containing three effective polymer–PFM tie points; however, for $X = 5$, the polymers could also contain five effective polymer–PFM tie points. For $X = 7$, the polymers could contain 3, 5, 7 effective polymer–PFM tie points, with the largest fraction being that for polymers containing three effective polymer–PFM tie points.

4.2. MWD for an LDPE–TAC system

A commercial LDPE with a polydispersity index $\overline{M}_w/\overline{M}_n = 6$, was used for the simulation. The initial MWD was assumed to follow Eq. (3), with $\sigma = 0.2$ and $u = 2571.4$. 1 wt.% of TAC was added as a crosslinking coagent. The parameters needed in the simulation are listed in Table 1. They were obtained from the gel content experiments and then calculated according to the explanations in Appendix A. It can be seen that the addition of TAC is very effective in promoting the crosslinking density. A 72% increase in crosslinking density was observed. However, only 51% of the PFM molcules took part in the crosslinking reaction. Fig. 6 shows the MWD for this LDPE–TAC system at various degrees of crosslinking reaction. When the degree of reaction exceeds the gel point, the MWD curves correspond to those for the sol fraction. In the beginning of a crosslinking reaction, the molecular weight distribution in the long molecule chain portion, increases at the expense of low molecular weight portion. The MWD curve for the crosslinking density at gelation point possesses the longest tail. After gelation, the molecular weight decreases as the longer chains attach to the gel molecule, and the distribution tail becomes shorter. The molecular weight for the residual sol fraction becomes lower and the distribution becomes narrower as the crosslinking density increases. After the completion of the crosslinking reaction, only small

Table 1
Parameters used in the simulation for the LDPE–TAC system

α[a]	ρ_1	ρ_2	ρ_2'	s	P_0	P_1	P_2	P_3
0.10	1.95×10^{-5}	2.10×10^{-5}	5.62×10^{-5}	0.064	0.9373	0.0614	0.0013	0.0000
0.27[b]	5.30×10^{-5}	6.43×10^{-5}	1.53×10^{-4}	0.174	0.8355	0.1548	0.0096	0.0002
0.50	9.75×10^{-5}	1.35×10^{-4}	2.81×10^{-4}	0.321	0.7125	0.2557	0.0306	0.0012
1.00	1.95×10^{-4}	3.35×10^{-4}	5.62×10^{-4}	0.641	0.4862	0.3964	0.1077	0.0098

[a] α is the extent of reaction.
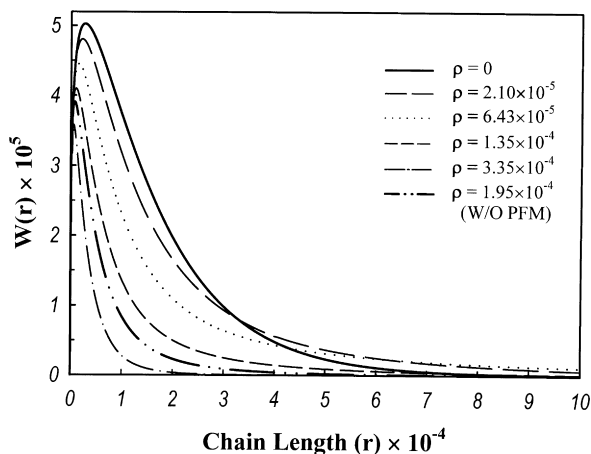[b] The onset of gelation.

Fig. 6. Molecular weight distributions at various levels of crosslinking density for the commercial LDPE–TAC system. A MWD curve for LDPE which crosslinks without TAC ($\rho = 1.95 \times 10^{-4}$) at the same conditions is included for a comparison. Notice that curves for $\rho > 6.43 \times 10^{-5}$ are the MWD for sol molecules.

