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Kinetic Gelation Model

Qualitative Percolation Study of Free-Radical Cross-Linking Polymerization

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SUMMARY

Simulations of a conceptually simple model for free-radical cross-linking polymerization have been performed in relation to experimental indications for (temporary) microgel particles. Many qualitative features ascribed to microgels show up in the simulation. In particular this model yields qualitative agreement with experiments on the conversion dependence of the number of pendant double bonds.

INTRODUCTION

The extent of inhomogeneity in amorphous polymeric materials is an unexpectedly difficult issue, experimentally as well as theoretically. While linear polymers are now believed to be homogeneous, there are strong indications that many cross-linked polymers are not. We are concerned with networks obtained by free-radical polymerization for which Dušek et al. (1) and Galina and Gordon (2) have summarized the arguments for inhomogeneity (see also (3)-(5)). The following picture emerges : Soon after the start of the reaction "microgel" particles are formed, macromolecules that are highly cross-linked and contain pendant double bonds (PDBs,i.e. unreacted vinyl groups on polymer segments) which are shielded (6) from further reaction by stiff, fully reacted polymer segments. In this context the sharp drop of the relative number of PDBs in the polymer at the beginning of the reaction (indicating strong cross-linking) followed by a very slow decrease (indicating shielding) is interpreted as one of the indications for inhomogeneity (7). In this paper a conceptually simple mathematical model is presented which accounts qualitatively for these experimental findings concerning (transient) inhomogeneity.

MODEL DESCRIPTION

The elegant analytic theory by Flory (8) and Stockmayer (9), formulated in terms of generating functions and extended by Gordon and co-workers (see e.g. (10)) describes many aspects of gelation quite satisfactorily, but is not able to treat the present case, where the formation of a cross-link strongly depends on the local concentration of cross-links that have already been formed (11). Therefore we resort to computer simulation to study the extent of inhomogeneity in a model system. The model we use was introduced by Manneville and De Sèze (12) and has been studied by several authors (see e.g. (13)-(18)). It is known as the "kinetic gelation model". We start with a square or cubic

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lattice of point-like monomer molecules so that the two vinyl groups of a divinyl monomer occupy the same lattice site. A fraction c_b of the molecules has two functionalities (one vinyl group), a fraction $1-c_b$ has four functionalities.

Initiation at a constant rate is simulated by transforming randomly chosen monomer sites into radical sites at a rate of time which is much slower than the propagation rate. Propagation is simulated in the following way. Every time unit we select a radical site and one of its neighboring sites at random. If the neighboring site has no free functionalities left (is fully saturated) nothing happens. Otherwise, a bond is formed and the number of unreacted functionalities for both sites is reduced by one. The radical is shifted to the neighbor site if this site does not contain a radical; if it does, the radicals are terminated by a combination reaction. In this way each radical performs a random walk on the lattice until it is terminated or trapped between fully reacted neighbors. In the literature this model is mainly used to describe properties in the neighborhood of the gel point. Sometimes a mixture of bi- and tetrafunctional units has been used to vary the cross-link probability (15-17); sometimes an unreactive solvent was present and solvent and monomer motions (not polymer-segment diffusion) were taken into account (16).

THE TOPOLOGY

In order to get a qualitative idea of the topology of the system in this model we have simulated the polymerization in various situations and produced snapshots of several stages for the two-dimensional case.

Figs. 1a-c are parts of such snapshots for a polymerization on a two-dimensional square lattice, all taken at the same value of the weight conversion α. Fig. 1a is a snapshot of a free-radical polymerization of pure tetrafunctional monomer; in Fig. 1b the fraction of bifunctional monomer is $c_b = 0.90$. There is no significant difference in inhomogeneity between these figures. However, at the given value of α the largest macromolecule is much larger for the first system than it is for the second, while the number of cross-links is a factor of ten smaller and the number of macromolecules a factor of six larger. Therefore, if we would introduce mobility of polymer segments, the second system, which contains many small macromolecules with few rings, has much more freedom than the first one to relax to a more homogeneous situation by the diffusion and swelling of macromolecules.

Fig. 1c shows a snapshot for step-wise polymerization with $c_b = 0$. This model, which is known as "restricted-valence percolation" (19), differs from the model for chain reactions in that all sites are eligible to chemical reaction with an arbitrarily chosen neighbor, whereas in the chain-reaction model only radical sites are. The difference in homogeneity and macromolecular sizes between Figs. 1a and 1c is striking.

Many such snapshots have been compared. For example we saw more ramification in a percolation model, defined by Pandey (17); in this model the probability of forming rings is reduced (20). In order to corroborate our results it is planned to calculate the radius of gyration as a function of macromolecular size for several reaction stages.

