

Monte Carlo Simulation of Non-linear Free Radical Polymerization Using a Percolation Kinetic Gelation Model (I): Free Radical Homopolymerization

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ABSTRACT

A kinetic gelation model that incorporates the kinetics of free radical homopolymerization is implemented to determine the effects of kinetics on polymerization statistics and microstructures. The simulation is performed on a simple cubic lattice that has 100 sites in each direction. A new algorithm for random selecting of the next step in a self-avoiding random walk and very efficient mechanisms of mobility of components are introduced to improve the generality of the predictions by removing commonly occurring deficiencies due to early trapping of radicals. A first order kinetics is considered for decomposition of initiator that enables us to consider the effect of temperature on polymerization reaction. Better understanding of microstructural evolution during polymerization and providing a framework to produce a realistic system of highly packed random chains within polymer network are among the benefits of model.

Key Words: kinetic gelation model, microstructure, bifunctional (vinyl) monomer, percolation threshold, self-avoiding random walk

INTRODUCTION

Free radical polymerization is a widely used method for synthesizing linear and cross-linked polymers. There are several advantages to this type of polymerization, including faster reaction time, easier manufacturing techniques, and rapid formation of high

molecular weight polymers [1,2]. Due to the random nature of growing macroradicals in the polymerization process, percolation theory is a very useful tool to describe such disordered systems [3]. The classical approach of percolation on the Cayley tree due to Flory [4] and Stockmayer [5] is regarded as the starting point in the theory of kinetic gelation model

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(KGM) which describes the chemistry of irreversible polymer gelation using a lattice model. The terminology of the theory was introduced by Broadbent and Hamersely [6]. 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) and two (usual vinylic monomer). Random connections are then initiated between the nearest neighbouring 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 [3]. The first percolation model proposed by Manneville and de Seze [8], referred as the kinetic gelation model, has been modified by a variety of researchers [7-14]. 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 model have been performed using KGM [7-9]. The effect of the initiator quantity and initiator decay have been considered as fast initiation [8], slow initiation [10,11] and exponentially or first order rate decay [11].

One of the first modifications to the KGM was the addition of solvent [9,11,12] to avoid early trapping before considerable reaction progress. Coniglio et al. [13] 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 were immobile during the course of reaction. The mobility of the solvent, monomers and clusters has been considered in recent studies [11,14,15]. The mobility of species was considered to affect the trapping of radicals with no change in overall trends in simulation. Furthermore, several authors used KGM to describe the irreversible gelation in vinyl/divinyl copolymerization [15].

Also there is a lot of interest in using this approach for instance to study the phase transition and structural evolution of thermoreversible gels [16] and kinetics of living/controlled radical polymeriza-

tion using the iniferter technique [17].

In this paper Monte Carlo simulations using kinetic gelation model are performed on a simple cubic lattice with periodic boundary conditions to investigate free radical homopolymerization processes.

MODEL DESCRIPTION

The model used in this work is based on the Flory-Stockmayer [4, 5] theory, which is identical to percolation on a Cayley tree (Bethe lattice). Manneville and de Seze [8] developed one of the first percolation models (KGM) to examine free radical polymerization.

We simulate free radical polymerization of vinylic (bifunctional) monomer by applying a Monte Carlo approach on a modified version of KGM. Monomers are considered as sites on a discrete simple cubic lattice with L^3 sites ($L=100$) and are randomly distributed on the lattice sites. Periodic boundary conditions are implemented on lattice faces to eliminate edge effects.

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 neighbouring sites and decomposes into two radicals based on the first order rate decomposition [11]:

$$[I]/[I_0] = \exp(-t/\tau) \quad (1)$$

Here, $[I]$ is the initiator concentration, $[I_0]$ is the initial initiator concentration, t is the simulation step (Monte Carlo step time), and τ is a time constant (the inverse of the initiator decay constant is considered as $\tau=5 \times 10^3$ s in this work). The first order decay of the initiator provides a more realistic and variable representation of the polymerization as compared to simulation that use fast or slow initiation. Secondly, when the initiator molecule decays, it generates two radicals each occupying its own site. The radicals can recombine and become inactive or propagate. In this manner the efficiency of initiator is introduced, since a pseudo-cage effect is introduced from close proximity of the two radicals upon decay.

Furthermore, the effects of varying temperature and changing the initiator type are considered by determining the proper value of τ . During a time interval consisting of consecutive time steps, the total number of radicals is kept constant (rather than the ones that are trapped) until a new pair of radicals is introduced.