molecules remain in the residual sol fraction. It is also very important to note that, although gelation occurs at the reaction extent $\alpha = 27\%$ ($\rho = 6.43 \times 10^{-5}$, see Table 2), the distribution curve for the reaction extent $\alpha = 10\%$ ($\rho = 2.10 \times 10^{-5}$) shows that very large molecules exist long before the reaction reaches the gel point. These very large molecules affect the rheological properties of the polymer profoundly. In processing these reaction systems, a minor premature crosslinking reaction (scorch) could cause catastrophic damage to the equipment. The MWD curve for the residual sol fraction for the crosslinking LDPE system is included in Fig. 6 for a comparison (the $\rho = 1.95 \times 10^{-4}$ curve). It can be seen that in the residual sol fraction, the LDPE–TAC system contains much smaller polymer molecules than the LDPE system does after the completion of crosslinking reaction. And one can see also from Table 2 that gelation occurs at a lower crosslinking density when PFM molecules are added to a crosslinking system. This is because the introduction of tri-functional crosslinking coagents increases the branching probability for the polymer–PFM system. But since the concentration for the tri-connected PFM molecules are low (only 0.12% of the reacted PFMs whose all three functional groups have reacted, as calculated from Table 1), the crosslinking densities for the incipient network formation for both systems are not far apart.
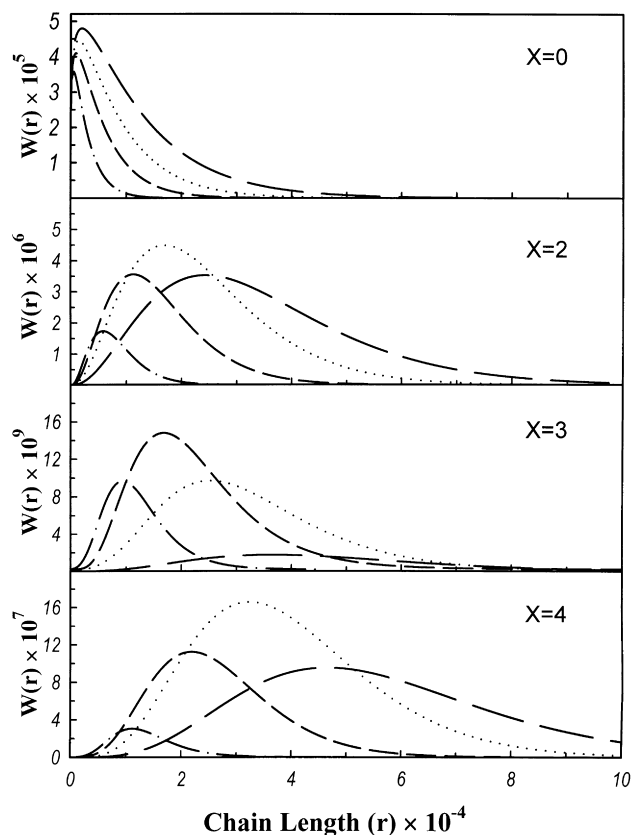

Fig. 7. Fractional MWDs in the LDPE–TAC system at various level of crosslinking density for polymers containing $X = 0, 2, 3, 4$ effective tie points. The symbols are the same as those used in Fig. 6.

Fig. 7 shows the fractional MWD ($W_x(r)$) for polymers with $X = 0, 2, 3$, and 4. It can seen from this figure that, throughout the crosslinking reaction, the proportion of polymers with $X = 0$ remains highest in the sol, as compared with each individual proportion with $X = 2, 3\ldots$. Also from Table 2, the fraction of sol molecules that do not react (Φ_o^{sol}, which is not equal to the $X = 0$ fraction) decreases first, reaches the lowest value at the gel point, and then increases again. At the end of reaction, 50% of the sol molecules remain intact throughout the crosslinking reaction. The $X = 3$ fractions are considerably lower than the other fractions shown in Fig. 7. This is, of course, due to the low concentration of tri-connected PFM molecules. If we discount those fractions with odd-numbered X, the fraction of molecules with higher number of effective tie points (X)

Table 2
Gel point prediction

	Polymer with a narrow initial distribution		Commercial LDPE	
	Without PFM	With PFM	Without PFM	With PFM
ρ[a] (theoretical)	4.98×10^{-3}	NA	6.48×10^{-5}	NA
ρ (simulated)	4.99×10^{-3}	4.91×10^{-3}	6.48×10^{-5}	6.43×10^{-5}

[a] The crosslinking density at gel point is given by $\rho = \sigma/\{(\sigma + 1)u\}$ [25].

