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Polymerization in non-uniform reaction fields: Monte Carlo description of structure buildup during photopolymerization

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Abstract. — A Monte Carlo 3D off lattice percolation in a non-uniform reaction field is reported. Monomers are simulated as point particles of functionality (coordination number), \( f = 3 \). The non-uniform field is expressed as an exponentially decaying reaction probability in one dimension tailored to simulate the photopolymerization process. It is argued that tubular reactors and other polymerizations in non-uniform fields will show similar qualitative features. Two cases of molecular mobility are studied. In the first limit molecules can only react in immediate neighborhoods corresponding to diffusion limited growth. In the second any two units can react. Results based on the distinction of whether one or both units must be activated before reaction are reported. It is found that for the particular type of non-uniform field considered reaction gradients result in inhomogeneous gelation at low conversions. Reaction gradients cause large spatial heterogeneities in the size distribution of the molecules and also introduce large polydispersities. These results are compared with recent experimental observations on photopolymerizations and tubular reactors.

Introduction.

Existence of reaction gradients, either as thermal or momentum non-uniform fields, or other external non-uniform sources like light, can significantly effect the structure of reacting materials. In this paper the effect of reaction gradients on structure evolution during polymerization is discussed. The simplest everyday example of non-uniform polymerization is the baking of bread or cookies, where the outer crust or skin is formed because of the higher temperatures experienced on the outside.

The classical models of structure evolution during polymerization are based on the mean-field assumption [1]. Mean-field models require that the field over which the particles interact (the entire reaction volume) be free of fluctuations [2]. Such models are suited for well stirred batch reactors with bulk stepwise polymerization [3]. However there are many cases where

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polymerization reactors are not well stirred resulting in non-uniform reaction fields. Non-uniform reaction fields can be loosely categorized as either self-generated or externally induced. Self-generated, non-uniform fields are always present to some extent in all polymerizations. For example, reaction kinetics introduce non-uniform thermal fields if the reactor is not sufficiently stirred. Similarly the viscosity and glass transition temperature changes accompanying polymerization may also result in non-uniform polymerization.

An illustration of an external non-uniform reaction field is a tubular flow reactor with a parabolic velocity profile which is of considerable technological importance [4-6] (see Fig. 1b). Here, since the material flowing closer to the walls spends more time in the reactor a gel layer is formed next to the wall which grows towards the center. Generally the flow in such reactors is laminar with little or no turbulent mixing.

Temperature profiles in the reactor also result in varying rates of reactivity for different functional units given by the Arrhenius temperature dependence of the kinetic rate constant.

![Diagram of exponential light gradient in a cylindrical photopolymer sample](image1)

![Diagram of laminar flow profile in a tubular reactor](image2)

Fig. 1. — a) Exponential light gradient in a cylindrical photopolymer sample. On the right the shading indicates varying level of polymerization, darker material being more reacted. b) Laminar flow profile in a tubular reactor. The bottom reactor shows the gel layer next to the wall.
Such non-uniform temperature profiles could be generated in a non-isothermal reactors by heat of reaction, or could be externally imposed along the length of the reactor [6].

A third kind of reaction gradient exists in photopolymerizations where polymerization is induced by a suitable light source. Here since the degree of polymerization is proportional to the intensity of light, and the intensity of light decays as it travels through the sample, non-uniform polymerizations are expected (see Fig. 1a).

The purpose of the present work is to investigate the effect of non-uniform reaction fields on structure evolution during polymerization. The case of photopolymerization is studied but the conclusions of this work apply to any polymerization in a non-uniform field. The results are reported for an off lattice percolation in a reaction gradient. To facilitate a clear physical understanding of the problem, the simplest possible chemistry, stepwise \( A_f \) homopolymerization, is studied, which is equivalent to a percolation model with particles of fixed coordination \( f \).

Most photopolymerizations are free radical, not stepwise chemistries [7]. Structure evolution in free radical polymerization is not satisfactorily understood and much less so with the added complication of a reaction gradient [8]. This limits any direct comparison of these simulations with experiments. Therefore in keeping with the philosophy of this work the present results should be taken as a qualitative measure of all effects studied. The stress here is on concepts and not numbers.

