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Microstructure evolution and simulation of copolymerization reaction using a percolation kinetic gelation model[☆]

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Abstract

A new kinetic gelation model that incorporates the kinetics of non-linear free radical copolymerization is presented. Copolymerization of bi- and tetrafunctional monomer mixtures is simulated to characterize kinetic effects on polymerization statistics and microstructures. An algorithm for random next step selection in a self-avoiding random walk and efficient mechanisms of component's mobility are introduced to improve the universality of the predictions by removing commonly occurring simulation deficiencies due to early trapping of radicals. The model has the capability to predict the onset of the sol–gel transition, and the effect of chemical composition on the transition point. It is shown that a better understanding of microstructure evolution during polymerization and chemical gelation is attained. Lastly, one important benefit of the simulation method is the ability to simulate very highly packed random chains or microgels within a polymer network. © 2001 Published by Elsevier Science Ltd.

Keywords: Kinetic gelation model; Microstructure; Percolation threshold

1. Introduction

During free radical copolymerization of a mixture of vinyl–divinyl monomers, the crosslinking reactions lead to the evolution of a three dimensional network. Kinetics [1,2] and statistical [3] models are commonly used to investigate the reaction mechanisms and microstructures.

Due to the random nature of growing macroradicals in the polymerization process, percolation theory is a very useful tool to describe such disordered systems [4,5]. The classical approach of percolation on the Caylee tree due to Flory [6] and Stockmayer [7] is regarded as the starting point in the theory of kinetic gelation model (KGM) which describes the chemistry of irreversible polymer gelation using a lattice model. The terminology of the theory was introduced by Broadbent and Hamersely [8].The polymer percolation model has been mainly used [3,4,9,10] to study the critical behavior near the gel point, where the assumption of a diffusion-limited process is likely to be accurate [9]. This behavior depends on the space dimensionality and not on the lattice geometry [10].

In the context of polymerization, a typical percolation model is a finite *d* dimensional lattice where each site is assumed to be occupied by a functional unit. The functionality number varies from zero (solvent or void), to one (initiator radical), two (usual vinylic monomer), and three or more (for example: divinylic monomer, crosslinking agent and some special chain transfer agent). Random connections are then initiated between the nearest neighbor sites to form a permanent or chemical bond.

Computer simulations based on percolation models describe polymers that undergo the self-avoiding random walks (SAW) on a lattice, to simulate the gelation process during polymerization of multifunctional monomers [11].

The first percolation model proposed by Manneville and de Seze [12], referred as the kinetic gelation model, has been modified by a variety of researchers [11–25]. They developed a computer model that took into account polymerization of a mixture of bi- and tetrafunctional monomers in absence of any solvent on a simple cubic lattice up to 32 sites in each direction. Extensive computer simulation studies of realistic models have been performed using KGM [11–15]. The effect of the initiator quantity and initiator decay kinetics [12–20], the addition of solvent [13–15,21], and the mobility of the components [19–21], were the early modification to KGM. Coniglio [22]

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developed a site-bond correlated percolation model to include the solvent effects. Most of studies have been restricted to static growth in the sense that the chemical constituents where immobile during the course of reaction. The mobility of the solvent, monomers and clusters have been considered in recent studies [19,23–25]. The species' mobility was considered to affect the trapping of radicals with no change in overall trends in the simulation. Furthermore, several authors used KGM to describe the irreversible gelation in vinyl/divinyl copolymerization in radical initiated [26] and light-induced processes [16,27].

The effect of inhomogeneity in the gelation and interaction between solvent and polymer [28] have been considered. Also there is a lot of interest in using this approach for example to study the phase transition and structural evolution of thermoreversible gels [28,29] and kinetics of living/controlled radical polymerization using the inferter technique [30].

