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Monte-Carlo modeling of degradation of polymer networks: 3. Lattice networks☆

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Abstract

The degradation of polymer networks with three functional junctions has been studied by using Monte-Carlo techniques. The networks were formed on 2D square or 3D cubic lattices in a random process with chains spanning junctions fixed at the distance not exceeding a predetermined value. This value has been found to have an effect on the degradation process that followed. The degradation degree at the gel–sol transition was the lowest for the networks formed in the nearest-neighbor percolation processes. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Percolation networks; Network structure; Model networks

1. Introduction

The processes of polymer degradation were modeled theoretically essentially for linear macromolecules only. The early models made use of statistical arguments [1–3]. A study on the degradation of branched polymers was carried out by Demjanenko and Dušek [4] who used the cascade theory. Similar systems were studied by Tobita [5]. Kinetics models were also used to study the evolution of polymer size distribution during degradation processes [6–8]. More recently, Monte-Carlo computer simulations were applied by Emsley and Heywood [9] who studied the degradation of linear chains with arbitrarily weighed probability of chain scission. Guaita et al. [10] used a Monte-Carlo algorithm developed by Malác [11] and followed the changes in polydispersity of a system comprising linear chains. A quick algorithm for a similar type of study was recently described by Shyichuk [12,13]. Yushanow et al. [14] and Gyure and Edwards [15] studied degradation of networks and lattice clusters, respectively, by using percolation models.

A Monte-Carlo degradation study of random model networks [16] and highly branched molecules [17] was described in our previous papers in the series. The degradation process has been found by us to be affected by the structure of a (virtual) network, namely by its topology. The latter, on the contrary, depended on the way the network was created in computer memory prior to the degradation experiment.

2. The model

The networks studied in this work were nearly ideal trifunctional networks. They consisted of 10^4 units (junctions) from almost all of which extended three links. One may assume that each link represented a linear chain. In the first step of the Monte-Carlo degradation experiment, a network was generated by linking junctions (units) placed on a lattice. A randomly chosen junction could be linked with a partner located in the hypercube of the edge length $2l + 1$ where l was the number of partner junctions on the lattice in a direction along its edge (cf. Fig. 1). Thus, the partner for the linking act was a unit selected from among $(2l + 1)^D - 1$ ones in the hypercube (D is the dimensionality of lattice). This procedure is known as the so-called *long-range bond percolation* [18,19]. It became the “ordinary” or the *nearest-neighbor percolation* when l was 1. In most of our experiments the square lattice was used with the usual periodic boundary conditions [20].

A fragment of the lattice at which the network is formed is presented in Fig. 1. The junction selected at random (filled circle) may be linked only with a partner located within its

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☆ Part 2, see H. Galina, J. Lechowicz, Polm. Gels Networks 6 (1998) 247.

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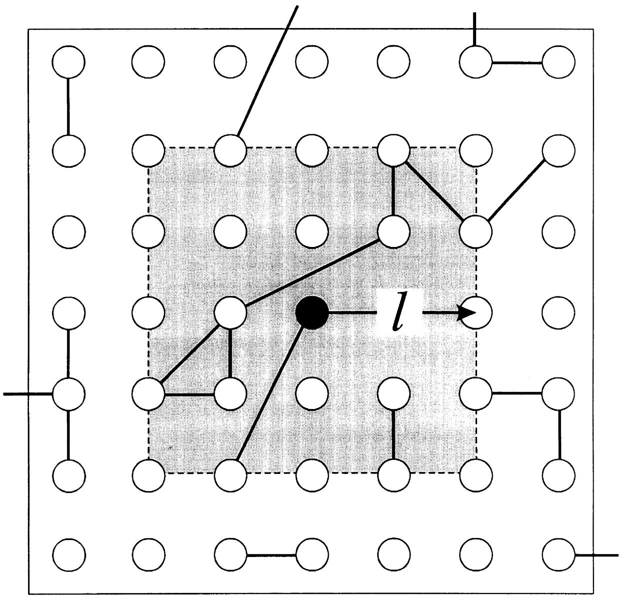

Fig. 1. A reacting system on the square lattice. The linking range $l = 2$. The junction selected at random (filled circle) may react only with the partners within the shaded square. The already existing links are shown.

vicinity determined by the largest distance l latter referred to as the linking range.

The linking range significantly affects the structure of the resulting lattice animals (molecules). The network formation process approaches the classical or mean-field end-linking one when l becomes sufficiently large. Only then the cycle closing links can appear between junctions located at an arbitrary distance from each other. Consequently, in the linking process, the probability of selecting junctions belonging to the same molecule becomes small, particularly prior the gel point when the molecules are generally small. Therefore, in the large-linking-range networks the number of cycles prior to the gel point is negligible.

