Monte Carlo Simulation of Chemical Gelation Using a Percolation Kinetic Gelation Model

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A B S T R A C T

A Monte Carlo approach based on kinetic gelation model is used to simulate the kinetics of non-linear free radical copolymerization of vinyl-divinyl monomer mixtures or chemical gelation, and to characterize kinetic effects on polymerization statistics and microstructures. New algorithm for random selection of the next neighbour site in a self-avoiding random walk and efficient mechanisms of mobility of components 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 of predicting the onset of the sol-gel transition and the effect of chemical composition on the transition point. It is shown that there is attained a better understanding of microstructure evolution and appearance of gel phase during polymerization and chemical gelation. Finally, one important benefit of the simulation method is the ability of characterizing system in which, the dominant combination reaction leads to highly branched structure.

INTRODUCTION

During free radical copolymerization of a mixture of vinyl-divinyl monomers, the cross-linking reactions lead to the evolution of a three dimensional network and the kinetics models are commonly used to investigate the reaction mechanisms and microstructures [1].

Due to the random nature of growing macroradicals in the polymerization process, percolation theory is a very useful tool to describe such disordered systems[2]. The classical approach of percolation on

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the Caylee tree due to Flory[3] and Stockmayer[4] is regarded as the starting point in the theory of kinetic gelation model (KGM) which describes the chemistry of irreversible polymer gelation by using a lattice model. The polymer percolation model has been mainly used [2,5] to study the critical behaviour near the gel point, where the assumption of a diffusion-limited process is likely to be accurate. This behaviour depends on the space dimensionality and not on the lattice geometry [5].

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 of any given site introduces the number of possible chemical bonds it makes with its neighbouring sites.

Computer simulations based on percolation models describe polymers that undergo the self-avoiding random walks (SAW) on a lattice. They simulate the gelation process during polymerization of multifunctional monomers. The first percolation model proposed by Manneville and de Seze [6], referred to as the kinetic gelation model (KGM), has been modified by many researchers [6-12]. They developed a computer model that took into account the 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 by using KGM [6-12]. The effect of the initiator s quantity and decay kinetics [7-10], the addition of solvent [8-10], and the mobility of the components [11] were the early modification of KGM. 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 [10-11] 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 by initiated radicals [11].

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.

The next section describes the computational model, and defines the model properties, and then the results of our computer simulations are presented.

Simulation

The model used in this work is based on the Flory-Stockmayer[3,4] theory, which is identical to percolation on the Caylee tree (Bathe lattice). Manneville and de Seze[6] 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 and divinylic monomers by using a modified version of KGM. Monomers and initiators are considered as sites on a discrete simple cubic lattice with L3 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 neighbours, however due to previous bond in each chain head; each site has at most five possible neighbouring sites to form a bond. The next step is to initiate the growing process. This is done by randomly placing a free radical (active centre) on a monomer site. Each initiator molecule is considered as two near neighbouring sites and decomposes into two radicals based on the first order rate decomposition [9, 11].

To form a chemical or permanent bond, each radical recognizes the capability of each nearest neighbouring site for reaction, if there is at least one monomer or another active site the reaction takes place. If there are 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 its neighbours. 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 centre transfers to the reacted site. In each Monte Calro step (MCS) this process will be done by all of the

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active centers.

To determine polymerization quantities (i.e. reacted sites) the Hoshen-Kopelman algorithm [12] is used. In this algorithm all monomers in the percolation network are labeled in such way that those with same labels belong to the same cluster. When a bond is formed the reacted site becomes 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, in this work, we use two important modifications that we presented in previous works [13, 14]:

(i) Successive steps evaluation of a growing radical.

(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 neighbours has capability to react, so a radical is trapped. To avoid or at least delay this problem, we used the following algorithm. 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-neighbouring sites (layer of first step of walker), the second-nearest-neighbour (second layer) and so on. 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 its 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, new-born 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 neighbouring sites. In multiple-site movements we consider three types of movements:

(1) The active centre in a macroradical head moves to a neighbouring 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).

(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.

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 that are normalized by total number sites in lattice.

G the gel fraction (order parameter of system) is defined as:

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

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 units; 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.,

$$DP_w = \frac{\sum_s n_s s^2}{\sum_s n_s s} \qquad (2)$$

where n_s is the number of clusters containing s monomers; and R_s is the radius of gyration defined as:

$$R_s^2 = \frac{1}{S} \left\langle \sum_{i=1}^{s} (r_i - r_0)^2 \right\rangle \qquad (3)$$

where

$$r_0 = \sum_{i=1}^{s} r_i / s \qquad (4)$$

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

$$R_s \sim s^{1/De} \tag{5}$$

where D_e is interpreted as the fractal dimension of the infinite cluster. These quantities are monitored at each MCS time.

