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Kinetic Monte-Carlo simulation of network formation

II. Effect of system size

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Summary

The simulation described in Part I was applied to random step polyaddition of a trifunctional monomer and the results were compared with exact solution for an infinite system. The gel point conversions, the weight-average degree of polymerization before (P_w) and beyond ($P_\mathrm{w,sol}$) the gel point, the sol fraction and the cycle rank were used for comparison. The best way for detection of the gel point conversion is the extrapolation of the gel fraction, w_g, to $w_\mathrm{g} = 0$. The largest fluctuations are exhibited by P_w and $P_\mathrm{w,sol}$. To get results closer to the exact ones, one can repeat several experiments with smaller number of units or increase the number of units, the former way being somewhat more economical. Typical orders of magnitude used were 10^7 monomeric units.

Introduction

In Part II, the results of testing of the computer program described in Part I [1] are described. To be able to compare the results with the exact solution, a simple system, random polycondensation of a trifunctional monomer, has been chosen.

The main objectives of the study are as follows:

(a) simulation of the weight-average degree of polymerization, P_w, and its value, $P_\mathrm{w,sol}$, for the sol, weight fraction of gel, w_g, and cycle rank, ζ, as a function of the number of units used in simulation, N;

(b) investigation of fluctuation of results by repeating the experiment;

(c) finding the best criterion for determining the critical conversion at the gel point.

Random polycondensation of a trifunctional monomer

Only irreversible ideal step polyaddition (polycondensation) is considered. The kernel (eq. (15) of Part I)

$$K_\mathrm{I}(l_j, l'_k; \mathrm{x}, \mathrm{x}', \ldots) = k_{jk}\, k(\mathrm{x}, \ldots)\, k(\mathrm{x}', \ldots)\, l_j^a\, l_k'^{a'} \tag{1}$$

becomes for $l_j = l_k = l$; $k_{jk} = k$; $k(x, ...) = k(x', ...) = 1$; $aa' = 1$

$$K_\mathrm{I}(l, l') = k\, l\, l' \tag{2}$$

and the equation determining the changes in the concentrations of molecules $A(\mathbf{x},\mathrm{l})$ (cf. eq. (9) of Part I, $f = 3$) reads

$$\frac{dc(x,l)}{dt} = \frac{1}{2}k\sum_{x'=1}^{x-1}(l-l'+1)\,(l'+1)\,c(l-l'+1,x-x')\,c(x',l'+1) - k\,c(x,l)\sum_{x'=1}^{\infty} l\,l'\,c(x',l') \quad (3)$$

As was pointed out in Part I, all finite molecules in an infinite system must have only a tree-like structure. For tree-like molecules, a fixed relation between l and x holds

$$l = x\,(f-2) + 2 \quad (4)$$

because $x - 1$ bonds out of all possible $fx/2$ bonds are sufficient to connect x molecules.

The initial conditions for $t = 0$ are

$$c(x,l) = \begin{cases} c_0 & \text{for } x = 1 \text{ and } l = 3 \\ 0 & \text{otherwise} \end{cases} \quad (5)$$

where c_0 is the initial monomer concentration.

Calculated parameters

Typical parameters calculated to test the simulation procedure and the exact solutions obtained by the theory of branching processes (cf. e.g. refs. 2 and 3) for an infinite system are listed below:

Weight-average degree of polymerization including (P_w) and excluding ($P_{w,sol}$) the largest molecule

In a simulated (finite) system distinguishable molecules can be numbered and the corresponding quantities denoted by subscripts $i = 1, \ldots, n_{type}$. Formulas for P_w and $P_{w,sol}$ then read

$$P_w = \sum_{i=1}^{n_{type}} x_i^2 N_i \Big/ \sum_{i=1}^{n_{type}} x_i N_i \quad (6)$$

$$P_{w,sol} = {\sum_{i=1}^{n_{type}}}' x_i^2 N_i \Big/ {\sum_{i=1}^{n_{type}}}' x_i N_i \quad (7)$$

These formulas differ only in the range of summation: in P_w, there are included all molecules and in $P_{w,sol}$, all but the largest molecule which is expressed by prime at the summation sign. Before the gel point, the difference between P_w and $P_{w,sol}$ decreases to zero with increasing system size. After the gel point, contribution to P_w from the largest molecule (gel) is prevailing and for infinite systems it diverges.

The exact solution for infinite system reads:

$$P_w = 1 + 3\alpha/(1-2\alpha) \qquad \text{for } \alpha < \alpha_g \quad (8)$$

$$P_{w,sol} = 1 + 3\,(1-\alpha)/(2\alpha - 1) \qquad \text{for } \alpha > \alpha_g \quad (9)$$

where gel point conversion $\alpha_g = 0.5$. Up to the gel point $P_{w,sol} = P_w$.