On the contrary, in the short-linking-range network formation, the amount of cycles is significant from the very beginning of simulation. This is the result of the limited number of partner junctions for the selected one to react. One observes the formation of many multiple links that practically do not appear in the large-linking-range networks. These multiple links are in later procedures treated as cycles. One should bear in mind, however, that in the final network prepared for the degradation experiment, the total amount of cycles is necessarily the same for any linking range since nearly all "functional groups" are reacted. To summarize, the difference between the random networks prepared at various linking ranges is in the cycle sizes and the amount of multiple links.

The virtual random networks created as described above were then the subject of degradation experiments. The algorithm used in the experiments was the same as that already described [21]. It was constructed in such a way that the rate at which a link was split depended on the substitution degree of the adjacent units. The contribution of this substitution effect was modeled in the same way as proposed by Gordon and Scantlebury [22], i.e. the rate constants had the product form [21]. The effect of junction substitution degrees is not, however, presented in this paper. As usual, the binary degradation mechanism was adopted, i.e. only one link could split in the single degradation step. Although the individual links represented polymer subchains, they were disregarded in the further process as soon as they happened to get split.

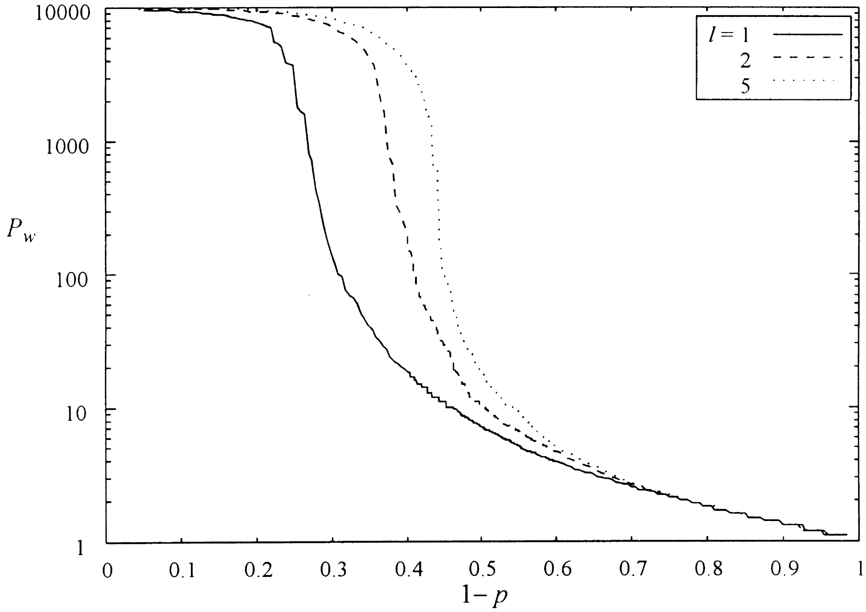

Fig. 2. The weight average degree of polymerization during the degradation of networks prepared with the linking range $l = 1$, 2, and 5 on the 2D square lattice.

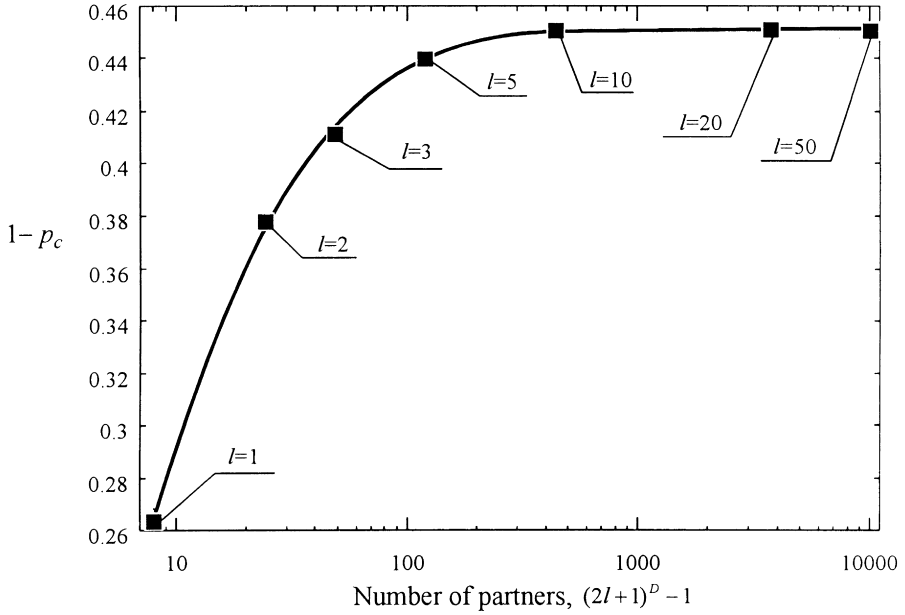

Fig. 3. The critical degradation degree at the gel–sol transition for 2D networks vs. the number of reaction partners at the formation stage. The corresponding linking ranges during the network formation are indicated. The critical degradation degrees are average values from at least five simulations. The standard deviation of their determination did not exceed 0.01.

