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Percolation analysis on free radical linear polymerization with instantaneous initiation

Churl-Young Park and Son-Ki Ihm*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology,
P.O. Box 150 Cheongryang, Seoul, Korea

Summary

Free radical linear polymerization with instantaneous initiation was simulated on the simple cubic lattice. The monomer conversion, polydispersity index and average degree of polymerization were predicted by using the percolation model which was based on computer-simulated self-avoiding walks on the lattice. The adjusting parameters such as reactivity, termination modes, coordination number of given lattice were introduced.

Introduction

So far the average degree of polymerization (DP) and the polydispersity index (Q) for free radical polymerization have been predicted by solving the kinetic differential equations (1, 2). This process is based on spatially averaged concentrations of monomer and polymer, and concentrations are assumed to be uniform throughout the bulk phase. The active polymers in the reaction system grow competitively and spatial hindrance by neighbouring polymer or diffusion limitation by the dilution of local monomer concentration will affect the properties mentioned above. It is believed that this spatial effect in free radical linear polymerization with instantaneous initiation could be explained through percolation approach.

Percolation theory was applied to branched polymers by Flory(3) and Stockmayer(4) for Bethe lattice (or tree-like lattice) in order to predict the critical phenomena for gelation(5). Although analytical solution was available, a ring formation could not be expected due to the nature of the Bethe lattice. The inhomogeneity produced by chain reaction with crosslinking was investigated through a "chain reaction percolation" on the simple cubic lattice in which the bond formation was represented as time-invariant random walk (6, 7).

In this paper the chain growth of linear polymer by the free radical polymerization with instantaneous initiation is analyzed through the computer simulated temporal self-avoiding walk in cubic lattices based on percolation. The spatial effects on monomer conversion, Q, DP and number of polymers are predicted in terms of the participation extent of active polymers in propagation reaction (EOP) and the termination modes by two radicals (MOT). The competitive growths are simulated on three types of cubic lattices such as simple, body centered and face centered cubic lattices, and especially for the simple cubic lattice were considered the second neighbour interactions.

Theoretical

In Fig. 1-a, a snapshot of a simulated polymerization with instantaneous initiation in two dimensional square lattice is shown to illustrate the growths of four active polymers at the inception. Each site is considered as a point-like monomer molecule (site percolation). Firstly arbitrary monomer sites, which are selected at random by Monte Carlo method, are changed into

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*To whom offprint requests should be sent

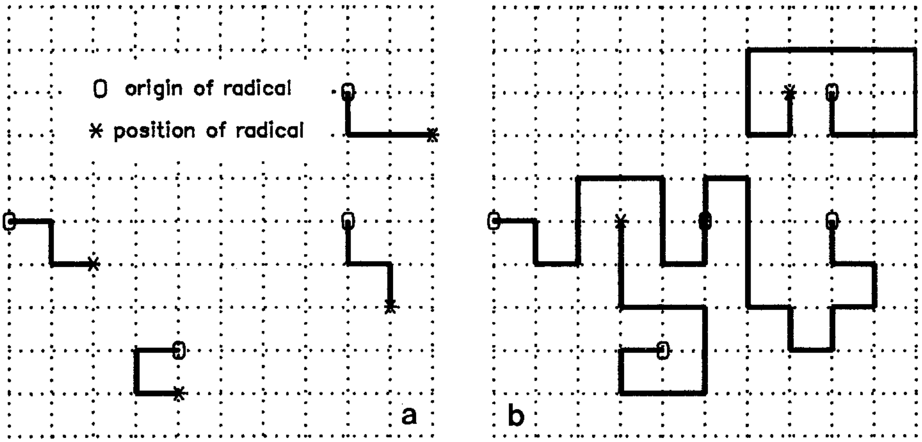

Figure 1 Snapshots for simulation on states of a) initiation/propagation and b) termination of 4 radicals.

radicals represented as open circles (initiation step). A bond is formed when a radical of active polymer chooses an unreacted neighbour monomer randomly. The radical marked as asterisk in Fig. 1-a moves from the penultimately connected monomer to the newly connected one. The radical function performs a self-avoiding walk on the lattice, thereby connecting a series of monomers by chemical bonds (propagation step). In order to avoid boundary effect (or end effect), the lattice is projected on a torus, so that a side can be connected to its counter part (6, 7). The walk continues randomly until two radicals meet at the same site or until a radical is unable to walk self-avoidingly (that is, the radical is trapped between reacted monomer sites) as shown in Fig. 1-b (termination step). The existence of trapped radicals was confirmed by electron spin resonance measurements (8). The linear polymers thus formed are called dead-end polymers and accounted as dead polymers since the term dead polymer signifies the cessation of growth for the propagating radical (6, 7, 9).