Table 3
Simulated results for LDPE–TAC system

ρ	ρ_c	Φ_o^{sol}	$\displaystyle \int_{r=0}^{\infty} W_{c=0}(r) \Big/ \sum_{X=0}^{\infty} \int_{r=0}^{\infty} W_X(r)$	$\displaystyle \sum_{X=0}^{6} \int_{r=0}^{\infty} W_X(r) \Big/ \sum_{X=0}^{\infty} \int_{r=0}^{\infty} W_X(r)$	$\rho_r^{sol}\big|_{r\to\infty}$	ρ^{gel}	$\rho_{c,r}^{sol}\big|_{r\to\infty}$	ρ_c^{gel}
2.10×10^{-5}	3.60×10^{-5}	0.521	0.580	0.964	7.71×10^{-5}	–	3.82×10^{-5}	–
6.43×10^{-5}	9.43×10^{-5}	0.271	0.295	0.713	1.29×10^{-5}	–	9.98×10^{-5}	–
1.35×10^{-4}	1.65×10^{-4}	0.357	0.376	0.915	1.81×10^{-4}	1.96×10^{-4}	1.72×10^{-4}	1.76×10^{-4}
3.35×10^{-4}	2.94×10^{-4}	0.500	0.510	0.972	2.65×10^{-4}	3.89×10^{-4}	2.92×10^{-4}	3.06×10^{-4}

decreases as X increases. Polymers with higher number of effective tie points tend to have higher molecular weights, but their fractional MWD is broader. In the beginning of crosslinking reaction, only a small fraction of molecules with higher molecular weights have the chance to crosslink, and the resultant molecules will have very high molecular weights. At a constant X, the fractional distribution shifts toward smaller molecules as the crosslinking density increases and smaller molecules have more chances to crosslink. Past the gel point, long chain molecules begin to gel; and most sol molecules contain only a low number of effective tie points at a high level of crosslinking density. From Table 3, it is clear to see that, only in the vicinity of the

gel point ($\rho = 6.43\times10^{-5}$), molecules with higher number of effective tie points (e.g. $X > 6$) will take up a higher fraction (29%) of the sol molecules. When the crosslinking density is much lower or much higher than the density at the gel point, most molecules in the sol contain only a couple of effective tie points.

Fig. 8 shows the fractional distribution for polymers containing 0, 1, 2 and 3 PFM molecules. Similar trends as those revealed in Fig. 7 can be found in this figure. But the distributions are more uniform for polymers containing various numbers of PFM molecules. Most sol molecules contain only a low number of PFM molecules, except in the vicinity of the gel point. Actually, we can also see from the $\int_{r=0}^{\infty} W_{c=0}(r)/\sum_{X=0}^{\infty}\int_{r=0}^{\infty} W_X(r)$ column in Table 3 that a large portion of sol molecules does no contain any PFM molecule.