Weight fraction of gel, w_g

$$w_g = x_{i_{\text{largest}}} N_{i_{\text{largest}}} \Big/ \sum_{i=1}^{n_{\text{type}}} x_i N_i \tag{10}$$

where i_{largest} is an identification label of the largest molecule. The exact solution is

$$w_g = 1 - (1 - \alpha + \alpha v)^3 = 1 - \left(\frac{1-\alpha}{\alpha}\right)^3 \tag{11}$$

where v is the extinction probability; in this case $v = \left(\frac{1-\alpha}{\alpha}\right)^2$

The cycle rank, ζ

The cycle rank is an important quantity in rubber elasticity theories. By definition, the cycle rank is equal to the number of bonds (edges) which must be split in a graph with cycles to obtain a spanning tree (a connected graph with tree-like structure). The number of bonds in the molecule $A(x, l)$ is $(fx - l)/2$ and the minimum number of bonds to connect x units into a tree-like molecule is $x - 1$ (cf. eq. (4)), hence

$$\zeta = x\,(f-2)/2 - l/2 + 1 \tag{12}$$

(here $f = 3$).

For a perfect network, there exist one-to-one relation between the cycle rank, number of network chains (ν) and junctions ($\mu = x$) in the gel, because for an infinite system $x - 1 \approx x$

$$\zeta = \nu - \mu = \frac{f-2}{2}\,\nu \tag{13}$$

For an imperfect network, the corresponding relation reads

$$\zeta_e = \nu_e - \mu_e = \frac{f_e - 2}{2}\,\nu_e \tag{14}$$

where ζ_e, ν_e and μ_e mean the elastically effective cycle rank, the number of elastically active chains and elastically active junctions, respectively; f_e is the average effective functionality which is equal to 3 if $f = 3$. The exact solution for ζ related to a monomeric unit ($\zeta_e' = \zeta_e/x$) read

$$\zeta_e' = \frac{3}{2}\,\alpha^3\,(1-v)^3 - \alpha^3\,(1-v)^3 = \frac{1}{2}\,\alpha^3\,(1-v)^3 = \frac{1}{2}\left(\frac{2\alpha-1}{\alpha}\right)^3 \tag{15}$$

The cycle rank per monomeric unit in the gel

$$\zeta_{eg}' = \zeta_e'/w_g = 2\,\frac{(2\alpha-1)^2}{(2\alpha-1)^2+3} \tag{16}$$

Simulation results

Two main tasks were pursued: the determination of the critical conversion and the changes of various parameters listed above as a function of conversion of functional groups in dependence on the number of monomeric units used in the simulation and on the number of repetitions of the experiment.

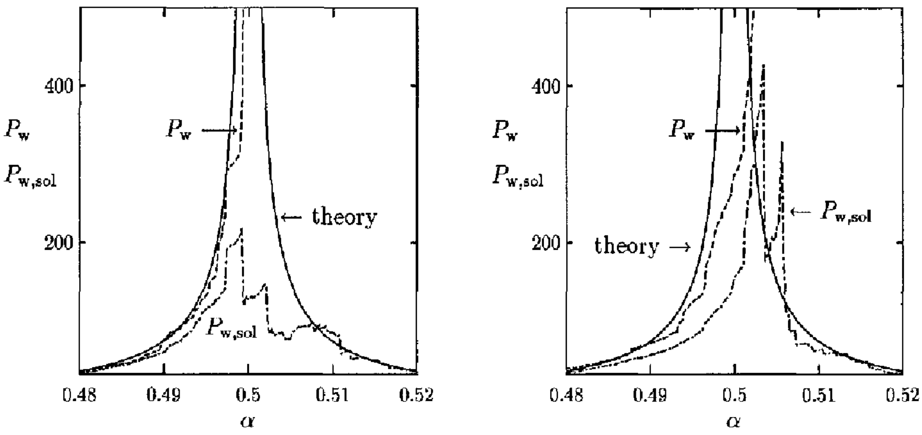

Figure 1: Examples of P_w and $P_{w,sol}$ evolution for two experiments with $N = 10^6$ units.

Gel point conversion

Two criteria for the gel point have been examined:

(1) maximum of the weight-average degree of polymerization of sol, $P_{w,sol}$, which, in an infinite system, diverges at the gel point and falls again,

(2) the gel fraction, w_g, which, in infinite system, is zero at the gel point and $w_g > 0$ for $\alpha > \alpha_g$.

(1) In the infinite system, all molecules contribute to P_w and beyond the gel point the infinite structure is excluded from $P_{w,sol}$. Before the gel point, $P_{w,sol}$ and P_w are identical because the contribution of the largest molecule (largest here means that its degree of polymerization is as large as any finite number) by its weight is negligible compared to that of all other molecules.