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 **k** times and a statistical average is taken. We consider 50 to 100 runs depending on the fluctuations observed, however for large lattices increasing of **k** does not affect the accuracy of the results [10].

RESULTS AND DISCUSSION

We consider a simple cubic lattice of size L=100 in which initially all sites are considered as vinylic monomers (functionality of 2). The initial initiator concentration is 1% on mole basis, very common in bulk polymerization, and it 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 place or a branch or side-branch is formed and the two chains with different labels unit together and takes the same label. During the reaction, this process will be repeated and thus the numbers of junctions or branches increase.

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 a (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 [5-11] 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.

As the reaction proceeds, the polymerization quantities and the microstructure of gel phase, such as entangled chains, loops, and pendant double bonds can be distinguished and characterized.

Figure 1 shows the conversion of monomers p, as a function of Monte Carlo step (MCS) time, for six increasing tetrafunctional monomer concentrations (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.

Figure 2 shows the gel 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 appears at earlier stages of the reaction.

Figure 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
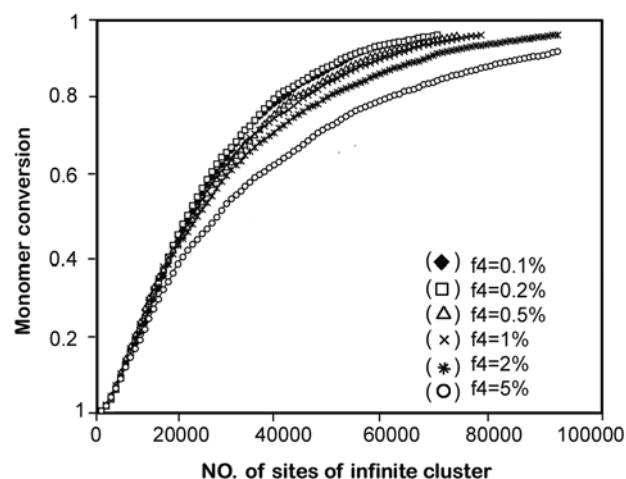

Figure 1. Monomer conversion, p, as a function of Monte-Carlo step time for tetrafunctional monomer concentration, f4: 0.1%, 0.2%, 0.5%, 1%, 2%, and 5%.
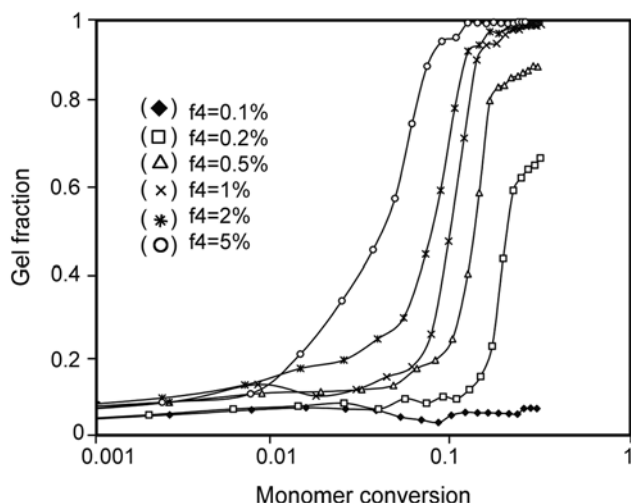
Figure 2. Gel fraction, G, of monomer conversion for tetra-functional monomer concentration, f4: 0.1%, 0.2%, 0.5%, 1%, 2%, and 5%.

Figure 4. Concentration at the gel point or critical conversion, P_c, as a function of tetrafunctional monomer concentration.

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 concentrations of tetrafunctional monomers, the number of cross-linked sites or microgels is lower than the number of chains. Therefore, 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.
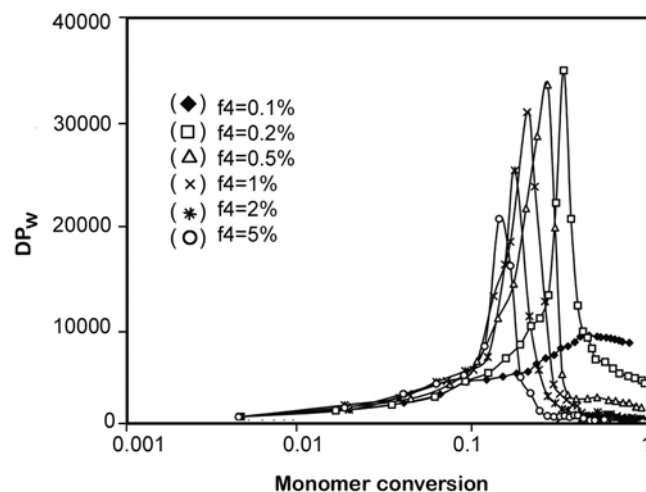
Figure 4 shows the gel fraction of polymer as a function of monomer conversion. It also shows the conversion at gel point or the critical conversion p_c as a function of tetrafunctional monomer concentration. The figure shows the same observed trend in experimental results[17], and also shows that at high concentration of tetrafunctional monomer the gel phase appears earlier, and most of the monomer sites react with the growing cluster.