One can also use this simulation to obtain the average crosslinking density in a polymer chain, ρ_r, as a function of chain length and the result is shown in Fig. 9. The value of ρ_r increases with increasing chain length r and increasing overall crosslinking density ρ and becomes asymptotically constant as r becomes extremely high. This asymptotic value of ρ_r, denoted as $\rho_r^{sol}\big|_{r\to\infty}$, is very important for the
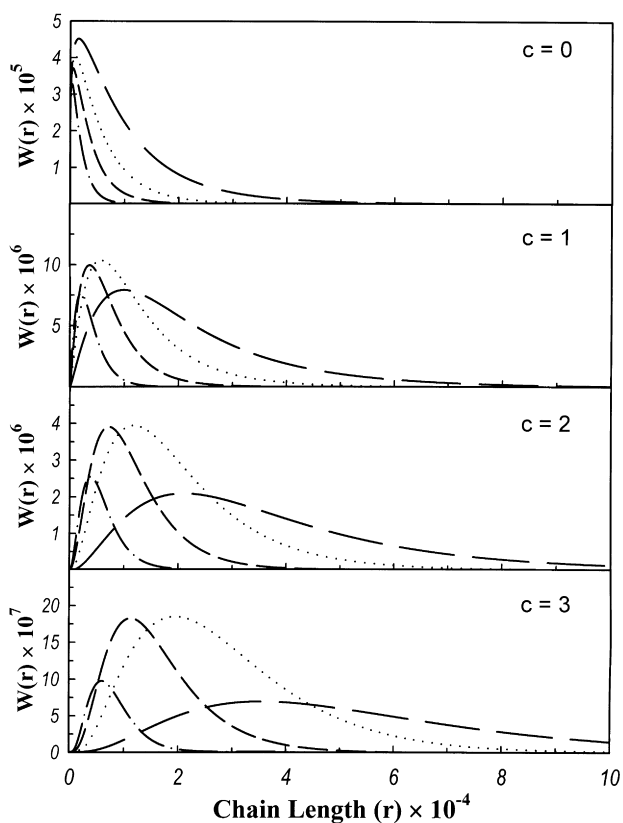

Fig. 8. Fractional MWDs in the LDPE–TAC system at various level of crosslinking density for polymers containing $c = 0$, 1, 2, 3 PFM molecules. The symbols are the same as those used in Fig. 6.
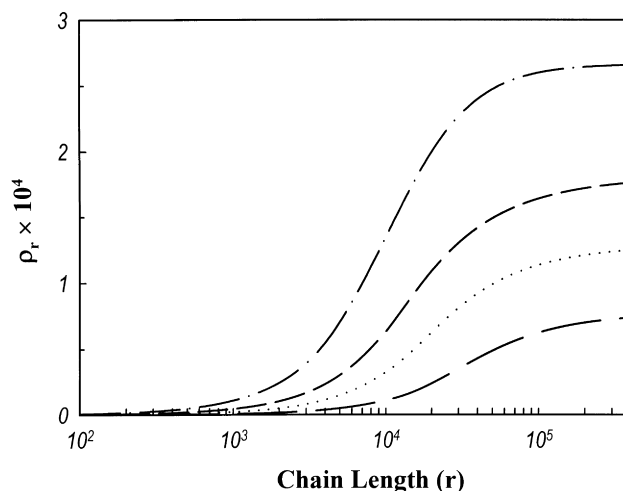

Fig. 9. Average crosslinking density in a polymer chain, ρ_r, as a function of chain length at various level of crosslinking density in the LDPE–TAC system. The symbols are the same as those used in Fig. 6.
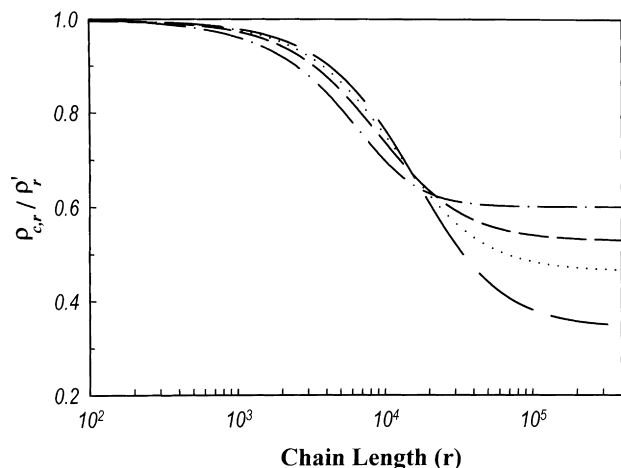
Fig. 10. $\rho_{c,r}/\rho_r'$ as a function of chain length at various level of crosslinking density in the LDPE–TAC system. The symbols are the same as those used in Fig. 6.

interpretation of the elusion curve obtained in a gel permeation chromatography measurement [11].