It is important to note that the model used in this work is not a lattice model, but a percolation model. In the standard percolation model, many types of networks or lattices are used for space discretization. This is the first step in our model and may be considered as a lattice model, but subsequent steps are unrelated to those used in lattice models. The numerical values of all percolation quantities depend on the microscopic details of the system, such as its coordination number. But near the percolation threshold, most percolation quantities obey scaling laws that are largely insensitive to the network or lattice structure and other microscopic details. Even some characteristic exponents are completely universal, i.e. they are independent of the microscopic details of the system and depend only on the dimensionality of the system. Furthermore, the evolution of microstructure of the formed gel is largely insensitive to the network type. Thus we believe that the percolation model used in this work is a very suitable and powerful tool to predict the scaling behavior of gelation processes and we consider the percolation model in a different category rather than lattice models.

In this paper, Monte Carlo simulations using kinetic gelation model are performed on a simple cubic lattice with periodic boundary conditions to investigate microstructural evolution during copolymerization of a mixture of multifunctional monomers. For this purpose, we introduce an algorithm to overcome the trapping of radicals in the early stages of reaction. Section 2 describes the computational model, and defines the model properties, and Section 3 presents the results of our computer simulations.

2. Simulation

The model used in this work is based on the Flory–Stockmayer [6,7] theory, which is identical to percolation on a Caylee tree (Bathe lattice). Manneville and de Seze [12] developed one of the first percolation models (KGM) to examine free radical polymerization. This model was used to study the structural evolution of polymer networks that form during the polymerization of multifunctional monomers.

We simulate free radical copolymerization of a mixture of vinylic (bifunctional) and divinylic (tetrafunctional) monomers by using a modified version of KGM. Monomers and initiators are considered as sites on a discrete simple cubic lattice with L^3 sites. Any given component is randomly distributed on the lattice sites and periodic boundary conditions are implemented on lattice faces to eliminate edge effects. The coordination number of a simple cubic lattice is six, which means that each site has six nearest neighbors, however due to previous bond in each chain head, each site has at most five possible neighbor sites to form a bond. The next step is to initiate the growing process. This is done by randomly placing a free radical (active center) on a monomer site. Each initiator molecule is considered as two near neighbor sites and decomposes into two radicals based on the first order rate decomposition [19].

To form a chemical or permanent bond, each radical recognizes the capability of each nearest neighbor for reaction; if there is at least one monomer or another active site, the reaction takes place. If there is more than one accessible site for the reaction, one of them is randomly selected to form a bond, and finally if there is no site the radical will be trapped.

By defining a random number between zero and n, an active site selects one of these neighbors. Because each site occupies no more than one monomer, the path of the active site will be a self-avoiding random walk on a simple cubic lattice. After forming a bond, the active center transfers to the reacted site. In each MCS, this process will be done by all of the active centers.

To determine polymerization quantities (i.e. reacted sites), the Hoshen–Kopelman algorithm [31] is used. In this algorithm, all monomers in the percolation network are labeled in such way that those with same labels belong to same cluster. When a bond is formed, the reacted site gets the active site label. At each time step, the total number of reacted sites is determined and considered as the extent of reaction. The number of formed bonds in three directions is measured in consecutive time intervals to assure directional randomness of bond formation.

To improve the efficiency of the KGM, we use in this work, two important modifications that we presented in previous work [32]: (i) successive steps evaluation of a growing radical and (ii) mobility of components in the lattice. Both improvements allow to model late stage phenomena, when few monomers remain in the lattice.

One of the most important problems in KGM is the trapping of a radical, when none of the nearest neighbors has capability to react, so a radical is trapped. To avoid or at least delay this problem, we used the following algorithm.

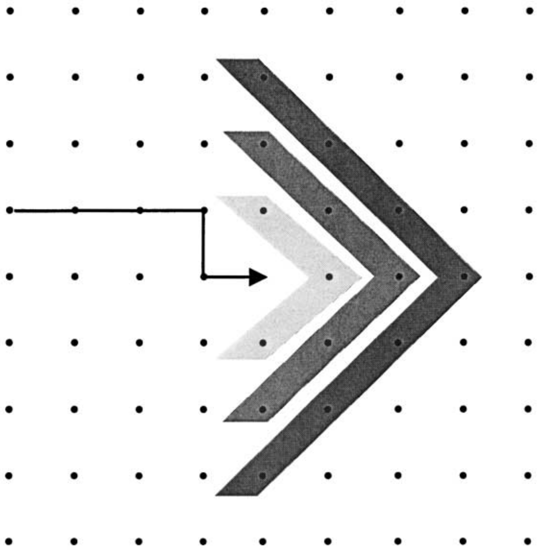

Fig. 1. Schematic of the geometry of successive layers of neighboring sites. ░: first accessible layer (first neighboring sites); ▒: second accessible layer (second neighboring sites); ▓: third accessible layer (third neighboring sites).