The rest of the paper is arranged as follows: a brief description of the Monte Carlo method follows this introduction. Then the results for the various cases are reported followed by a discussion.

**Monte Carlo Code.**

The Monte Carlo code on which the present work is based was originally reported for a study of diffusional effects in \( A_f \) homopolymerization by Gupta et al. [9]. The complete structure of the algorithm as well as the basic philosophy is discussed in that paper. The barest details are reproduced here with emphasis on the new developments.

\( N \) point particle monomers of \( f = 3 \) functionality (coordination number) are randomly distributed in a cube. For the purposes of calculating the dimensions of the cube they are imagined to have the volume of a sphere of unit radius. Periodic boundary conditions cannot be used in the \( z \) direction because of the reaction gradient so they are only used in the other two directions. To compensate for the enhanced finite size effect in \( z \) direction the cube length in the \( z \) direction-\( \ell_z \) is twice as long as in the \( x \) and \( y \) direction-\( \ell_x, \ell_y \). Then if \( \eta \) is the free volume in the system, or the vacancy volume, \( ( = 0.1 \) in all results reported here) the volume of the cube is given as:

\[
\ell_x \ell_y \ell_z = \frac{4 \pi N}{3(1 - \eta)} \tag{1}
\]

For uniform polymerization, two functional groups are randomly selected from the entire population until both groups are previously unconnected. Then, the probability of reaction of these two random sites is calculated and compared with a random number. If the random number is less, the sites are connected. The cluster size distribution is then upgraded and the procedure is repeated. For the Flory mean-field limit the probability of reaction is always unity irrespective of the spatial separation of the clusters and other factors. This correspondence was established in the previous work [9]. One simple way of introducing fluctuations is to reduce the interaction range from the entire volume, as in the Flory theory, to a smaller range. This effect was studied in the previous work by allowing sites to react only if they are within a distance \( r_h \) of each other [9]. Thus the reaction is mean-field within a sphere of radius

\[ r_h = \frac{1}{\sqrt{6}} \]
around each particle. Qualitatively, it can be argued that \( r_h \) represents, on the average, the distance a site traverses before encountering a successful reaction collision. The real picture is much more complicated because polydispersities and other effects must be considered. However this simple description reveals several interesting features. It was found that when \( r_h \) is only about 4 monomer radii the resulting growth is experimentally indistinguishable from the Flory limit for such parameters as gelation threshold and weight-average degree of polymerization \((\text{DP})_w\). This helps understand the rather surprising success of mean-field models in this context.

For non-uniform polymerization the probability of reaction must be biased by the reaction field. In photopolymerization the reaction field is exponentially decaying, proportional to the intensity of light. This can be incorporated in the reaction probability calculation with an additional term:

\[
p = k_1 e^{-k_2 z}
\]

Here \( z \) is the dimensionless coordinate measured from the surface where light enters the system. If both units must be activated before reaction the pair probability is used. In this paper results are reported for different values of \( k_2 \) with \( k_1 = 1 \). The case of reaction radius \( r_h = 2 \) is studied in detail. This corresponds to a process limited by mobility of the particles, activation and reaction are instantaneous. Results are also reported when \( r_h = \infty \), but here since the mean-field argument applies only with respect to molecular mobility and not activation the picture is rather artificial.

At regular conversion intervals structural characteristics of the population are calculated. The first three normalized moments of the size distribution function \( \Phi(n, \alpha) \): number-average \((\text{DP})_n\), weight-average \((\text{DP})_w\) and \( z \)-average \((\text{DP})_z\) degree of polymerization are:

\[
(\text{DP})_n = \frac{\sum n \Phi(n, \alpha)}{\sum \Phi(n, \alpha)} \quad (3a)
\]

\[
(\text{DP})_w = \frac{\sum n^2 \Phi(n, \alpha)}{\sum n \Phi(n, \alpha)} \quad (3b)
\]

\[
(\text{DP})_z = \frac{\sum n^3 \Phi(n, \alpha)}{\sum n^2 \Phi(n, \alpha)} \quad (3c)
\]