The monomer chain transfer are generally small for most monomers and the chain transfer to initiator such as BPO and AIBN can be negligible. It was assumed for linear polymerization that there was no chain transfer to polymer which results in the production of a branched polymer.

Since the spatial effect is dependent upon the history of chain growth of each polymer, the time-dependent percolation model is needed. It was assumed that only one bond in an active polymer could be formed per unit time ($\Delta t = 1$).

In view that the possibility of self-avoiding walk increases with increasing the number of coordination (NOC) which is defined as the number of bonds leaving each site, the walk was investigated on three types of cubic lattice such as the simple one with NOC = 6, the body centered one (bcc) with NOC = 8 and the face centered one (fcc) with NOC = 12. Additionally, for the simple cubic lattice the interactions of the second neighbours were considered, and the NOC becomes 18. When the length of bond is l in the simple cubic lattice, it is possible for bond with length of l or $\sqrt{2}\ l$ to be formed. The strength of interaction was discriminated by assuming that the possibility of bond formation was inversely proportional to the square of its length.

Model simulation and Discussion

The concentrations of monomer and initiator are replaced by the number of sites in the lattice. The total number of sites is 8000 for the simple cubic lattice, 8192 for the body centered one and 8788 for the face centered one,

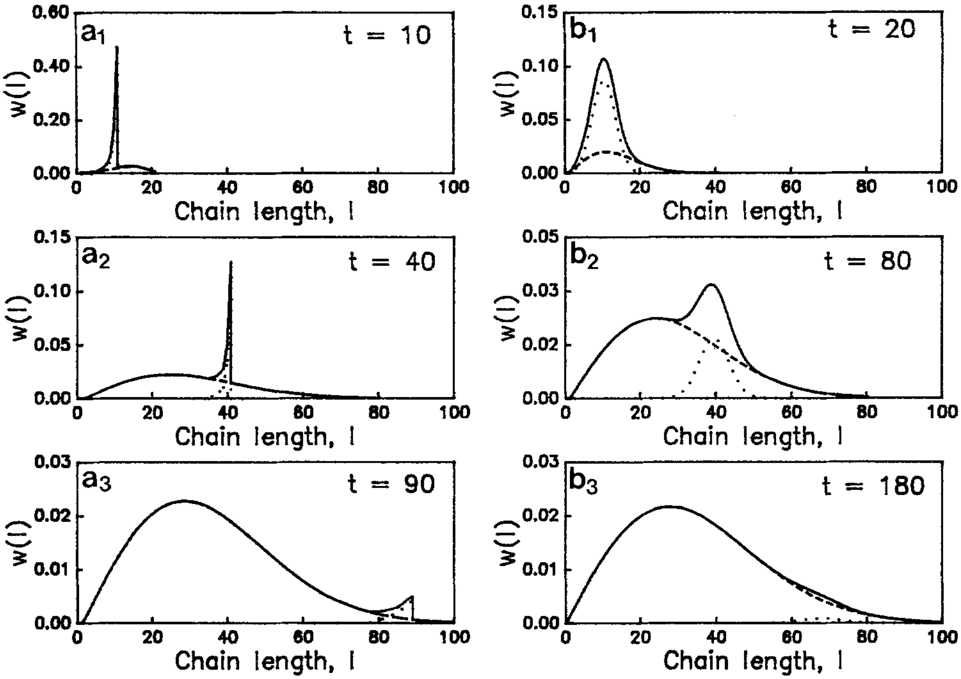

Figure 2 Molecular weight distributions at MOT = 1.0 and NOC = 6 for a) EOP = 1.0 and b) EOP = 0.5: polymer, solid; active polymer, dotted; dead polymer, dashed line.

respectively, which corresponds to the number of monomer molecules. The initial concentration of initiator was chosen 2.5 mol% which is rather larger than that normally used, but it is expected that the spatial effect can be more obviously demonstrated. In order to consider instantaneous initiation, the decomposition rate constant of initiator was chosen 1.0. It was confirmed from the simulation that the physical properties were almost independent of the constant if it was larger than 1.0.

