

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

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ABSTRACT

A kinetic gelation model that incorporates the kinetic of non-linear free radical copolymerization of a mixture of bi- and tetrafunctional monomers is used to simulate the kinetics effects on polymerization statistics and microstructures. An algorithm for random next step selection 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 to account into several free radical polymerization mechanisms such as cross-linking, branching, and also to predict the onset of sol-gel transition, and the effect of chemical composition on the transition point. It is shown that a better understanding of microstructure evolution and appearance of gel phase during polymerization and chemical gelation is attained. Finally, one important benefit of the simulation method is the ability to produce a system of very highly packed random chains or clusters within a polymer network.

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

INTRODUCTION

Several kinetic [1] and statistical [2] models are introduced and used to describe copolymerization of a mixture of multifunctional monomers in which the linear and cross-linked polymers are produced and it

is sometimes argued [2] that kinetic models are better suited for nonlinear free radical polymerization.

It was shown that the percolation approach is a very powerful tool to clarify the disordered phenomena [3]. The main reason is that the percolation model is based on randomly distribution of clusters within a

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network that resembles the macrochain growth. The classical works of Flory [4] and Stockmayer [5] on a Bethe lattice were considered as the original point of kinetic gelation model (KGM) that used to model the chemical gelation in polymerization reactions. KGM has been mainly used [3–6] 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 [7, 8].

In modelling a polymerization process by a percolation approach, a finite three-dimensional regular network would be considered as polymerization loci in which each site is assumed as a functional monomeric unit that can react randomly with its neighbouring sites. The number of formed chemical or permanent bonds is in according to the functionality number of the site.

To simulate the gelation process during polymerization of the mixture of multifunctional monomers [7], several computer algorithms based on percolation model describe the polymer chains behaviour that shows a self-avoiding random walk (SAW) on a finite lattice.

The first computer simulation that used the percolation theory was proposed by Manneville and de Seze [8] that was named later as kinetic gelation model. 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.

Many features of chemical gelation in vinyl/divinyl copolymerization have been studied by using different version of KGM [9–17].

In this paper Monte Carlo simulation (MCS) using kinetic gelation model are performed on a simple cubic lattice with periodic boundary to investigate free radical copolymerization of mixture of multifunctional monomers referred as chemical gelation.

Model Description

Manneville and de Seze [8] 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/divinylic monomers with cross-linking of growing chains by applying a Monte Carlo approach used in a modified version of kinetic gelation model. Monomers (bi- and tetrafunctional unit) are considered as sites on a discrete simple cubic lattice with L^3 ($L=100$) sites, and are distributed randomly. To neglect the effects of limited domain in the network, the periodic boundary conditions are imposed on lattice faces.

The growing process 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 [12].

Each active center in head of a macroradical recognizes its neighbouring sites to evaluate how many of them have capability to make a chemical bond. If the selected neighbouring site is a vinylic monomer, another radical or a multifunctional monomer then the propagation, termination and branching reactions take place.

By definition a random number between zero and n , (number of accessible neighbouring sites) selects one of the 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 active centers.

To know that which site belongs to which one of the clusters, the labeling mechanism of Hoshen-Kopelman algorithm is modified and used [18]. The only difference between the homopolymerization and copolymerization cases is that if an active center senses a reacted multifunctional monomer within a chain or a cluster, in this case the two clusters with two different labels react with each other so it would be necessary to omit the unsuitable label from the two and all the parameters related to the omitted label are modified.

For better suitability of the model, both modifications proposed in previous works [19–21] consisting of components mobility and successive algorithm layers are used.

As stated before [21] the most important measuring quantities of the model are as follows: p is total percentage of reacted monomers, DP_w is weight average degree of polymerization defined as :

$$DP_w = \frac{\sum n_s S^2}{\sum n_s S} \quad (1)$$

Which is the ratio of the second to the first moment of the cluster size distribution. The correlation length is defined as:

$$\xi = \left[\frac{\sum n_s S^2 R_s^2}{\sum n_s S^2} \right]^{1/2} \quad (2)$$

which is again the ratio of R_s multiplied to the second moment of that distribution and n_s and R_s are the mass and radius of gyration of cluster containing s sites.