\( \alpha \) is the fraction of total sites that are connected. The summation for finite size simulations runs from 1 to \( N \)-the population size. For infinite population gel point is the conversion where \((\text{DP})_w\) and higher moments diverge. Techniques for estimating the gel conversion for finite size simulations have been discussed before \([9, 10]\). The reduced-average degree of polymerization \((\text{RDP})_w\) (same as \((\text{DP})_w\) with the largest cluster excluded in the sum), the slope of \((\text{DP})_w\) and the fluctuations of \((\text{DP})_w\) in phase space are used for ascertaining the gel conversion. The spatial heterogeneity induced by the gradient is studied in two different ways. The cube is divided into three equal zones \((j = 1, 2, 3)\) in the \( z \) direction. The weight-average degree of polymerization \((\text{DP})_w^z\) based on the center of mass of molecules in each of the zones is reported. The first three moments \((i = 0, 1, 2)\) of the center of mass \((\text{cm}_i^z)\) of the molecules are reported (projected on \( z \) axis):

\[
\text{cm}_i^z = \frac{\sum z_j n_j^i}{\sum n_j^i} \quad (4)
\]
The summation is over all molecules $j = 1$, $N$ of size $n_j$. $z_j$ is the $z$ coordinate of the center of mass of the $j$-th molecule.

Results.

There are two major sources of approximations in computer simulations: finite size effects and consequences of working in a limited phase space. In order to minimize the latter, all results are reported as averages and fluctuations for ten runs. For the former runs were performed for three different populations and are discussed first.

**Finite Size Effects.** — In the previous work a detailed analysis of FSE was reported [9, 10]. It was found that for a population of 100,000 monomers it is possible to determine the gel conversion and pre-gel structural information within 1% of the exact values. In the previous work periodic boundary conditions (pbc) were imposed in all three directions. In the present work pbc cannot be used in the $z$ direction because of a reaction gradient. Three monomer population sizes, $N = 1,000$, 10,000 and 100,000 were studied for the case of $r_h = 2$, $k_2 = 5$ and where both units must be activated before reaction. In figure 2a $(DP)_n$ is plotted and in figure 2b the fluctuations in $(DP)_n$ for ten runs are shown. It is noted that FSE are more pronounced for reaction in a non-uniform field. However, a two order of magnitude increase in $(DP)_n$ at the gel point is sufficient to determine the gel conversion accurately. The gel points as determined by the maximum in $(RDP)_n[\alpha_c^{\text{m}}]$ and the inflection point in $(DP)_n[\alpha_c^{\text{i}}]$ are compiled in Table I. The conversion at which the first maximum in fluctuations of $(DP)_n$ appears $[\alpha_c^{\text{d}}]$ is also tabulated in Table I. It is observed that $\alpha_c^{\text{m}}$ and $\alpha_c^{\text{i}}$ agree within 1%
Table I. — Gel conversion of different populations for $5 \otimes 5$ and $r_h = 2$. $\alpha_c^1$ from the maximum in the reduced weight-average molecular weight, $\alpha_c^2$ from the maximum in the rate of change in $(DP)_w$, and $\alpha_c^3$ from the maximum in fluctuations in $(DP)_w$ over ten runs.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\alpha_c^1 - (RDP)_w$</th>
<th>$\alpha_c^2 - d(DP)_w/d\alpha$</th>
<th>$\alpha_c^3$-fluctuations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,000</td>
<td>0.238 ± 0.008</td>
<td>0.237 ± 0.007</td>
<td>0.237</td>
</tr>
<tr>
<td>10,000</td>
<td>0.233 ± 0.005</td>
<td>0.239 ± 0.004</td>
<td>0.242</td>
</tr>
<tr>
<td>100,000</td>
<td>0.226 ± 0.002</td>
<td>0.228 ± 0.003</td>
<td>0.235</td>
</tr>
</tbody>
</table>

for the largest population and $\alpha_c^3$ is less accurate. Similar conclusions were reached in the previous work [9].