The probability of bond formation is called as "reactivity", which makes the molecular weight of polymer being distributed. It should be determined prior to the selection of the direction of chain growth whether or not a bond is formed (that is, whether or not an active polymer participates in propagation reaction). The reactivity or the probability of bond formation could be represented by a parameter which is the participation extent of active polymers in propagation reaction (EOP). For example, EOP = 0.5 implies that 50% of active polymers participates in the propagation. It is noted that the propagation rate for EOP = 0.5 is slower by twice than that for EOP = 1.0.

In Fig. 2 the molecular weight distribution (MWD) as a density function w(l) is plotted against chain length for polymerization with termination by combination (MOT = 1.0). In case of EOP = 1.0 (or the probability of 1.0) the chain length of active polymer corresponds to its elapse time and the molecular weight of active polymer increases significantly with increasing chain length as shown in Fig. 2-a. However, the MWD of active polymer for EOP = 0.5 is like a normal distribution as illustrated in Fig. 2-b. At the inception most of polymers are active polymers and then the shape of MWD is changed into bimodal because the fraction of dead polymer increases with reaction time. As polymerization proceeds further (i.e., t = 180), the resulting MWD in Fig.

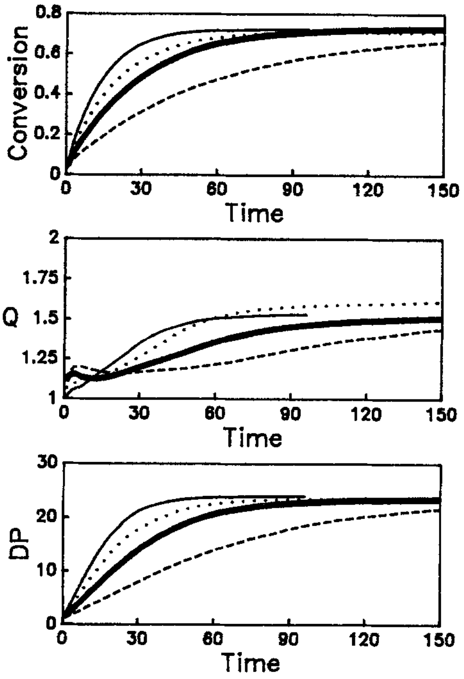

Figure 3 Effect of EOP on conversion, Q and DP with time at MOT = 1.0 and NOC = 6 (sc): EOP of 1.0, solid; 0.75, dotted; 0.5, heavy solid; 0.25, dashed line.

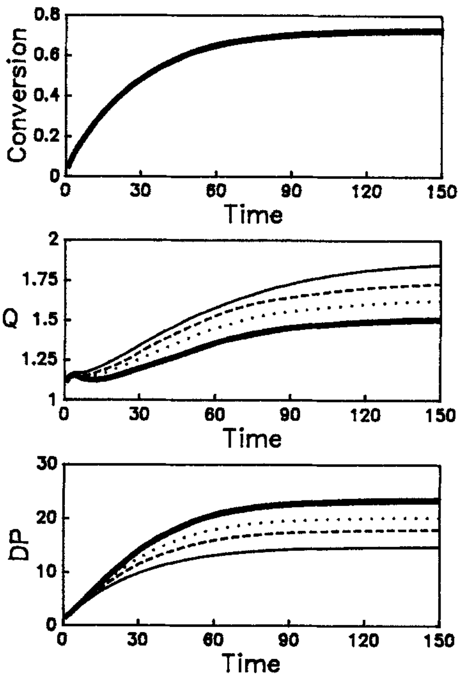

Figure 4 Effect of MOT on conversion, Q and DP with time at EOP = 0.5 and NOC = 6 (sc): MOT of 0.0, solid; 0.5, dashed; 0.75, dotted; 1.0, heavy solid line.

2-b3 is like a log-normal distribution which nearly corresponds to the distribution of EOP = 1.0 as shown in Fig. 2-a3.

Fig. 3 shows the effect of EOP on the transient behaviors of the conversion, Q and DP respectively. The conversion and DP increase with increasing EOP and the curve of Q shows a maximum value at the inception and then increases monotonically. However it can be seen that each of them approaches asymptotically the same value being independent of EOP. The variation with EOP did not affect the asymptotic values of properties mentioned above but the shape of MWD at EOP = 1.0 was different from these at the other values as confirmed in Fig. 2.