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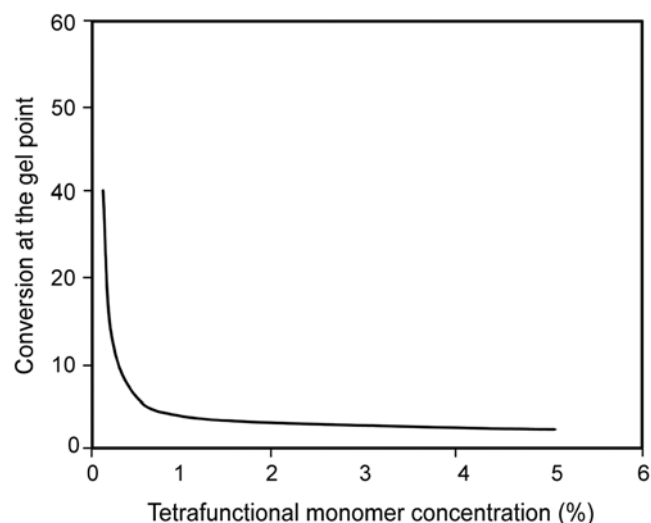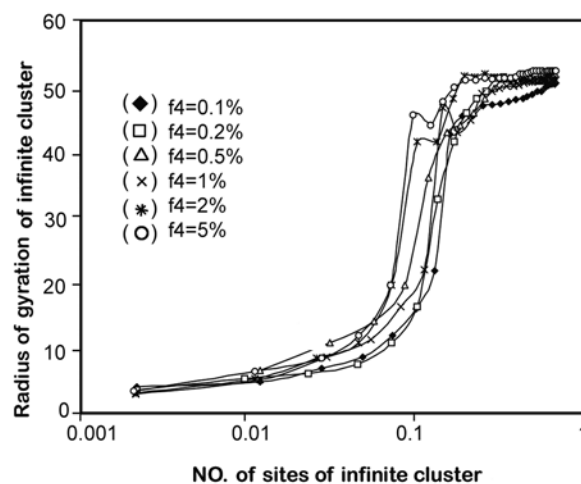

Figure 5. Radius of gyration of the infinite cluster, R_s, as a function of monomer conversion, p, for tetrafunctional monomer concentration, f4: 0.1%, 0.2%, 0.5%, 1%, 2%, and 5%.
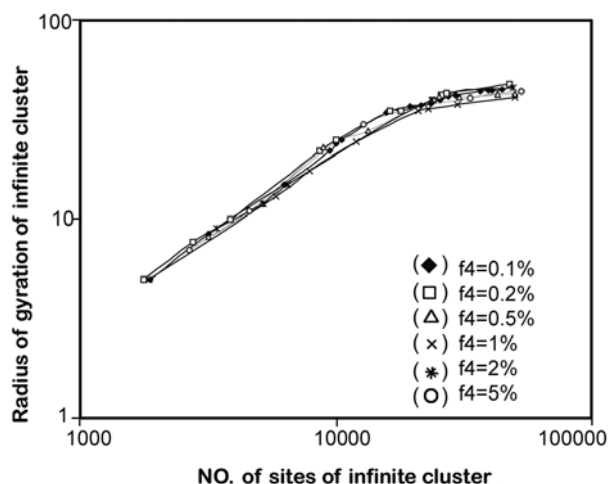
Figure 6. Radius of gyration of the infinite cluster as a function of number of sites that belong to it for tetrafunctional monomer concentration, f4; 0.1%, 0.2%, 0.5%, 1%, 2% and 5%; The fractal dimension of the infinite cluster, $D_e = 1.53 \pm 0.06$

Figure 5 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.

Figure 6 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 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 [2] and experimental [18] results, and confirms the self-similarity of the fractal structure of the chemical gels.

CONCLUSION

A new kinetic gelation model has been presented to describe non-linear free radical copolymerization of a mixture of bi- and tetrafunctional monomers referred as chemical gelation. The simulation can also be used to investigate several polymer reactions like branching, cross-linking, and vulcanization of long chain polymers. The new simulation involves improvements such as exponential decay of an initiator molecule into two initiator radicals at neighbour 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 behaviour 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 informations 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 behaviour of polymer-monomer system and its dependence on chemical composition of the system is considered. The starting point of the sol-gel transition behaviour 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.

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