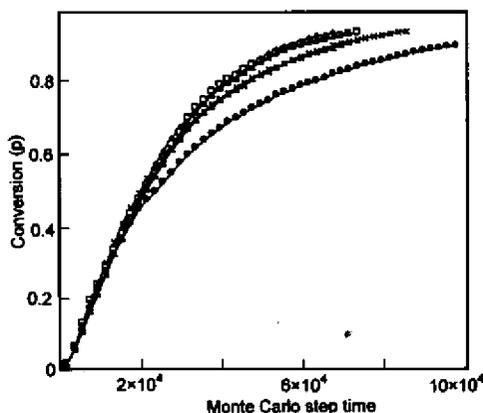
The changes in these quantities and also those related to all components are continuously monitored during the simulation and saved for the next use. To ensure the certainty of all measurements, the related statistical criteria are applied in each set of results.

RESULTS AND DISCUSSION

A simple cubic lattice of size $L=100$ in which initially all sites are assumed as vinylic (difunctional, $f=2$) monomer is considered as a model network. A specified number of tetrafunctional monomers that have four functional groups ($f=4$) 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. The process of chain growth is the same as the polymerization of vinylic monomer [21] except that the tetrafunctional monomer within a chain has capability to react again. When an active site selects a tetrafunctional monomer in a polymer chain, a cross-linking reaction takes place, or a branch or side-branch is formed and the two chains with different

labels unite together and acquire the same label. During the reaction this process will be performed more and more and the number of junctions or branches increases. Gradually large chains with side branches react with each other and at some point a very big cluster appears and spans through the whole system called the infinite cluster or the gel phase. The system also consists of small clusters that are not so large, called the sol phase. Thus at a specific conversion, 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 [7–16] are considered the best simulation tool for characterizing these processes involving chemical gelation. The transition value 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, pendant double bonds pendant chains, can be distinguished and characterized.

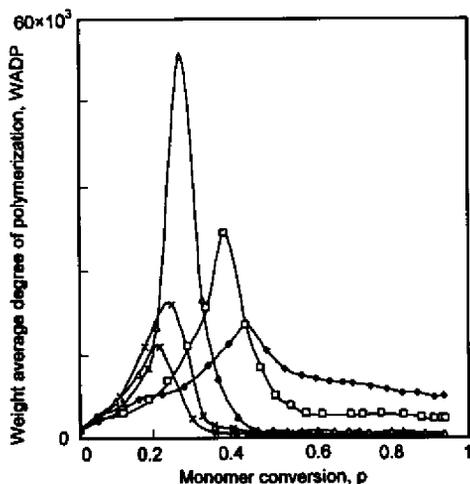
Figure 1 shows the conversion of monomers p ,



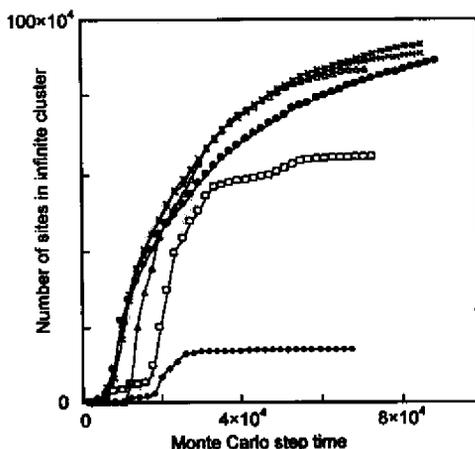
• Tet = 0.1 %; □ Tet = 0.2 %; Δ Tet = 0.5 %; × Tet = 1 %; * Tet = 2 %; ● Tet = 5 %.

Figure 1. Monomer conversion (p) as a function of time for the tetrafunctional monomer concentrations: 0.1 %, 0.2 % and 5 %.

as a function of step time, for six increasing tetrafunctional monomer concentration (Tet) and 1% initiator. The results show that the conversion profiles are very similar. The conversion curves grow in the same trend to a final value, meaning that up to 95 % of the total sites react. Figure 2 shows the weight average degree of polymerization of sol phase (excluded infinite cluster) for the same system as the result for 5% concentration is excluded. The figure shows a local maximum for each concentration. This effect is due to the fact that at low concentration of tetrafunctional monomers, the number of cross-linked sites or microgels is lower than the number of chains so that the weight average degree of polymerization (WADP) increases. At the higher concentration of tetrafunctional monomers, the largest cluster forms and the rest of the chains are not very long and the WADP decreases. Figure 3 shows the number of the sites that belong to the infinite cluster as a function of step time for the same concentration levels of the tetrafunctional monomers. As the concentration of tetrafunctional monomer increases, the infinite cluster grows up to 90 percent of total number of sites. The



