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Off-Lattice Long-Range Percolation Modelling of a Network Polymerisation

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SUMMARY: A system involving homopolymerisation of a 3-functional monomer has been studied by using an off-lattice long-range percolation model. The elementary reaction steps were controlled by substitution effects and by local concentrations of units. The latter were controlled by setting a constant value to a range-of-reaction parameter called the capture radius. The critical conversion at gelation in the system turned to the classical one as the value of capture radius increased.

Introduction

The physics of aggregation processes is often classified into two groups. The first is the *chemically limited aggregation*(1) where chemical reactions between species are the aggregation driving force. The other group constitutes the *diffusion-limited aggregation*(2,3) processes with the mass transport determining aggregation mechanisms. Network polymerisation clearly belongs to the first group. The specific properties of polymers, however, cause network polymerisation to change from a purely chemically limited process to a diffusion-limited one. Even in a system where, at the beginning of the polymerisation, the reacting species (units, reactive groups, reactive sites, etc.) wander essentially freely through the whole system before a chemical reaction step takes place, the conditions of aggregation change dramatically when the system passes the gel-point conversion. Then, an increasing part of the system becomes more or less motionless. In particular, the assumption typical for the mean-field or classical approaches(4,5) usually applied to model network polymerisations, namely the lack of spatial correlations or, in other words, the equal probability of reaction between any pair of reactive sites in the system, often cannot be met in reality. This was one of the reasons why, beside the classical models of network polymerisation, both statistical and kinetic ones(6-8), computer-based models have frequently been used. The latter either allow for the relaxation of some unrealistic assumptions, such as the lack of cyclization (pseudo-classical models), or make use of site percolation modelling either on lattice or off-lattice. Lattice site percolation is a series of computer experiments which start with molecules or their

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fragments placed on the nodes of a lattice of predetermined geometry.$^{9-11)}$ Links are introduced at random and the changes in the size distribution of resulting aggregates are accounted for. In most cases, the molecules are left motionless during percolation experiments. In the so called off-lattice simulations$^{12-15)}$ the reacting system is just diluted compared to the lattice experiments since any set of two, three or more numbers determines an available position of a node in the system of dimensionality two, three, or more, respectively. The accuracy of the number representation in the computer determines the lattice mesh size in the 'off-lattice' experiments.

The gel-point conversion and the system structure in its vicinity of the gel-point is a very sensitive measure of the course of a network polymerisation. The critical gel conversion depends first of all on the functionalities of reagents and on the amount intramolecular links$^{16)}$ closing cycles. It also depends on the availability of the reaction partners in the system as the big molecules have a limited freedom of finding reaction partners in the vicinity of and beyond the gel point.

In this work we have studied the effect of availability of units for reaction by restricting the distance over which a unit could move by, say, diffusion, until it binds a partner. This range of distance, called the capture radius, was changed in the model from the close neighbourhood of the unit to the entire reacting system.

The Model

A simple off-lattice model of network polymerisation has been used. The model was partly based on ideas of Eichinger et al.$^{12,13,15)}$ The following standard assumptions were made:

1. Reactions between units were assumed to be second order.
2. The reactivity of functional groups did not depend of the size of molecule to which they were attached (Flory's postulate).
3. The reactivity could, however, depend on the substitution degree of the unit the group belonged to (units react according to the *first shell substitution effect*$^{6)}$).
4. Cyclization reactions were neither excluded nor promoted.

The units were gradually placed at random positions in the virtual reaction space and remained motionless during the whole simulation. The reaction space was a cube of size 1.

A fragment of the polymerisation system is shown schematically in Fig. 1. A unit chosen at random could react with any partner present in its vicinity, i.e., laying within the sphere of predetermined radius z ($0 < z \leq 1$), called the capture radius. At $z = 1$ the system was the classical one.

The other parameter affecting the number of potential reaction partners of a given unit was the concentration of units. In this work, the simulations were carried out in 3D space and the concentration of units was constant and equal 10^{-5}. The standard periodic boundary conditions[17)] were used while building the reaction system.