At each step time, each active site recognizes and evaluates the capability of its future successive sites for reaction (or the future steps in a walk) as the first nearest-neighbor sites (layer of first step of walker), the second nearest-neighbor (second layer) and so on, as shown in Fig. 1. The number of total accessible sites for each of the six (or actually five) directions in all consequent layers is determined and the walker selects the nearest site that has the highest number of accessible sites. This method reduces the trapping process even in the last stages of reaction, and adapts according to the diffusion of radicals. The second improvement of this model is the ability of all the species in the reaction to move. We categorize the movements as single-site and multiple-site movements. In single-site movement, the monomers, solvent, newborn radicals and voids are allowed to exchange their positions with each other. All movements are in such a way that monomers move in one of the randomly selected directions to neighboring sites. In multiple-site movements, we consider three types of movements: (1) the active center in a macroradical head moves to a neighbor site and all the reacted monomers in the chain follow its path (reptation), (2) a cluster or chain is allowed to move in one of the six directions (central-mass or translational diffusion [29]), (3) one or more sections in a polymer cluster or chain are allowed to exchange their positions with surrounding sites (segmental diffusion).

All of these movements are restricted to one lattice unit displacement, and more importantly, all bonds are preserved and the polymer configuration remains almost unchanged. The main goal of these movements is to delay the trapping of radicals and also to allow trapped radicals to become active in later steps. Thus all movements are done in such a way that the total number of accessible sites for an active site in each MCS increases.

2.1. Model properties

The quantities and variables of the model are as follows. p is the extent of reaction defined as the total number of reacted sites that belong to the clusters normalized by total number sites in lattice; G, the gel fraction (order parameter of system) is defined as:

$$G = \frac{\phi_G}{\phi_S + \phi_G} = \langle |G| \rangle = \frac{n_G}{N} \tag{1}$$

where ϕ_G is the fraction of the infinite cluster or gel phase and ϕ_S is the fraction of the finite clusters in sol phase, i.e. $\phi_G = n_G/(n_S + n_G)$ and $\phi_S = n_S/(n_S + n_G)$, where n_G and n_S are the number of monomers in gel and sol phases, respectively, and $n_G + n_S = N$ is the total number of polymer unit; $\mathrm{DP_w}$ is the weight-average degree of polymerization, which is the ratio of the second moment to the first moment of the mass distribution, i.e.

$$\mathrm{DP_w} = \frac{\sum_s n_s s^2}{\sum_s n_s s} \tag{2}$$

where n_s is the number of clusters containing s monomers; ξ is the correlation length (z-average of the radius of gyration [29]), which is the measure of the spatial extension of the connectivity, is given by:

$$\xi^2 = \frac{\sum s^2 n_s R_s^2}{\sum s^2 n_s} \tag{3}$$

where R_s is the radius of gyration defined as:

$$R_s^2 = \frac{1}{s}\left\langle \sum_{i=1}^{s} (r_i - r_0)^2 \right\rangle \tag{4}$$

with

$$r_0 = \sum_{i=1}^{s} \frac{r_i}{s} \tag{5}$$

and r_i denotes the position of ith connected site. R_s is also given by a power law relation:

$$R_s \sim s^{-1/D_e} \tag{6}$$

where D_e is interpreted as the fractal dimension of the infinite cluster.

These quantities are monitored at each MCS time. Since we used the concept of percolation on a lattice, it is expected to see a percolation threshold or a scaling relation such as:

$$\mathrm{DP_w} \sim |p - p_c|^{\gamma} \tag{7}$$

This relation is used as p approaches p_c, the threshold value, but it is possible to extend its applicability far from this point. Different exponents were determined and even the universality of them is controversial [4,5,10,21,28,29].