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

Different polymerization reactions such as propagation, termination (combination and disproportionation) and branching reactions will be simulated in this way if the attacked site is a monomer, a radical or a polymer chain, respectively. Each vinylic monomer is bifunctional, so it can react with two neighbouring sites. Unlike the kinetic gelation model approach, the resulting macromolecules in this case will be only linear chains.

We consider the digit one as unit number if the neighbouring site has the capability of reaction and otherwise zero, so each active site possesses an integer number n equal to the total number of neighbouring sites that have the capability to form bond. By defining a random number between zero and n , an active site (here is considered as a drunken walker) selects one of these neighbours. Because each site occupies no more than one monomer, the path of 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 [18] 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 chain. When a bond is formed the reacted site acquires the active site label. The different labels between two reacted neighbour radicals become equal if the combination reaction

takes place and remain constant if disproportionation occurs. 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 used in this work the two important modifications that we introduced in previous works [19,20]: (i) successive steps evaluation of a growing radical and (ii) mobility of components in the lattice.

Successive Steps Evaluation

One of the most important problems in KGM is trapping of a radical, when none of the nearest neighbours has capability to react, and so a radical is trapped. In early trapping, all of the radicals stop reacting, so the results of such run are rejected. 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 future steps in a walk) as the first-nearest-neighbour sites (layer of first step of walker), the second-nearest-neighbour (second layer) and so on, as is shown in Figure 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; it means our walker is so conscious that recognizes his first, second and so on, steps to home. This method reduces the trapping process even in the last stages of reaction, and adapts itself according to the diffusion of radicals.

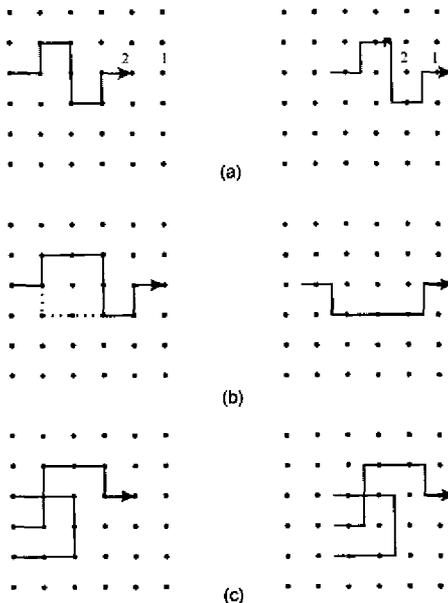
Mobility

One of the novel features 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 radical and void 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 the case of a solvent, void or

radical site, this movement allows trapped radical the possibility of becoming active in later steps of reaction. In multiple-site movement we consider three types of movements:

First, the active center in a macroradical head moves to a neighbouring site and all the reacted monomers in the chain follow its path (Figure 2a). This movement changes only the position of the first and the last sites in the chain and resembles chain reptation. Second one or more sections in polymer cluster (chain) are allowed to exchange their positions with surrounding sites referred to as segmental diffusion (Figure 2b). These segments move independently of each other, and any movement involves no bond breaking, or changes in bond length, except at the first and the last site in each segment. Thirdly, a whole cluster (chain) is allowed to move in one of the six directions, to produce a central-mass or translational diffusion (Figure 2c).

All of these movements are restricted to one lattice unit displacement, and more importantly, all bonds are preserved and the polymer configuration



a- Reptation movement. The chain crawls one site from head to tail and the chain head goes to the next site.
 b- Segmental movement of a chain section, the sites in a portion of chain exchange their positions with unoccupied neighbouring sites.
 c- Translational or cluster movement, each site in a chain or cluster moves to its next site so that the whole cluster moves one lattice unit.

Figure 2. Different types of cluster or chain movement.

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 made in such a way that the total number of accessible sites for an active site in each MCS increases.