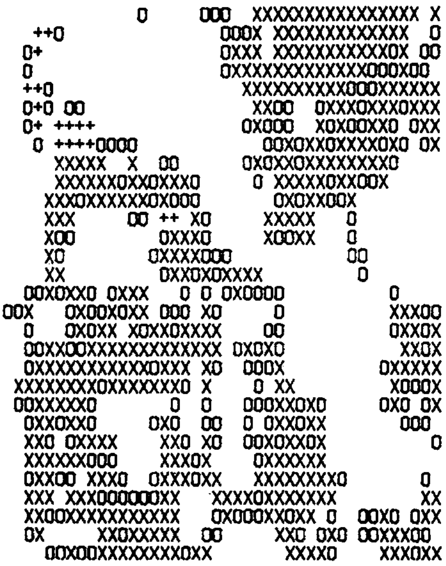

Fig. 1a. Chain reaction $c_b=0$
$\alpha_b=0.47$, $n_x=917$, $m=6$

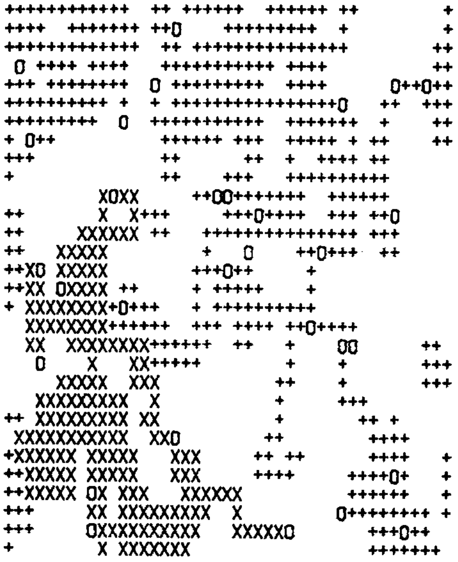

Fig. 1b. Chain reaction $c_b=0.9$
$\alpha_b=0.30$, $n_x=93$, $m=35$

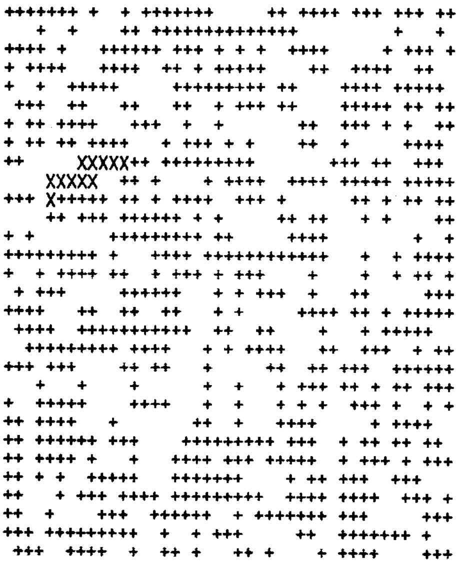

Fig. 1c. Step reaction $c_b=0$
$\alpha_b=0.22$, $n_x=141$, $m=482$

Fig. 1. Parts of snapshots of simulations on periodic 50x50 lattices for the weight conversion $\alpha=0.44$. A blank denotes a monomer site, X a site belonging to the largest cluster and + any other polymer site. In figs. 1a and 1b for chain reactions 0 denotes a (shielded or unshielded) PDB; in fig. 1c partly and fully reacted sites are not differentiated.

c_b is the fraction of bifunctionals;
α_b is the bond conversion;
n_x is the number of cross-links;
m is the number of clusters.

PENDANT DOUBLE BONDS

In Figs. 1a and 1b the PDBs are indicated by O. One sees that some of the PDBs within polymer-rich regions are completely shielded from further reaction by fully reacted sites; a high concentration of unshielded PDBs is found at the boundaries of the polymer-rich regions. In Fig. 2 b(α), the number of PDBs per divinyl repeat unit in the polymer, is plotted for three dimensions as a function of weight conversion α.

The drawn and dashed curves are model calculations for $c_b = 0.70$ and 0.92. The upper drawn and dashed curves are obtained if we exclude the return of a radical to a position it has just left; the lower ones are obtained without such restriction. This extra rule may be relevant for styrene/divinyl benzene polymerization where the benzene ring forms a stiff bridge between the vinyl groups so that a vinyl group cannot react with two ends of the same divinyl unit for steric reasons. Results of such experiments by Malinský et al. (7) are also shown in the figure, together with their calculation (dotted curve) for $c_b = 0.70$. They attribute the difference between their experiment and their calculation, which is based on homogeneous reaction conditions, to the existence of local inhomogeneity.