RESULTS FOR $r_h = 2$. — Four different cases were studied. If $a \otimes b$ reflects $k_2 = a$ for the first choice and $k_2 = b$ for the second choice with $k_1 = 1$ (see Eq. (2) for the exponential gradient term) then these four cases correspond to $5 \otimes 5$, $5 \otimes 0$, $2 \otimes 2$ and $0 \otimes 0$. Figure 3 shows some results for these four cases. From figure 3a, where $(DP)_w$ is plotted, if reactions occur only in local neighborhoods, as is the case here for $r_h = 2$, then there is no significant difference in whether both units must be activated or just one (see the case $5 \otimes 5$ and

![Fig. 3a](image1.png)

![Fig. 3b](image2.png)

![Fig. 3c](image3.png)

Fig. 3. — Structure buildup for $r_h = 2$ with different non-uniform fields. Results for $N = 100,000$ monomers and all results averaged over 10 runs. In figure 3a: (O) for $5 \otimes 5$ and (■) for $5 \otimes 0$. In figure 3c, dark lines for $5 \otimes 5$ and light lines for $0 \otimes 0$. In figures 3b and 3c arrows point to the gel conversion.
This is not unexpected since the close proximity of the reaction pair imply similar probability of being activated. This is in contrast to the case of larger $r_h$ as shall be shown later. The important effect of reaction in a non-uniform field is low gel conversion. For a non-uniform field of $5 \otimes 5$ the gel point is at 23% bulk conversion as compared with 67% conversion for uniform reaction field ($0 \otimes 0$). This is a consequence of the fact that the gradient preferentially reacts molecules in one zone — where the light intensity is high. This results in the largest molecule growing at the expense of all others and forming a non-uniform gel while the others are still unreacted.

Figure 3b shows the fluctuations in $(DP)_w$ for ten runs. For reaction in a uniform field the fluctuations are only concentrated in a small window around the gel point but the fluctuations for reaction in a gradient grow with conversion after the gel point. This reflects the highly non-uniform nature of growth in gradient polymerizations.

$(RDP)_w$ and $d(DP)_w/d\alpha$ are plotted for two cases in figure 3c ($5 \otimes 5$ and $0 \otimes 0$). Figure 3c shows that the gel point can be accurately estimated as the conversion at the maximum in these two quantities.

The first three moments of the $z$ center of mass of the molecules are plotted in figure 4 for $5 \otimes 5$ and $0 \otimes 0$. The length in the $z$ direction is normalized between 1 and $-1$, with 0 being the center of the cube and $z = 1$ corresponding to the face at which light enters the sample. As expected in the absence of a reaction gradient all three moments of the center of mass projected on the $z$ axis lie approximately in the center of the reactor. Thus neither the molecules, the monomers, nor the weight of the system has any spatial non-uniformity. For the case of polymerization in a gradient the following is observed: the monomers are still equally distributed in the $z$ direction, therefore $cm^1_z = 0$. However, most of the molecules are in the bottom half (away from the light source) of the cube, therefore $cm^2_z$ is negative. The molecules in the top half of the cube are few but have the largest sizes, therefore $cm^2_z$ is positive. It is noted that the minimum in $cm^0_z$ (or maximum in $cm^2_z$) can also be used to determine the gel conversion.

![Figure 4](image_url)

**Fig. 4.** — Projection of moments of the average center of mass of molecules on the $z$ axis as a function of conversion for $r_h = 2$. The upper curve for the second moment, lower curve for the zeroth moment and (O) symbols (middle line) for the first moment for reaction in a $5 \otimes 5$ gradient. The three moments for reaction in a uniform field $0 \otimes 0$ are all on the middle dashed line.

The effect of a non-uniform field is most easily seen in the compartmentalized $(DP)_w$. $(DP)_w$ in three equal compartments in the $z$ direction is plotted in figure 5 for $5 \otimes 5$ and $0 \otimes 0$. In non-uniform polymerization most of the weight-average mass is concentrated in the top half of the system. As expected, for uniform polymerization the weight-average mass is evenly distributed.
Fig. 5. — $(DP)_w$ in three compartments of the reactor for $r_h = 2$ and 100,000 monomers. Dark line for gradient $5 \otimes 5$ and light line for reaction in a uniform field $0 \otimes 0$. Light enters the sample from the top compartment.

The above results reveal two important characteristics of growth in non-uniform fields: early gel conversions and spatial heterogeneity of sizes. The third characteristic feature is the large dispersity of sizes. This can be gauged as the relative ratio of the various moments of the average degree of polymerization. The first of these is $P_1 = (DP)_w/(DP)_n$ and is shown in figure 6 for the cases $5 \otimes 5$ and $0 \otimes 0$.