3. Results and discussion

The degradation of polymer networks consisting of 3-functional junctions created on 2D and 3D lattices has been studied. In two dimensions, the square lattice of size 100×100 junctions was used. The 3D lattice was the simple cubic one of the size 22^3. Hence, in both cases the reaction system consisted of ca. $N = 10^4$ junctions. For each set of parameters the simulations were carried out at least five times. Some simulations were made for larger systems of 2.5×10^5 units with apparently no effect to the results compared to those for the standard system size.

The changes in the weight average degree of polymerization, P_w, taking place during the degradation of a network on the square lattice are shown in Fig. 2. As in our previous works [16,17,20], the degradation degree $1 - p$ was used as the measure of the extent of degradation (p was the fraction

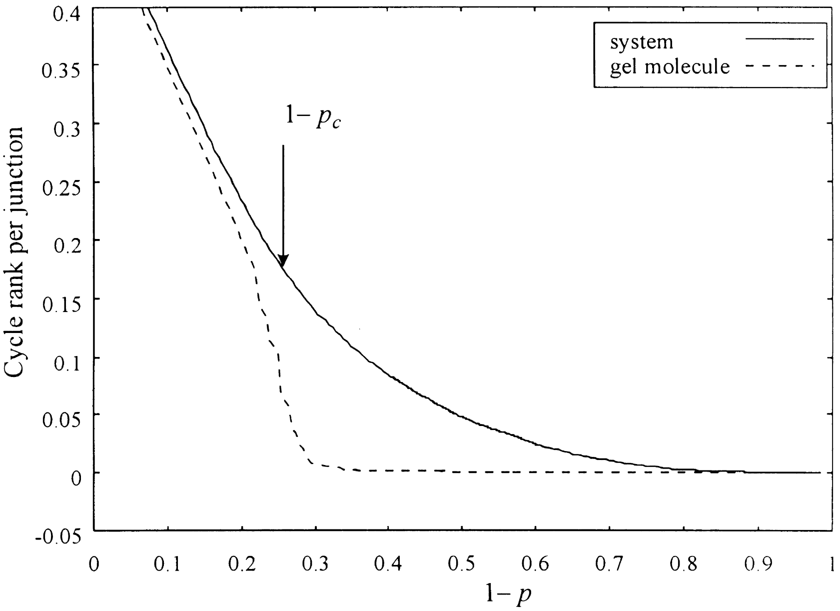

Fig. 4. The number of cycles per junction in the whole system (solid line) and in the gel molecule (broken line) during the degradation of a 2D network prepared by the nearest-neighbor percolation (linking range $l = 1$).

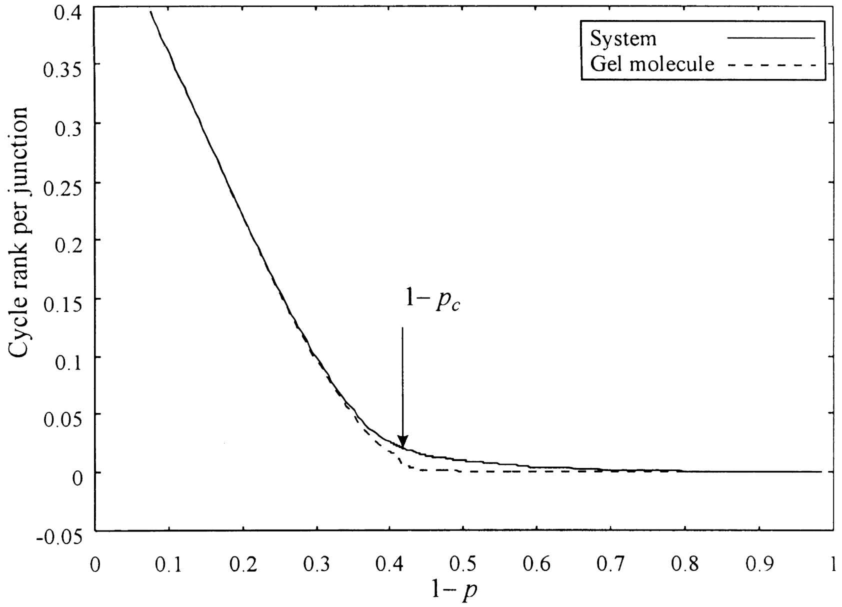

Fig. 5. The number of cycles per junction in the whole system (solid line) and in the gel molecule (broken line) during the degradation of a network prepared on the square lattice with the linking range $l = 3$.

of all possible chains that could extend from junctions; there were at most $3N/2$ such chains).