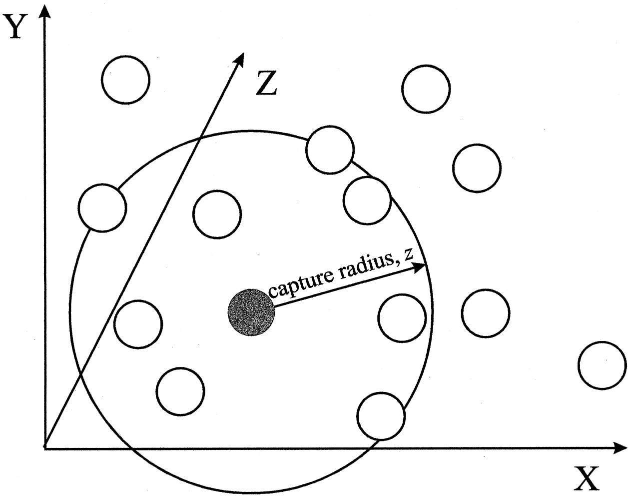

Fig. 1: A fragment of reacting system in the model network polymerisation. A reaction partner for the selected unit (shaded one) had to lay within the sphere of radius *z*.

The substitution effect was modelled as proposed by Gordon and Scantlebury[6)] and since widely used in polymerisation modeling[4,18,19)]. Accordingly, up to 6 types of elementary reactions could be distinguished in the homopolymerisation of a 3-functional monomer. These were the reactions between units of different substitution degrees. The appropriate rate constants took the form

$$K_{i,j} = (f - i)k_i \cdot (f - j)k_j \tag{1}$$

where the actual rate constant $K_{i,j}$ for the reaction between f- functional units of substitution i and j is the product of elementary rate constants k_i and k_j representing reactivities of respective unreacted functional groups.

The Algorithm

An one-dimensional array of N entries was defined in the computer memory to keep track of the reaction state of all N units. Each unit was identified by vector $\mathbf{b} = (x, y, z, s)$ where x, y, z were the position coordinates ($0 \leq x, y, z \leq 1$) and s was the number of the molecule to which the unit belonged. Other parameters describing the actual state of the system were the vectors $\mathbf{H} = (H_0, H_1, H_2, H_3)$ storing the numbers of units of substitution degree 0,..,3 and $\mathbf{N} = (N_1, N_2, \ldots N_i)$ with the numbers of molecules having different polymerisation degrees, (the size distribution vector). The extent of reaction was expressed in terms of the conversion degree, p defined as the ratio of reacted to total functional groups. The probability of a given reaction step was controlled by the values of the elementary rate constants, k_0, k_1, k_2.

The computer code contained procedures performing the following steps:

1. Create the system and initialise all parameters.
2. Choose a unit to react.
3. Identify the unit neighbourhood (controlled by capture radius).
4. Select a partner unit to the chosen one within the neighbourhood.
5. Calculate reaction probability.
6. Verify whether or not the reaction can occur and, if not, return to point 2.
7. Introduce the link between selected units and update the reacting parameters.
8. Return to point 2 unless the system has reached full conversion.

Depending on the set of input parameters, a single simulation for the system of size $N = 10^5$ units took from one hour to several days on an average PC.

Results and Discussion

The model polymerisation system consisting of N=10^5 units of functionality 3 was studied. Since in the long-range percolation simulations, the threshold probability (gel-point conversion) cannot be determined in the typical way, i.e., by analysing connectivity, we have applied the method used in the pseudo-classical modelling of polymerisation.[5,16)] The method involved determination of the peak value of weight-average polymerisation degree of the sol fraction. Fig. 2 illustrates the changes of this value for different capture radii. It is not difficult to see that as the capture radius increases, the percolation probability (here equivalent to the critical conversion at gelation) approaches that of the classical, mean-field value of $p = 0.5$.[20)]

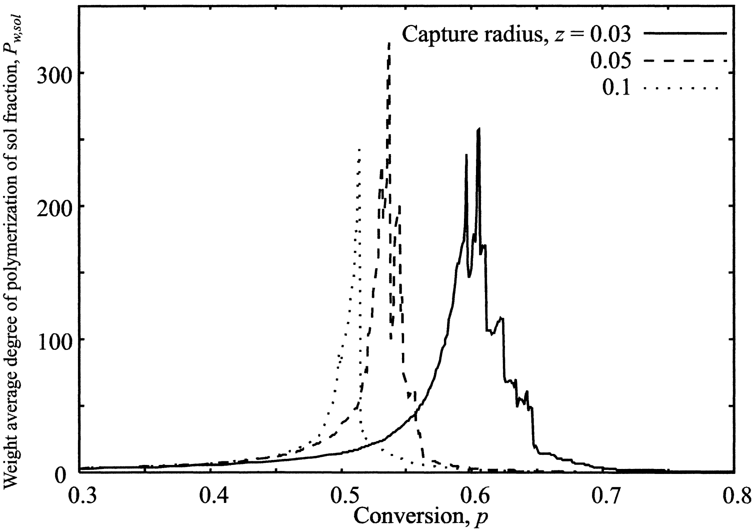

Fig. 2: The weight-average polymerisation degree of sol fraction vs. conversion of functional groups at 3 different values of capture radius z. The system size N=10^5. No substitution effect is taken into account: k_0=k_1=k_2=1.