The simulation results are seen to be in qualitative agreement with experiment in the sense that the initial sharp drop is described correctly and that both in experiment and model a slow decrease of b(α) follows this sharp drop. (From additional calculations it is found that this qualitative behavior also occurs for one macromolecule growing on an infinite lattice. If we raise the initiation concentration to unusually high values, b(α) is raised for low conversion but not for high conversion, so that the initial drop becomes less pronounced.) A clear difference between theory and experiment is that the slow decrease is slower in the experiment than in the model for $c_b = 0.70$ and $c_b = 0.85$. This leads to important discrepancies at high conversion. A further, possibly related difference is the effect of varying c_b. This effect is much greater in the experiment than in the model and it is of the opposite sign.

Similar conclusions are obtained from a comparison between the present model and an experiment by Aso (21) on ethylene glycol dimethacrylate (c_b = 0). For step reactions quantities similar to b(α) have been calculated. In that case there is no qualitative difference between a simulation model and a model without local structure.

DISCUSSION

The present simulation model accounts qualitatively for the experimental conversion dependence of the number of PDBs. In view of the simplicity of its rules and the lack of adjustable parameters the agreement at low conversion is remarkably good. The disagreement at high conversion may be due to the underestimation of the shielding of PDBs by fully reacted polymer in the model, but it cannot be excluded that part of this disagreement may be explained by the occlusion of monomer within fully reacted polymer. This would cause incomplete extraction and hence an underestimation of the weight conversion determined in the experiment (except, possibly, for experiments at high c_b). However, we do not believe that monomer occlusion alone will explain the differences between model and experiment. We hope that the results of the model will stimulate further experimentation, especially on the high-conversion behavior of the number of PDBs.

These results are qualitative. They show that the main features ascribed to inhomogeneities in free-radical polymerization follow from a simple simulation model that does not include polymer segment diffusion, polymerization shrinkage and specific information, like e.g. the chemical structure of the monomer.

Polymer segment diffusion can only be introduced in an off-latice model to avoid artificial constraints. Such a simulation would be very hard, but it is considered to study the growth and relaxation of one macromolecule in order to estimate the importance of diffusion. The extra mechanisms that influence compaction if diffusion is included are

- the improbability for an accidentally dense (and thus highly cross-linked) cluster in the statistical ensemble to expand, and the high probability of an extended macromolecule to relax to a more probable, denser configuration by brownian motion;
- a possible preference of polymer segments to polymer-segment neighbors, especially in the presence of a bad solvent for the polymer;
- the longer lifetime of a growing radical in a dense cluster compared to one in a more dilute environment; in reality, radical termination is controlled by diffusion (not by growth, as it is in our model) and diffusion is slow within dense clusters;
- the difference in swelling behavior, which causes macromolecules to be less compact in systems that contain a higher fraction of bifunctionals; this effect, which we discussed in connection with Fig. 1b, may qualitatively explain the fact that systems with a high concentration of cross-linking agent (small c_b) have a low viscosity (22) or a high permeability (3).

Polymerization shrinkage may also lead to inhomogeneity, if the local shrinkage is only slowly converted to total-volume shrinkage (23). These effects cannot easily be incorporated in a numerical model. However, they are not necessary for a qualitative interpretation of experimental results ascribed to inhomogeneity in free-radical polymerization.

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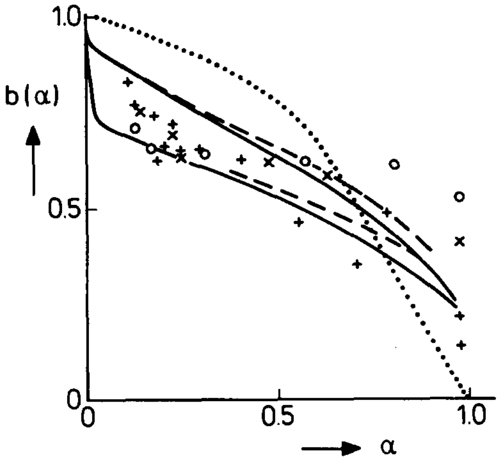

Fig. 2. b(α), the number of PDBs per divinyl repeat unit as a function of weight conversion α. Experimental results (7) are indicated by 0 (c_b=0.7), x(c_b=0.85) and + (c_b=0.92). The dotted curve (7) is calculated for c_b=0.7 by disregarding local structure. Drawn curves are averages over 50 runs of the present model on a 20x20x20 lattice for c_b=0.7; dashed curves for c_b=0.92. The upper drawn and dashed curves are obtained if a radical cannot "step back"; the lower ones are obtained without this restriction.

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