RESULTS FOR $r_h = \infty$. — This case is somewhat incongruent: the functional units are considered frozen for the purposes of determining if they are activated for reaction, but they are allowed infinite mobility once they are activated. The results here are qualitatively similar to the case of $r_h = 2$ discussed above. $(DP)_w$ for three cases, $5 \otimes 5$, $5 \otimes 0$ and $0 \otimes 0$, is shown in figure 6. The last case corresponds to the ideal mean-field solution: $(DP)_w = (1 + \alpha)/(1 - 2 \alpha)$, $\alpha$ is the fraction of total sites connected. Here it is important whether one or both units must be activated before reaction, as evidenced in figure 7. If both units must be activated the gel conversion is even earlier, the spatial heterogeneity is more dramatic, and the polydispersities larger, than the case where only one unit need be activated before reaction.
Discussion.

Results of this study reveal several features of growth in a reaction gradient, but these should be taken in perspective. Photopolymerizations to which the simulations are directly tailored are usually free radical polymerizations. This makes experimental mapping of this study of stepwise chemistry difficult. It is important to note that polymerization is normally much more sensitive to the detailed reaction chemistry than to the physics of the reaction process. The present study is deficient in as much as it only concentrates on the physics of the growth by studying the simplest possible chemistry. Three major effects of gradient are shown in this study. These effects are early gel conversion, spatial size heterogeneities and large polydispersities.

Experimentally, a detailed characterization of non-uniform polymerization has not yet been reported. A few qualitative studies exist and can be related to this work. The first of these are experimental studies of polyurethane polymerization in tubular reactors [5]. Unlike typical photopolymerizations, polyurethanes grow by a stepwise mechanism and are therefore chemically similar to the present work. In tubular flow reactors it is found that gel forms next to the wall, where the molecules have longer residence times, and then grows in. The experimental results are for the gel layer kinetics and subsequent pressure rise in the reactor. Detailed studies of the polymer structure as a function of both the radial and axial position are unavailable.

Some effort can be made towards an analytic description of polymerization in a tubular reactor. Consider, for reasons to be understood later, that instead of continuous reactor feed, a delta feed is introduced in a tubular reactor at time \( t = 0 \). Assume further that the material is a Newtonian fluid throughout its journey in the reactor and is therefore described by a parabolic velocity profile. Since the material is polymerizing, the viscosity of the material must be a function of both the radial \( r \) and axial \( z \) position. While this effect is not insignificant (the viscosity will strictly diverge when the material gels) it shall be ignored at this level. Assume the polymerization reaction to be locally mean-field, that is, at any given location, the gel condition is that the local conversion: \( \alpha_c(r, z) = 1/(f - 1) \) for \( A_f \) homopolymerization. Under
these assumptions, the surface of the gel for a bimolecular reaction is given by the equation:

\[
\left( \frac{r_{\text{gel}}}{R} \right)^2 = 1 + \frac{z(f - 2)}{t_0 v_{\text{max}}} \tag{5}
\]

\( R \) is the radius of the reactor, \( t_0 \) is the reaction time constant, \( t_0 = 1/2 kA_0 \) for a bimolecular reaction, \( k \) is the reaction rate constant, \( A_0 \) the initial concentration of the reactant \( A \), \( v_{\text{max}} \) is the velocity at the center of the reactor, for laminar flow \( v_{\text{max}} = R^2 \Delta P/4 \eta \Delta x \), \( \eta \) is the viscosity and \( \Delta P/\Delta x \) the pressure drop. In order to describe polymerization of a continuous feed we can consider another delta feed entering a paraboloid instead of a cylindrical reactor, and so on. Since even the equations of motion of a fluid in a paraboloid are not tractable, this problem is not easily described analytically. Experimentally it is observed that growth of the gel layer is not a paraboloid as this analysis predicts but cylindrical. It is speculated that either back diffusion is important or shear degradation occurs at the walls, tearing the gel layer and carrying it in the flowing stream.