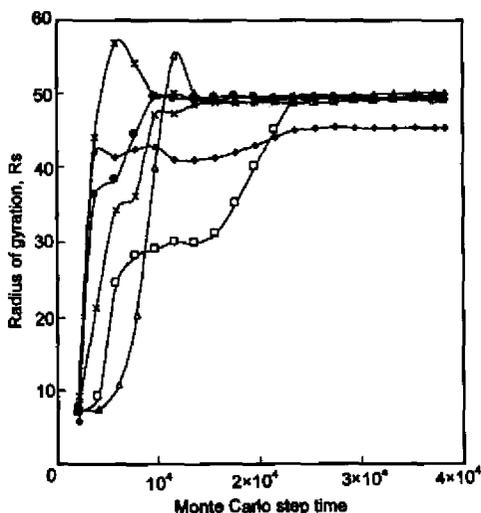
♦ Tet = 0.1 %; □ Tet = 0.2 %; Δ Tet = 0.5 %; x Tet = 1 %; * Tet = 2 %.
Figure 2. Weight average degree of polymerization of sol phase as a function of monomer conversion for tetrafunctional monomer concentrations: 0.1 %, 0.2 % and 5 %.



♦ Tet = 0.1 %; □ Tet = 0.2 %; Δ Tet = 0.5 %; x Tet = 1 %; * Tet = 2 %; • Tet = 5 %.
Figure 3. Total-Number of sites in the largest cluster as a function of time for tetrafunctional monomer concentrations: 0.1 %, 0.2 % and 5 %.

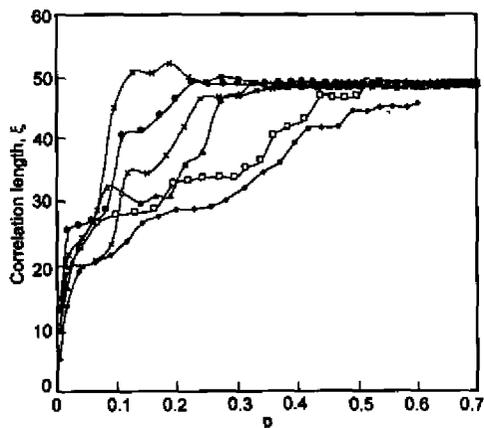
sharp increase in the number of sites belongs to the largest cluster in some cases is due to the high number of reaction between different clusters.

Figure 4 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 very rapidly and approaches a final value. 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 5 shows the correlation length as a function of monomer conversion for the same concentrations. As the concentration of tetrafunctional 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 correlation length depends on concentration, but at the final stages the amount of ξ approaches the final, $L/2$. Figure 6 shows the critical conversion or starting point of the sol-gel transition, p_c as a function of tetrafunctional monomer. As the



• Tet = 0.1 %; □ Tet = 0.2 %; △ Tet = 0.5 %; × Tet = 1 %; * Tet = 2 %; ● Tet = 5 %.

Figure 4. Radius of gyration of the infinite cluster as a function of time for tetrafunctional monomer concentrations: 0.1 %, 0.2 % and 5 %.



• Tet = 0.1 %; □ Tet = 0.2 %; △ Tet = 0.5 %; × Tet = 1 %; * Tet = 2 %; ● Tet = 5 %.

Figure 5. Correlation length, ξ as a function of monomer conversion for tetrafunctional monomer concentrations: 0.1 %, 0.2 % and 5 %.

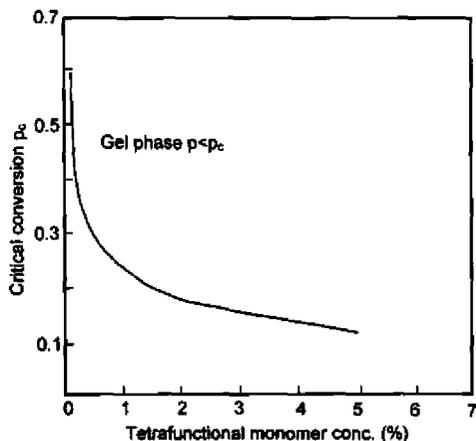


Figure 6. Critical monomer conversion p_c as a function of tetrafunctional monomer concentrations.

concentration of tetrafunctional monomer increases the gel phase appears at lower conversions and the final amount of gel phase increases.

CONCLUSION

A new kinetic gelation model has been presented to describe non-linear free radical copolymerization of mixture of bi- and tetrafunctional monomers.