Model Quantities

The quantities and variables of the model are as follows: p , is the total number of reacted sites that belong to a chain; ρ is the conversion of monomer, defined as the total number of reacted sites p normalized by the total initial number of monomer sites; WADP is weight average degree of polymeriz-

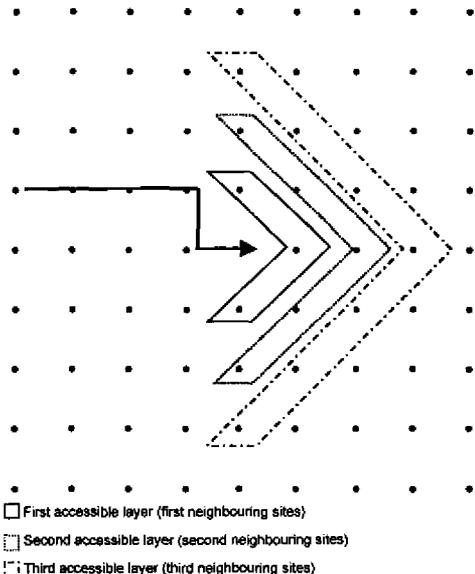


Figure 1. Schematic geometry of successive layers of neighbouring sites.

ation or weight average molecular weight defined as:

$$WADP = \frac{\sum s^2 n_s}{\sum s n_s} \quad (2)$$

where, n_s is number of clusters (chains) that contains s reacted monomers, ξ is typical correlation length defined as:

$$\xi^2 = \frac{\sum R^2 s^2 n_s}{\sum S^2 n_s} \quad (3)$$

where:

$$R_s = \sum \frac{(r_i - r_0)^2}{s} \quad (4)$$

and

$$r_0 = \frac{\sum r_i}{s} \quad (5)$$

R_s is radius of gyration of a cluster, and r_i is the length vector from a reference point to site i . 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:

$$WADP \sim |p_c - p|^\gamma \quad (6)$$

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 [7,12,16].

For linear clusters in lattice, the threshold value p_c and the critical exponent γ deviate from usual site or bond percolation values or even random walk exponents. The p_c value is estimated by finite size-scaling method for an infinite lattice [7,12].

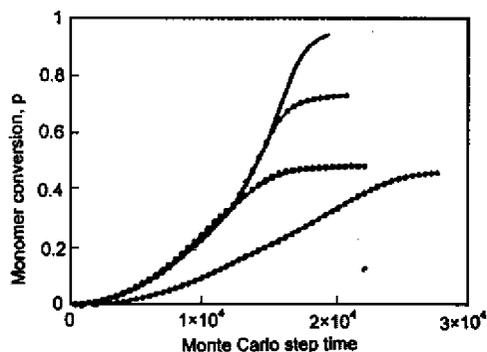
During each simulation, the information history of all components and clusters in the lattice is stored for future use. The whole procedure of distribution and growth is performed N times and a statistical averages is obtained. We consider 50 to 100 runs depending on the fluctuations observed; however, for large lattices increasing N does not affect the accuracy of the results [14].

RESULTS AND DISCUSSION

We consider a simple cubic lattice of size $L=100$ in which initially all sites are considered as vinylic monomer. Then monomers are randomly distributed in the lattice. Each monomer site carries a number ($f=2$) of reactive groups or functionality capable of forming chemical bonds in pairs. Other components are considered as solvent or void ($f=0$) and radicals ($f=1$).

In this work free radical homopolymerization of vinylic monomers is considered. The system consists only of difunctional monomers, as in bulk polymerization of simple vinyl monomers. Active sites grow and form long random chains with different sizes. The total number of sites that belong to all growing chains is considered as the monomer conversion p . The initial initiator concentration is 1% on a mole basis, being very common in bulk polymerization, and is introduced randomly with first order kinetics. Figure 3 shows conversion as a function of time step for four systems differing in mobility (in Successive Steps Evaluation section). In the simplest case D, no mobility is considered in the system and all active sites perform a completely self-avoiding random walk without preference to the next step.

As it is seen, the reaction stops as early as when half of the sites react, implying that half of the



— A: Mobility-successive layers; × B: Mobility-first neighbouring sites; Δ C: No mobility-successive layers of neighbouring sites; □ D: No mobility-first neighbouring sites

Figure 3. Effect of successive layers and mobility algorithm on the extent of polymerization, (monomer conversion, p).

monomers remain virgin and are not sensed by active sites. These results are compatible with the previously mentioned conclusions [7,12] that for a random walk in a static system, up to half of the sites remain unseen and should be considered as inactive sites or solvent.

The conditions in case C are the same as in case D but any active site can perform the new proposed successive layers of neighbouring sites algorithm. The conversion goes to slightly higher amount in longer times but with no considerable increase. In case B, the effect of mobility is considered and the conversion approaches to higher point means the great effect of different types of mobility in the system. Finally, in case A the use of the successive step evaluation algorithm and mobility of all the components, leads to more than 95 percent conversion.