With the help of the Monte Carlo simulation method, $\rho_r^{\text{sol}}|_{r\rightarrow\infty}$ can be effectively estimated for the reacting polymer–PFM system. It is found in Table 3 that, in the pre-gelation period or when the gel content is low, the value of $\rho_r^{\text{sol}}|_{r\rightarrow\infty}$ is higher than the value of the overall crosslinking density. As the gel content increases to a certain degree, since the highly crosslinked molecules have gelled, the value of $\rho_r^{\text{sol}}|_{r\rightarrow\infty}$ is lower than the overall crosslinking density. The relationship between $\rho_r^{\text{sol}}|_{r\rightarrow\infty}$ and ρ for a random crosslinking reaction without the presence of PFM molecules is known at gel point, namely, $\rho_r^{\text{sol}}|_{r\rightarrow\infty} = 2\rho$. It is interesting to find that this relationship also holds when PFM molecules are involved in the random crosslinking reaction. The crosslinking density in the gel, ρ^{gel}, can be easily calculated with known distributions of $W(r)$ and ρ_r and the results are listed in Table 3. The value of ρ^{gel} is always higher than both the value of $\rho_r^{\text{sol}}|_{r\rightarrow\infty}$ and ρ. As gel content increases, the value of ρ^{gel} approaches the value of ρ. For random crosslinking of a polymer without the presence of PFM molecules, the relationship among ρ^{gel}, ρ and gel content w^{gel} is given by

$$\rho^{\text{gel}} = \rho(2 - w^{\text{gel}}) \tag{8}$$

This relationship also holds for the random crosslinking of a polymer–PFM system.

For the random crosslinking of a polymer–PFM system, in addition to the crosslinking density distribution, the PFM molecule density distribution, defined as the number of PFM molecules per structural unit in a polymer chain and denoted as $\rho_{c,r}$, is also an important aspect that must be considered. The ratio between $\rho_{c,r}$ and the tie point density in a polymer chain, denoted as ρ_r', provide us with more insight into the molecular constitution and is shown in Fig. 10. For all four crosslinking densities, the value of $\rho_{c,r}/\rho_r'$ decreases with

increasing chain length r and becomes asymptotically constant as r becomes extremely high. The asymptotic value of $\rho_{c,r}$, denoted as $\rho_{c,r}^{\text{sol}}|_{r\rightarrow\infty}$, for each crosslinking density is also listed in Table 3. For the low chain length portion of the curves, the value of $\rho_{c,r}/\rho_r'$ is close to unity, which indicates that the tie points are mainly polymer–PFM ones. As the chain length increases, more polymer–polymer or polymer–PFM–polymer tie points are present and the value of $\rho_{c,r}/\rho_r'$ decreases. Notice that as ρ increases, the ratio between the values of overall PFM density, ρ_c, and ρ decreases. This is due to more PFM molecules connecting with more than one polymer molecule, and the PFM molecules crosslink more effectively. However, the asymptotic value of $\rho_{c,r}/\rho_r'$ increases with increasing ρ. This indicates that, since more PFM molecules have reacted as the extent of reaction increases, very large sol molecules contain higher proportion of pedant PFM molecules. Those molecules with highly connected PFM molecules have gelled already. We also see a similar trend in $\rho_{c,r}^{\text{sol}}|_{r\rightarrow\infty}$, as exhibited in $\rho_r^{\text{sol}}|_{r\rightarrow\infty}$, but the value of $\rho_c^{\text{sol}}|_{r\rightarrow\infty}$ is very close to the value of the overall PFM density, ρ_c. The value of ρ_c^{gel} is always higher than both the values of $\rho_{c,r}^{\text{sol}}|_{r\rightarrow\infty}$ and ρ_c. All these evidences indicate that the average number of polymer–PFM crosslink points for each PFM molecule in the gel fraction is higher than that in the sol fraction.