A very efficient self-avoiding random walk, such as 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, 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 site and to decrease the number of trapped radicals, as well as 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 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 information to describe the chemical nature of the resulting gels. It is also possible to consider the solvent effect 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 are considered. The starting point of the sol-gel transition behaviour and the related threshold conversion for realistic cases are investigated. 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. The model has an 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 unreacted or single sites, suitable to model polymer systems via the network approach.

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REFERENCES

1. Flory P.J., *Principles of Polymer Chemistry*, Cornell University, Ithaca, 1953 and Odian, G., *Principles of Polymerization*, John Wiley, New York, 1991.
2. Tobita H., "Statistical derivation of kinetic molecular weight developments in nonlinear free radical polymerization", *Macromol. Theory Simul.*, **6**, 641, 1997.
3. Sahimi M., *Applications of Percolation Theory*, Taylor and Francis 1984, Stauffer D., Coniglio A., and Adam M., "Gelation and critical phenomena", *Adv. Poly. Sci.*, **44**, 103, 1982.
4. Flory P.J., "Molecular size distribution in three dimensional polymers", *J. Am. Chem. Soc.*, **63**, 3083; 3091; 3096, 1941.
5. Stockmayer W.H., "Theory of molecular size distribution and gel formation in branched-chain polymers", *J. Chem. Phys.*, **11**, 45, 1943.
6. Stauffer D., *Introduction to Percolation Theory*, Taylor and Francis, Philadelphia, 1985.
7. Family F., Landau, D.P., *Kinetics of Aggregation and Gelation*, North-Holland, Amsterdam, 1984
8. Manneville P. and de Seze L., "Percolation and gelation in additive polymerization", in Della Dora, J., Demongeot J., Lacolle B., *Numerical Methods in the Study of Critical Phenomena*, Springer, Berlin, 1981.
9. Hermann H.J., Landau D.P. and Stauffer D., "New universality class for kinetic gelation", *Phys. Rev. Lett.*, **49**, 412, 1982 and "Computer simulation of a model for irreversible gelation", *J. Phys. A: Math. Gen.*, **16**, 1221, 1983.
10. Boots H., Kloosterboer J.G., Van de Hei G. and Pandey R., "Inhomogeneity during the bulk polymerization of divinyl compound", *Brit. Polym. J.*, **17**, 219, 1985.
11. Boots H. and Dotson N., "The simulation of free-radical cross-linking polymerization", *Polym. Comm.*, **29**, 346, 1988.
12. Bowman C.N. and Peppas N., "A kinetic gelation method for the simulation of free-radical polymerization", *Chem. Eng. Sci.*, **47**, 1411, 1992.
13. Anseth K.S. and Bowman C.N., "Kinetic gelation model prediction of cross-linked polymer network microstructure", *Chem. Eng. Sci.*, **49**, 2207, 1994.
14. Matthews-Morgan D., Landau D.P. and Hermann H., "Effect of solvent in a kinetic gelation model", *Phys. Rev. B*, **29**, 6328, 1984.
15. Chiu Y.Y. and Lee L.J., "Microgel formation in the free radical cross-linking polymerization of ethylene glycol dimethacrylates", *J. Polym. Sci., part A*, **33**, 269, 1995.
16. Gupta A.M., Hendrickson R.C. and Macosko C.W., "Monte Carlo description of A_r homopolymerization", *Chem. Phys.*, **95**, 2097, 1991.
17. Liu Y., Pandey R.B., "Computer simulation studies of kinetic gelation", *Phys. Rev. B*, **55**, 8257, 1997.
18. Hoshen J. and Kopelman R., "Percolation and cluster distribution. I. Cluster labeling technique and critical concentration algorithm", *Phys. Rev. B*, **14**, 3428, 1976.

19. Ghiass M., Rey A.D. and Dabir B., "Simulation of non-linear free radical polymerization using a percolation kinetic gelation model", submitted to *Macromol. Theo. Simul.*
20. Ghiass M., Rey A.D. and Dabir B., "Microstructural evolution and simulation of non-linear free radical polymerization using a percolation kinetic gelation model", submitted to *Comput. and Theo. Polym. Sci.*
21. Ghiass M., Rey A.D. and Dabir B., "Monte Carlo simulation of non-linear free radical polymerization using a percolation kinetic gelation model, (I): Free radical homopolymerization", *Iran. Polym. J.*, **10**, 5, 2001.