Figure 4 shows the weight average degree of polymerization WADP, as a function of monomer conversion p , for a polymerization system with 1% initiator. The WADP has a local maximum around $p=0.3$. This threshold value indicates that before and after this point there are different mechanisms in a general percolation model. For $p < p_c$ each active site has a high number of accessible neighbouring sites and the random selection of neighbouring sites is dominant. For $p > p_c$ the total accessible sites decrease and the radicals select the next site from 1 or 2 possible neighbouring sites, so that the total accessible monomer concentration decreases.

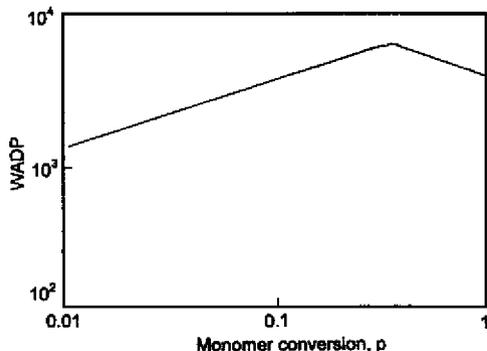
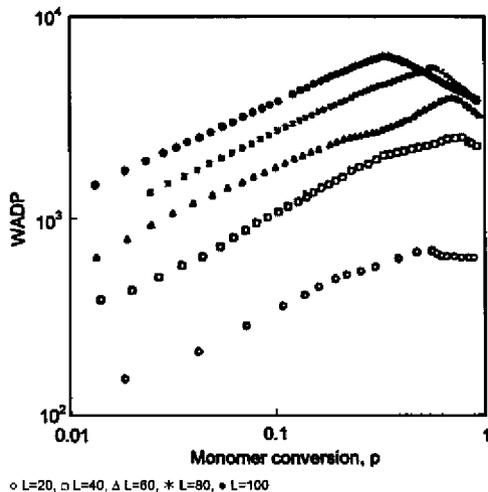


Figure 4. Weight average degree of polymerization as a function of monomer conversion, $L=100$ and $[I]=1\%$.



○ L=20, □ L=40, △ L=60, * L=80, ◆ L=100

Figure 5. Weight average degree of polymerization as a function of monomer conversion for different lattice sizes; 20, 40, 60, 80 and 100.

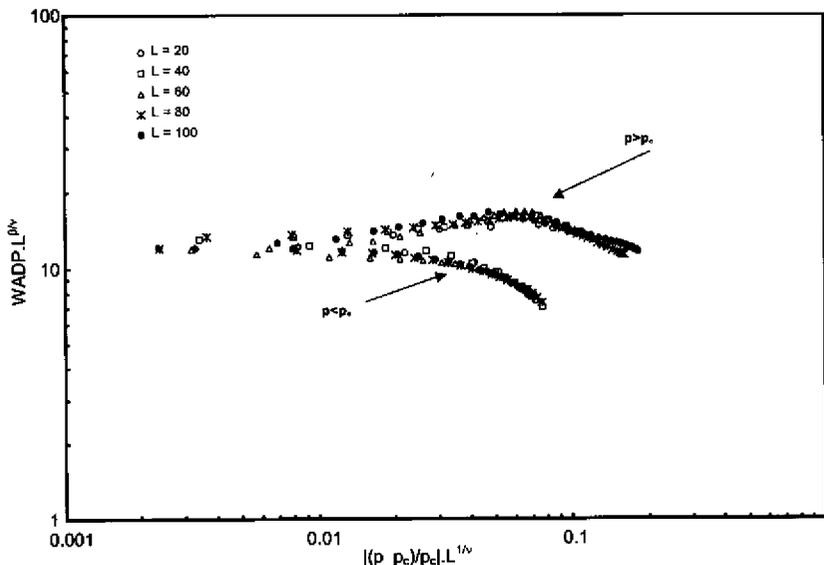
Furthermore, the new radicals, continually generated, lead to growth of small chains within the system and to the decrease in the weight average degree of polymerization. Figure 5 shows the weight average degree of polymerization as a function of monomer conversion p , for five increasing lattice length, L : 20,40,60,80 and 100. The WADP has the same behaviour in all levels, showing that the lattice size does not affect strongly the system properties.