During each simulation, the information history of all components and clusters in the lattice is stored for future use. The whole procedure of distribution and growth is performed N times and a statistical averages is taken. We consider 50–100 runs depending on the fluctuations observed; however, for large lattices increasing N does not affect the accuracy of the results [24].

3. Results and discussion

We consider a simple cubic lattice of size $L = 100$ in which initially all sites are considered as vinylic (difunctional) monomers (functionality of 2). The initial initiator concentration is 1% on a mole basis — very common in bulk polymerization — and is introduced randomly with first order kinetics. A specified number of tetrafunctional monomers in accordance with tetrafunctional monomer concentration (f4) that have four functional groups (functionality of 4) are randomly distributed in the lattice, instead of monomer sites. Since the functionality of these sites is four, they have the capability of forming bonds in four directions. When an active site selects a tetrafunctional monomer in a polymer chain, a crosslinking reaction takes places, or a branch or side-branch is formed and the two chains with different labels unit together and get the same label. During the reaction, this process will be repeated and thus the number of junctions or branches increases. Gradually large chains with side branches react with each other and at some point, a very large cluster called the infinite cluster or gel phase forms and spans through the whole system. The system also consists of small clusters that are not so large, known as the sol phase. Thus at a specific conversion p, there is a sudden change from a high number of small clusters to one (or more) very large cluster along with a lower number of small clusters. In a real system of such monomers, at the sol–gel transition, the appearance of the large cluster or insoluble gel phase takes place. This critical value of monomer conversion is called the threshold value, p_c. So far, percolation network models used [11–25] are considered the best simulation tool for characterizing chemical gelation. The transition value p_c depends on the chemical nature of system (i.e. concentration of tetrafunctional monomers) but the power law scaling relation is applicable [4,5,16,23,24]. As the reaction proceeds, the polymerization quantities and the microstructure of gel phase, such as entangled chains, loops, pendant double bonds pendant chains, can be distinguished and characterized.

Fig. 2 shows the conversion of monomers p, as a function of Monte Carlo step time, for six increasing tetrafunctional monomer concentration (f4), and 1% initiator (these conditions are the same for all figures unless stated). The results show that the conversion profiles are weak functions of tetrafunctional monomer concentration. The conversion curves grow with the same trend to a final value, close to 95% of the total monomer sites. Fig. 3 shows the weight-average degree of polymerization of the sol phase (excluded infinite cluster) for the same system. The figure shows a pulse for each concentration level, whose amplitude and position (in p space) decrease as the concentration of the tetrafunctional monomer increases. This effect is due to the fact that at low concentration of tetrafunctional monomers, the number of crosslinked sites or microgels is lower than the number of chains so that the weight-average degree of polymerization, DP_w increases. At the higher concentration of tetrafunctional monomers, the largest cluster forms and the rest of the chains are not very long and the weight-average degree of polymerization decreases. Fig. 4 shows the gel

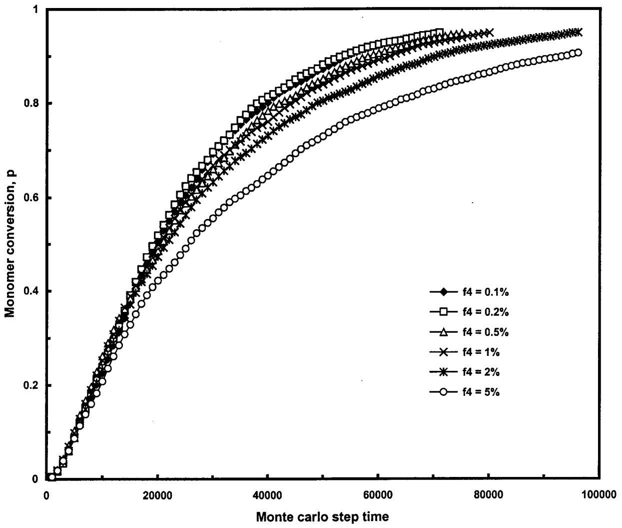

Fig. 2. Monomer conversion p, as a function of Monte Carlo step time for tetrafunctional monomer concentration, f4: 0.1, 0.2, 0.5, 1, 2 and 5%.