In order to predict the effects of mode of termination by two radicals, the fraction of termination by combination is assumed to vary from 0 (termination only by disproportionation) to 1.0 (termination only by combination). When two radicals encounter at the same site, if the given value of MOT is larger than a pseudorandom number, the termination by disproportionation takes place. Therby, each of active polymers becomes a dead polymer and this chain length is unchanged. For EOP = 0.5, the Q increases but the DP decreases significantly with decreasing MOT as shown in Fig. 4. This result seems reasonable because Q = 2 for polymerization with termination by disproportionation and Q = 1.5 with termination by combination (9). The curve of Q results in a maximum at the beginning and the variation is like a combined shape between the curves for termination by combination and by disproportionation. Yan and Cai (2) proposed that the curve of Q had a maximum value for termination by combination and it increased monotonically for termination by disproportionation.

In percolation, the type of lattice and/or the number of coordination (NOC)

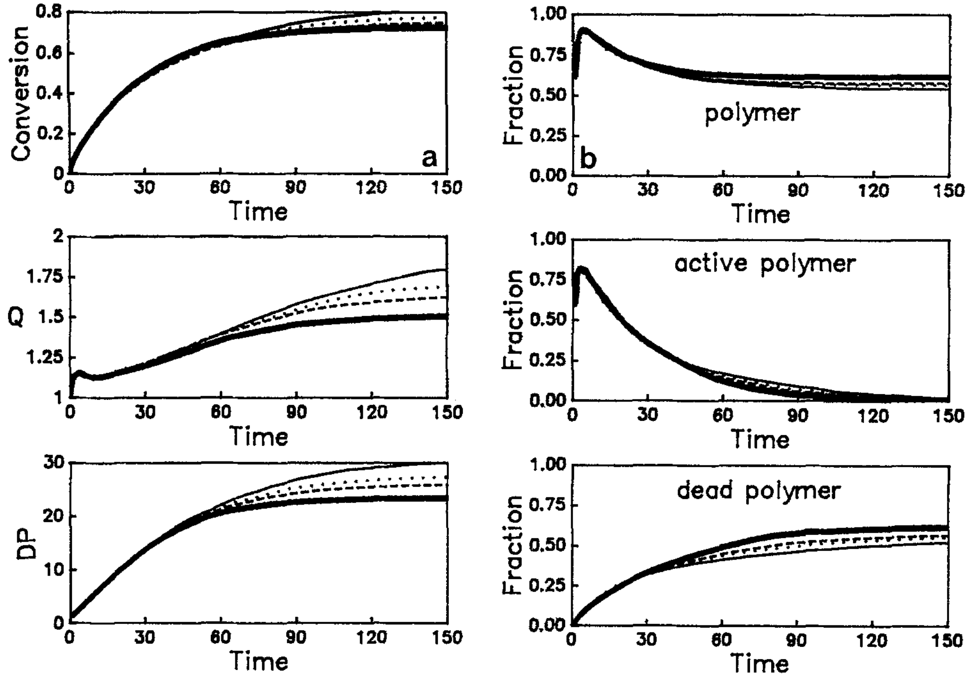

Figure 5 Effect of NOC at EOP = 0.5 and MOT = 1.0 on a) conversion, Q and DP and b) numbers of polymer, active polymer and dead polymer: NOC of 18 (sc), solid; 12 (fcc), dotted; 8 (bcc), dashed; 6 (sc), heavy solid line.

are the controlling parameters. The effects of NOC on the conversion, Q and DP are shown in Fig. 5-a. As NOC increases, all of the conversion, Q and DP increase. For a simple cubic lattice, the interaction with the second nearest neighbouring site results in significant influence as expected. Fig. 5-b shows the effect of NOC on the number fractions of polymers to the radicals generated during polymerization. The fractions of polymers and dead polymers decrease with increasing the NOC. However, the fractions of dead polymer are larger than 0.5. If all the termination were made by combination, the fraction of dead polymer would be 0.5. This difference must be due to the contribution from dead-end polymers formed by the cessation of self-avoiding walk. The contribution of dead-end polymer will decreases as the NOC increases; from 24% for NOC = 6 to 8% for NOC = 18.

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