The general behaviour of WADP suggests that this term scales with change in p as eqn. (6), in which γ is scaling exponent. This equation applies below and above the percolation threshold; however, the front factor may differ in two regions. The amount of p_c is evaluated by applying the finite-size scaling method [7,12]. WADP for limited values of L can be expressed in term of scaling function ϕ as:

$$WADP.(L,p)=L^{-\beta\nu}\phi\left[\frac{(p-p_c)}{p_c}\mid.L^{1/\nu}\right] \quad (7)$$

(β and ν are different scaling exponents used in finite-size scaling method)

In the asymptotic limit $L \rightarrow \infty$ and $p \rightarrow p_c$ the



○ L=20, □ L=40, △ L=60, × L=80, ● L=100

Figure 6. Finite-size scaling of rescaled weight average degree of polymerization for $L=20, 40, 60, 80$ and 100 ; $p_c=0.337$, $1/\nu=0.29\pm 0.04$ and $\beta/\nu=1.3\pm 0.04$.

eqn. (6) is recovered. Figure 6 is the finite-size scaling plot of WADP shows that the family of curves for different lattice length nearly collapses on a singly two-branched curve for p values below and above p_c . A very rough finite-size scaling estimates show $p_c=0.34\pm 0.005$ and scaling exponent $\gamma=0.26\pm 0.03$. It

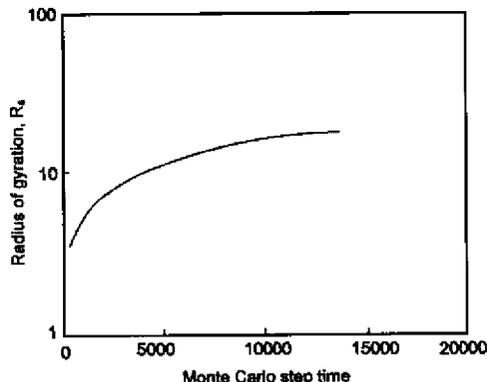


Figure 7. Radius of gyration, R_g , of the largest chain as a function of step time, $[I]=1\%$.

is expected that the value of p_c would give the critical conversion at the onset of the gel effect in bulk polymerization. Figure 7 shows the radius of gyration R_g of the longest chain as a function of step time for 1% initiator system. As the reaction proceeds, the

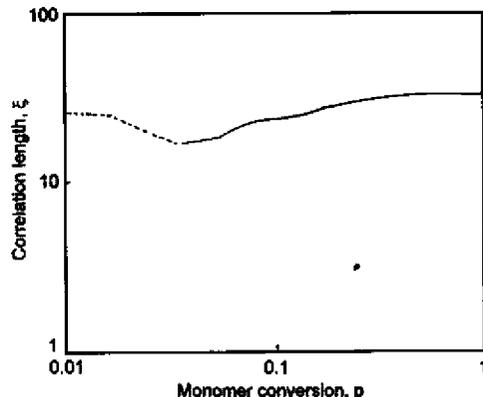


Figure 8. Correlation length, ξ , as a function of monomer conversion, $[I]=1\%$.

radius of gyration grows slightly to a final asymptotic value due to the constraints in the lattice boundaries.

This behaviour also shows a power law relation of the radius of gyration to chain length, or equivalently to the step times. Figure 8 shows the correlation length ξ , as a function of monomer concentration p for a 1% initiator system. This property plays a major role in percolation systems whose scaling behaviour relates percolation parameter p , to some mechanical properties (i.e., viscosity or elastic modulus). Due to the nature of linear chains in the linear free radical polymerization ξ grows very rapidly in early stages of polymerization ($p < 0.01$) and slightly increases to a final value, so the scaling relation in this case is no longer expected. In a general percolation system the correlation length is limited by the linear size of the lattice length L , and since in our case $\xi \ll L$ that means in a system of linear chains there is no such a big chain to span the entire lattice.

CONCLUSION

A new kinetic gelation model has been presented to describe non-linear free radical homopolymerization reactions of vinylic monomers. 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 exponentially decay of an initiator molecule to two initiator radicals as neighbouring sites. The efficiency of the initiator is introduced when radicals recombine and become inactive.

A very efficient self-avoiding random walk, the successive layer evaluation process, is introduced to remove or at least delay the trapping of radicals until the last stages of reaction, which allows one to efficiently simulate polymerizations with high levels of conversion without specifying sites as solvent. In addition, several mobility mechanisms for all the single sites and chains like chain reptation, segmental and chain diffusion are introduced. These improvements make most of the monomers accessible to react with active site and to decrease the number of trapped radicals, as well as trapping frequency; thus over-

coming 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 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 results are in agreement with experimental results for usual polymerization cases and show the onset of the gel effect in bulk polymerization. The chemical nature of different monomers that leads to different polymerization processes can be evaluated if the chemical interaction between monomer and resulted polymer is considered.

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