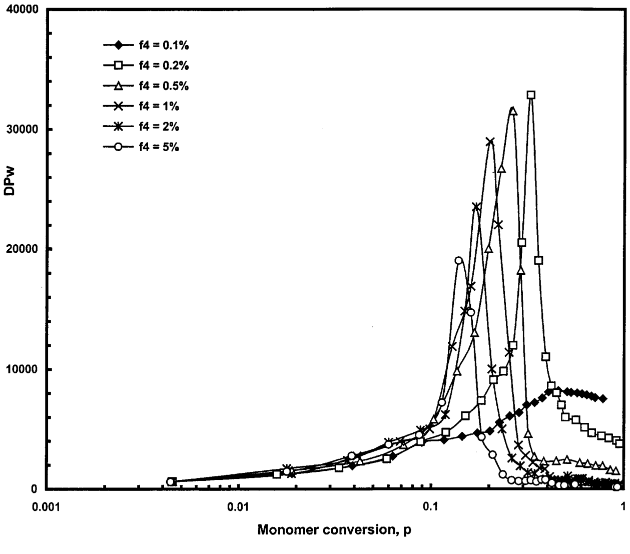

Fig. 3. Weight-average degree of polymerization DP_w, as a function of monomer conversion for tetrafunctional monomer concentration, f4: 0.1, 0.2, 0.5, 1, 2 and 5%.

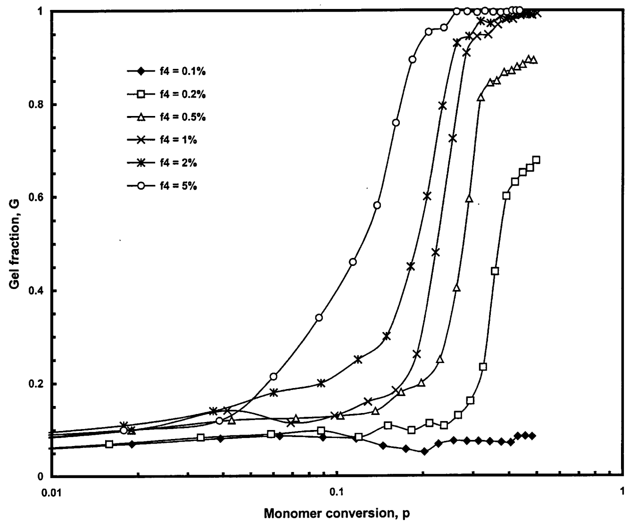

Fig. 4. Gel fraction G, as a function of monomer conversion for tetrafunctional monomer concentration, f4; 0.1, 0.2, 0.5, 1, 2 and 5%.

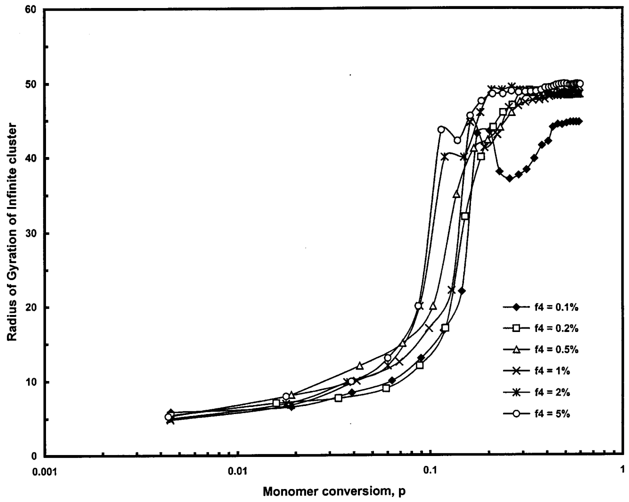

Fig. 6. Radius of gyration of the infinite cluster R_s, as a function of monomer conversion for tetrafunctional monomer concentration, f4: 0.1, 0.2, 0.5, 1, 2 and 5%.

fraction of polymer as a function of monomer conversion. The figure shows that at low concentration of tetrafunctional monomers, no gel forms, and as this concentration increases, more gel, and at earlier stages of the reaction, appear. Fig. 5 shows the conversion at gel point or the critical conversion p_c as a function of tetrafunctional monomer concentration. The figure shows the same observed trend in experimental results [33], and also shows that at high concentration of tetrafunctional monomer, the gel phase appears earlier, and most of the monomer sites react with the growing cluster.