Fig. 8. — Simulation pictures of growth for 1,000 monomers. Four states of conversion from left corner clockwise: \( \alpha = 0.12, \ 0.24, \ 0.51, \ 0.69 \). a) Reaction in a gradient with 5 \( \otimes \) 5 and reactive radius \( r_h = 2 \). Only the largest molecule (connected) and the unreacted monomers are shown. Gel conversion ca. 0.24. b) Growth without a gradient for a reactive radius \( r_h = 2 \). Only the largest molecule and the unreacted monomers are shown for ease of visualization. Gel conversion ca 0.69. c) Without a gradient for mean-field growth (\( r_h \) is the entire computer bath). All molecules are shown. Monomers on the same molecule are not connected. Monomers on the same molecule have the same color. Gel conversion ca 0.50.
Fig. 8 (continued).
The above exercise demonstrates the rather difficult situation in non-uniform polymer reactors. Several recent studies have taken the approach of numerically solving the combined transport equations along with the mean-field polymerization equation on a grid representing the mold [11]. In this work an alternate view is presented. Instead of treating the reactor as a continuum, a molecular simulation of reactors is suggested. The latter approach allows reactions to be treated in a non-mean-field way and presents possibility of incorporating difficult effects, such as viscoelasticity in simple reaction rules.

The second application of this study, for which some experimental work exists, is photopolymerizations. Photopolymers are used in diverse applications and while one would normally expect that non-uniform polymerizations are undesired, some novel applications readily suggest themselves. In polymer coatings at least two separate functions are demanded of the coatings. The outer exposed surface should be chemically resistive and mechanically strong while the inner surface should have good adhesion to the substrate. Interestingly both functions can be optimized in an uneven polymerization if light is used to cure the material. Then, the unexposed surface is undercured and the large fraction of tangling ends ensures good adhesion. At the same time, the highly cured outer surface would have the necessary strength and resistance. In general, uneven polymerizations can be harnessed for novel technology by custom varying specific properties along the polymer sample as a function of the degree of polymerization. A clear example is building a polymer fiber with refractive index gradient. Such fibers could then be used as optical guides. Since the refractive index is usually a sensitive function of degree of polymerization, the gradient itself can be rather easily tailored. The main problem in such cases may be ensuring that polymers are sufficiently cured such that they retain their desired properties. Recently a detailed rheological study of photopolymerizations has been reported [12]. While some deductions from the rheology can be used to comment on the structure of the polymers, a fundamental investigation of the structures is desirable. If the structural non-homogeneity is measurable, sections of the polymer should have different molecular weights — a well defined experimental study.

Another useful aspect of computer simulations is illustrative pictures that offer easy insights into physical effects. To end this report, a few such pictures are presented. Three cases of 1,000 monomers were simulated. These are $5 \otimes 5$ (gradient, Fig. 8a) and $0 \otimes 0$ (no gradient, Fig. 8b) for $r_h = 2$ and $r_h = \infty$ (no gradient, Fig. 8c). The dramatic growth of the gel molecule on the side where light enters the cube and the large concentration of monomers on the other side are clearly manifest in these figures. In fact, all three features that this report predicts can be deduced qualitatively from these two figures. Comparing just the mean-field case (8c) with $r_h = 2$ polymerization (8b) reveals that growth of the largest molecule is significantly faster and dominant in the mean-field case. At about 50 % conversion the system has already gelled in mean-field growth while the size of the largest molecule is only about 30 monomers (for a system of 1,000 monomers) for reaction with $r_h = 2$.

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References

[1] a) FLORY P. J., J. Am. Chem. Soc. 63 (1941) 3083;
    b) FLORY P. J., J. Am. Chem. Soc. 63 (1941) 3091;
    c) FLORY P. J., Principles of Polymer Chemistry (Cornell University Press, Ithaca, 1953);
    d) STOCKMAYER W. H., J. Chem. Phys. 11 (1943) 45;
    g) MILLER D. R. and MACOSKO C. W., Macromolecules 9 (1976) 206;
    i) GUPTA S. K. and KUMAR A., Reaction Engineering of Stepwise Polymerization (Plenum Press, New York, 1987);

    b) STAUFFER D. and ACHARON A., An Introduction to Percolation Theory 2nd Ed. (Taylor and Francis Ltd. Philadelphia, 1985);