5. Conclusions

An algorithm for the Monte Carlo simulation for the random crosslinking in polymer–PFM systems is proposed. A multimodal MWD is obtained for a polymer with an extremely narrow primary polymer molecule distribution. Each distribution peak corresponds to the crosslinking of $1, 2, 3, \ldots$ primary polymer molecules. The addition of PFM molecules makes the distribution peaks broader as compared to those without PFM molecules. The fractional distributions for polymers containing $0, 1, 2, 3, \ldots$ PFM molecules are also multimodal. By combining gel content experiments, this algorithm was applied to the study of the crosslinking behavior of a commercial LDPE–TAC system. Compared with the crosslinking LDPE system under the same condition, the LDPE–TAC system gels at a slightly lower level of crosslinking density. Except in the vicinity of the gel point, most molecules in the sol contain only a couple of effective tie points or PFM molecules. The crosslinking density for the sol molecules increases with increasing chain length. The values of crosslinking density in the gel, ρ^{gel}, are always greater than the value for the sol molecules with infinite chain length, $\rho_r^{\text{sol}}|_{r\rightarrow\infty}$. The tie points in the small sol molecules ($r < 1000$) are mostly polymer–PFM tie points. The PFM density distribution shows similar behavior as that exhibited for crosslinking density distribution. Throughout the crosslinking reaction, though, the values for the overall PFM density, ρ_c, the PFM density for the sol molecules with infinite chain length, $\rho_{c,r}^{\text{sol}}|_{r\rightarrow\infty}$, and

the PFM density in gel, ρ_c^{gel} are close to one another, with ρ_c^{gel} being always the highest among them.

Appendix A. Method for obtaining the needed parameters in the simulation

Let there be N_p segments (structural units) in the polymer system. After the crosslinking reaction, there are X_p polymer–polymer tie points in the homopolymer system. The crosslinking density is then

$$\rho_1 = \frac{X_p}{N_p} \tag{A1}$$

When N_C tri-functional monomer molecules are introduced into the system, additional X_T polymer–PFM tie points are created. Let N_0, N_1, N_2, N_3 be the number of PFM molecules in the system that have connected to 0, 1, 2, 3 polymer molecules, respectively. It follows

$$N_C = N_0 + N_1 + N_2 + N_3 \tag{A2}$$

and

$$X_T = X_P + N_1 + 2 \times N_2 + 3 \times N_3 \tag{A3}$$

and the overall tie point density becomes

$$\rho_2' = \frac{X_T}{N_P} \tag{A4}$$

Only those segments bearing PFM molecules which have connected to more than two polymer molecules can be counted as crosslinked segments. The number of crosslinked segments (effective tie points) then is

$$X_C = 2 \times N_2 + 3 \times N_3 \tag{A5}$$

The crosslinking density for the system with the presence of PFM molecules then becomes

$$\rho_2 = \frac{X_P + X_C}{N_P} \tag{A6}$$

Define P_0, P_1, P_2 and P_3 as the probabilities that a trifunctional monomer molecule has connected to 0, 1, 2, 3 polymer molecules, respectively. Then

$$P_0 = \frac{N_0}{N_C}, \qquad P_1 = \frac{N_1}{N_C}, \qquad P_2 = \frac{N_2}{N_C}, \qquad P_3 = \frac{N_3}{N_C} \tag{A7}$$

It follows

$$P_0 + P_1 + P_2 + P_3 = 1 \tag{A8}$$

The average number of polymer–PFM tie points for each PFM molecules, s, can be calculated according to the following equation:

$$s = \frac{N_1 + 2N_2 + 3N_3}{N_C} = P_1 + 2P_2 + 3P_3 \tag{A9}$$

Assuming that the probability that any one of functional groups in a PFM has reacted, p is the same for all functional groups. Then the probability, P_0, P_1, P_2, P_3 is given by a binomial distribution:

$$P_j = \binom{3}{j} p^j (1-p)^{3-j} \tag{A10}$$

Combining Eq. (A1), (A5) and (A6), we have

$$2P_2 + 3P_3 = (\rho_2 - \rho_1) \times \left(\frac{N_P}{N_C} \right) \tag{A11}$$

Since N_P and N_C are known values for the system, ρ_1 and ρ_2 can be obtained from gel content experiments, p can be obtained by solving Eq. (A11). The experimental values for ρ_1 and ρ_2 are 1.95×10^{-4} and 3.35×10^{-4}, respectively.

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