Fig. 6 shows the radius of gyration of the largest or the infinite cluster as a function of step time for the same concentrations. This figure shows that the radius of gyration grows and saturates very rapidly. This effect is due to the fact that for a randomly growing chain, the final value of radius of gyration in a lattice equals to $L/2$ and when the growing chain senses the periodic boundaries, the radius of gyration approaches its final value. At low concentration of the tetrafunctional monomer, the largest cluster is not so large that addition of the side-growing chains with the different orientations causes the decrease in the radius of gyration, while at high concentration of tetrafunctional monomer, the infinite cluster is so large that the addition of some chains does not affect its microstructure. Fig. 7 shows the radius of gyration of the infinite cluster as a function of the number of monomer sites that belong to it. The slope of the linear section of the curves in a logarithmic

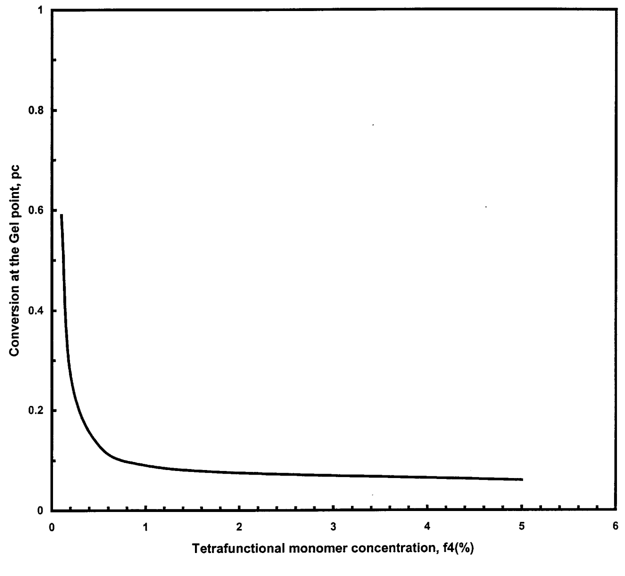

Fig. 5. Concentration at the gel point or critical conversion p_c, as a function of tetrafunctional monomer concentration.

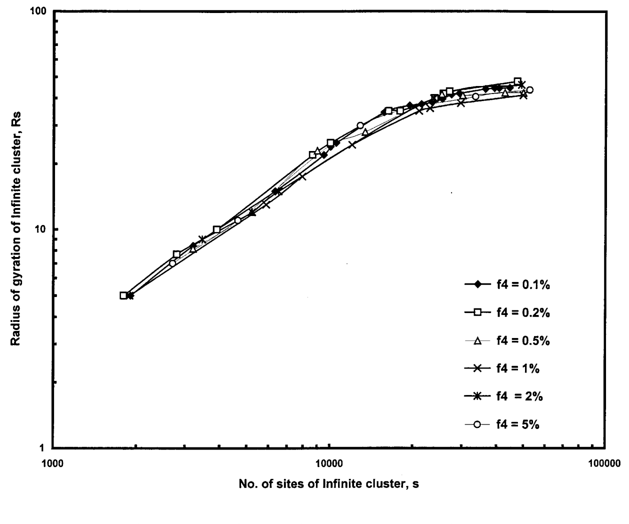

Fig. 7. Radius of gyration of the infinite cluster as a function of number of sites that belong to it for tetrafunctional monomer concentration, f4: 0.1, 0.2, 0.5, 1, 2 and 5. The fractal dimension of the infinite cluster $D_e = 1.53 \pm 0.06$.