The inflection point on the curves presented in Fig. 2 can be treated as the critical gel–sol transition point. As in our previous papers [16] the position of this point was determined as the degradation degree at which the weight average polymerization degree of the sol fraction reached its maximum. The sol fraction was the total of all molecules except the largest one. The latter was the gel molecule.

The position of the gel–sol transition point on the degradation degree scale was found to depend strongly on the network structure which in turn was related to the linking range during its formation. For the 2D networks, the critical degradation degree of the gel–sol transition is plotted in Fig. 3 against the number of reaction partners for the selected junction during the network formation. The corresponding linking ranges, l, are also shown. As one can see in Fig. 3, the critical degradation degree is shifted towards higher values as the linking range, l, increases. It seems that as small a range as $l = 10$ is

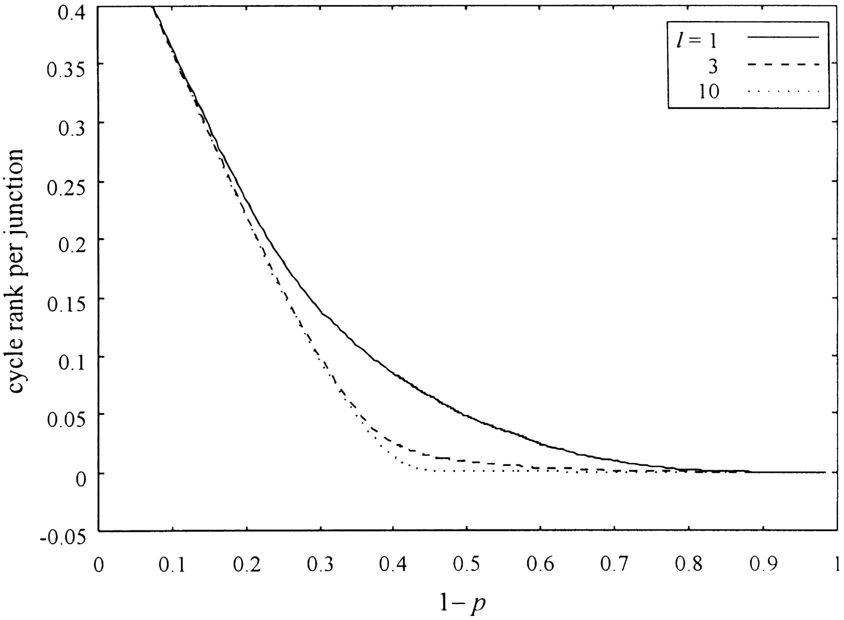

Fig. 6. The of cycle contents (per junction) vs. degradation degree in 2D networks prepared at various linking ranges.

sufficient for the critical degradation degree to reach its mean-field value of 0.45, the same as determined in [16]. Similar, but less pronounced effects were observed for the 3D networks. The mean-field critical value of the degradation degree was reached already at the linking range of $l = 3$. Even at l equal to 1 or 2, the gel–sol degradation degrees were smaller than the mean-field ones by several percent only.

The shift in the degradation degree in the critical gel–sol transition was caused by the differences in the network structures. As mentioned above, the lower the linking range, the larger was the number of multiple links between units. The effective cross-linking degree of such networks was therefore smaller than for the mean-field networks. Lesser number of scissions were necessary to split the network into smaller parts. Accordingly, the number of cycles in the fragments that were formed from the networks including the multiple links remained relatively large. The cycle rank (number of independent cycles) [23] per unit in the whole system and in the gel molecule alone are compared in Fig. 4 for the 2D network created with the range $l = 1$ (nearest-neighbor percolation). It is peculiar that the number of cycles in the gel molecule for that network rapidly decreases and becomes close to none just after the gel–sol transition. All the remaining cycles present in the system are distributed among the small sol molecules. Most of them are likely to be multiple links.

The 2D networks created with $l > 1$ behaved during degradation similarly as the mean-field ones. For the network prepared at the linking range $l = 3$ the curves showing the changes in cycle rank in both the whole system and in the gel molecule lay close to each other. It is shown in Fig. 5.

As one can see in Fig. 5, at the gel–sol transition point the number of cycles in both the whole system and in the gel molecule drops nearly to zero. At the still higher value of the linking range during the network formation, the curves similar to those presented in Figs. 4 and 5 become indistinguishable. The amount of cycles beyond the gel–sol transition is close to none. This suggests that sol particles are essentially acyclic. This conclusion well agrees with the classical interpretation of the degradation processes according to which it is the gel molecule that contains all the cycles.

The rate at which the number of cycles in the system approaches zero increases, as the reaction range at which the network was created becomes larger. It is shown in Fig. 6. This is another indirect evidence for the larger cycle size in the networks prepared in the long-range percolation experiments. The nearest-neighbor percolation method of modeling network formation is known for preferring formation of large amounts of small cycles [24].

Acknowledgements

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