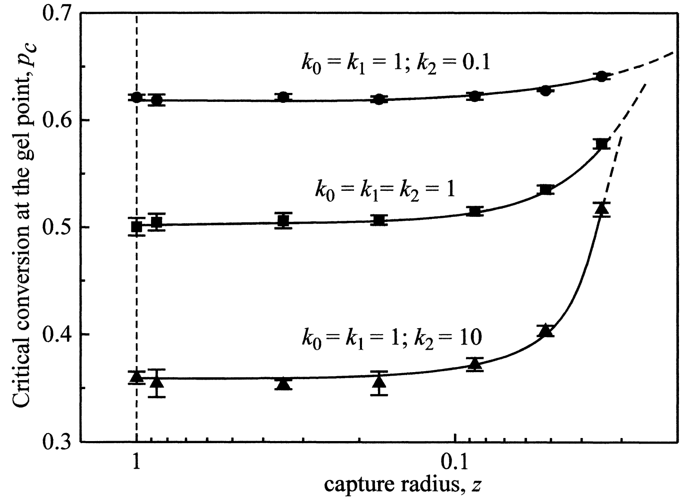

Fig. 3: Critical conversions at the gel point, p_c vs. capture radius at the specified sets of elementary rate constants.

The shifts in the gel point caused by both the substitution effects and variations of capture radius are summarized in Fig. 3. Each point is the average value from 6 simulations and error bars represent standard deviations.

The changes in gelation conversion depend on the capture radius in the similar way for each combination of elementary rate constants. The critical point move towards high conversion as the capture radius decreases. It is interesting that the shift is significant only when the capture radius becomes relatively small, i.e., less than ca. 0.1. Then, the critical conversion dependence on capture radius is marked; particularly for the case where the branching in the system is favoured ($k_2 = 10$). That system gels at the lowest conversion of functional groups. One should also bear in mind that for the very small z (say, less than 0.014) no reaction is possible since this value roughly corresponds to the average volume of just one unit. Hence, no gelation occurs for very small capture radii.

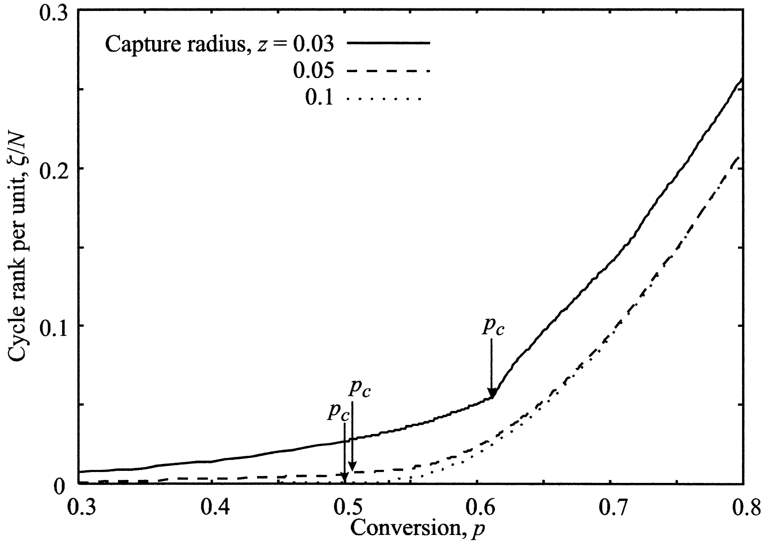

Fig. 4: The cycle rank (independent number of cycles) per unit in the model off-lattice network polymerisation of a 3-functional monomer. The system size, $N = 10^5$ units. No substitution effect is taken into account: k_0=k_1=k_2=1. The critical conversions at gelation, p_c, are shown in the plot.

At small values of z, the probability of selecting the same unit as the reaction partner is greatly enhanced as compared with the classical limit. The cyclization reaction becomes favoured and the number of cycles in the system increases accordingly. This is shown in Fig. 4 where the fractions of cycles formed in the system are plotted against conversion for different capture radii. Obviously, the fraction of cycles increases with conversion, but the increase is the more significant the smaller is capture radius. For small z the fraction of cycles in the system is relatively high, even prior to the critical conversion at gelation, p_c.

Acknowledgements

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