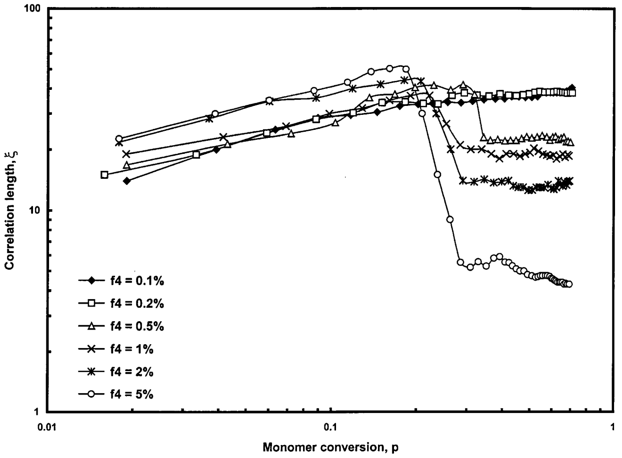

Fig. 8. Correlation length ξ, as a function of monomer conversion for tetrafunctional monomer concentration, f4: 0.1, 0.2, 0.5, 1, 2 and 5%.

scale (gel growing section) defines the reciprocal of D_e, the effective fractal dimension of branched polymer in solution. The present simulation yields, $D_e = 1.53 \pm 0.06$ which is in good agreement with theoretical [4,5] and experimental [34,35] results, and confirms the self-similarity of the fractal structure of the chemical gels.

Fig. 8 shows the correlation length as a function of monomer conversion for the same concentrations. As the conversion of monomer increases, the correlation length approaches its final value, $L/2$, which means that the largest cluster form at the early stages of reaction. Also the result shows that the initial values for the correlation length depend on the tetrafunctional monomer concentration, but near the critical conversion, the magnitude of ξ approaches the maximum value $L/2$. The decrease after the critical conversion is due to the fact that the correlation length after this point represents only the chains and microgels in the sol phase, and as the concentration of tetrafunctional monomer decreases, the formed chains and microgels have more chance to remain in the sol phase, thus the correlation length increases.

4. Conclusions

A new kinetic gelation model has been presented to describe non-linear free radical copolymerization of a mixture of bi- and tetrafunctional monomers. The simulation can also be used to investigate several polymer reactions like branching, crosslinking, and vulcanization of long chain polymers. The new simulation involves improvements such as exponential decay of an initiator molecule into two initiator radicals as neighbor sites. The efficiency of the initiator is introduced when radicals recombine and become inactive. A very efficient self-avoiding random walk, based on a successive layer evaluation process, is introduced to remove or at least delay the trapping of radicals until the last stages of reaction, which allows efficient polymerizations simulations with high conversions without the need of artificial specifying sites as solvent. In addition, several mobility mechanisms for all the single sites, chains, and clusters like chain reptation, segmental, and cluster diffusion are introduced. These improvements make most of the functional groups accessible to react with active sites, and to decrease the number of trapped radicals, as well as the trapping frequency, thus overcoming weaknesses of previous models. Polymerization reaction quantities, such as the weight-average degree of polymerization, and properties, such as the radius of gyration and the correlation length, are evaluated as quantitative measures of microstructure. The model has the ability to simulate several realistic conditions in polymerization systems. Finally, this work has provided an unified frame for producing a system consisting of highly packed chains or clusters with less than one percent of unconnected or single sites, suitable to model polymer systems via the network approach. The weight-average molecular weight results show a scaling behavior near a threshold value that signals the presence of a different mechanism before and after threshold value. The polymerization related quantities and the microstructural properties evolution provide information to describe the chemical nature of the resulting gels. It is also possible to consider the solvent effect—interaction between solvent and polymer—and the phase separation of gel phase during gel formation. The phase behavior of polymer–monomer system and its dependence on chemical composition of the system is considered. The starting point of the sol–gel transition behavior and the related threshold conversion for realistic cases is investigated. The chemical nature of different monomers that leads to different polymerization processes can be evaluated if the chemical interaction between monomer and the resulting polymer is considered.

Finally, in this work, our main goal was to understand the scaling properties of the gelation process and to test the capability to predict gel microstructure. In future work, we shall attempt to use experimental data to make quantitative assessments of the kinetic gelation model capabilities. Our special interest is the evolution of molecular weight distribution in the relatively highly crosslinked polymer network.

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