In finite systems, P_w defined by eq. (6) increases continuously through the "gel point" (in the infinite system it would diverge) and is thus of no use for detection of the gel point. On the other hand, the average $P_{w,sol}$, from which the contribution by the largest molecule is excluded, passes through a maximum value and decreases again. As expected, the maximum $P_{w,sol}$ is found at conversions higher than the asymptotic α_g given by $\alpha_g = 1/(f-1)$. Figures 1a,b show the dependence of P_w and $P_{w,sol}$ for two experiments with 10^6 monomeric units. Figure 2 illustrates similar dependences for the indicated number of monomeric units used in simulation. These dependences are averaged over several experiments as described in the legend. One can see that with increasing N the maximum value of $P_{w,sol}$ is shifted towards the expected gel point conversion, 1/2, valid for an infinite system. In Figure 3, the values of α corresponding to the highest values of $P_{w,sol}$, α_{max}, are plotted against the system size. The fluctuations of experimental values and the error bars corresponding to the root-mean-square deviation are also shown. The least-square plot of α_{max} vs. $N^{-1/2}$ for $N \to \infty$ gives a value very close to 1/2.

It can be concluded that α_g can be found with reasonable approximation (with deviation of the order of 0.003) for a relatively large system (e.g. 10^7 units) or if the mean value over several experiments (e.g. with $N = 10^6$) is taken.

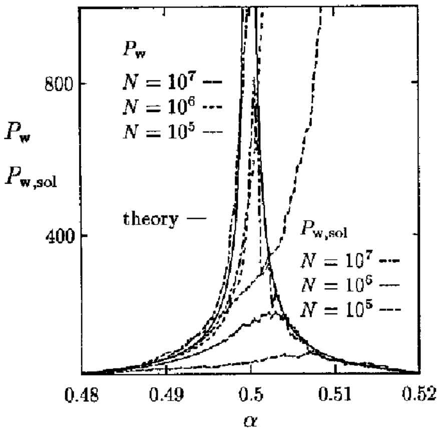

Figure 2: P_w and $P_{w,sol}$ for different sizes N (each averaged over several experiments).

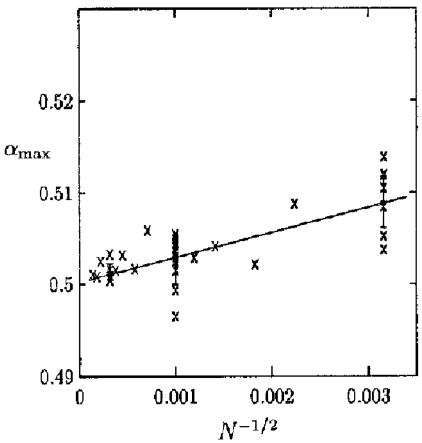

Figure 3: Values of α corresponding to the highest values of $P_{w,sol}$, α_{max} plotted against $N^{-1/2}$.

Another observation is still to be mentioned. The fluctuation pattern of several experiments for the same system size (10^6) shown in Fig. 4 does not look fully random as one might expect. In all individual experiments, one can see a series of steep and deep falls preceded by gradual but irregular climbs. The explanation of this "regularity" is that the deep fall corresponds to the reaction of the second largest molecules or one of the next largest molecules with the largest one. The status of this molecule is then changed from a countable molecule to the uncountable largest one, and the average $P_{w,sol}$ falls. When the largest molecule is added (to yield P_w), or when $P_{w,sol}$ is averaged over several experiments, the curves are much more featureless (Figs. 1 and 2). Beyond the gel point, such features of single-experiment $P_{w,sol}$ remain preserved.

(2) The other possibility to find the gel point conversion is the extrapolation of the weight fraction of the largest molecule (gel) to zero. Figures 5a–c show the dependence of w_g on conversion and system size at different scales of α. With the exception of $N = 10^5$ and the critical region, on a wider scale, the dependences practically copy the curve for an infinite system (Fig. 5c) and fluctuations are small. The w_g vs. α dependence is not linear. However, within a narrower α-range (Fig. 5b), the dependences for $N = 10^6 - 10^7$ are almost identical down to $\alpha = 0.503$ and almost linear up to $\alpha = 0.515 - 0.520$. Linear extrapolation gives $\alpha_g = 0.498 - 0.499$. Figure 5a shows that extrapolation of dependences for $N = 1 - 5 \times 10^7$ gives a value of $\alpha_g = 0.5 \pm 0.0005$.

Thus, the extrapolation of the gel fraction dependence is the best method of obtaining the value of the critical conversion.

Dependences of P_w, $P_{w,sol}$, w_g and ζ on conversion

It has already been stressed that the w_g vs. α dependence for an infinite system is very well simulated by system sizes $10^6 - 10^7$, and even the 10^5 system offers a reasonable approximation of the infinite system (at these relatively short distances from the gel point the experimental determination of w_g by extraction is much less accurate).

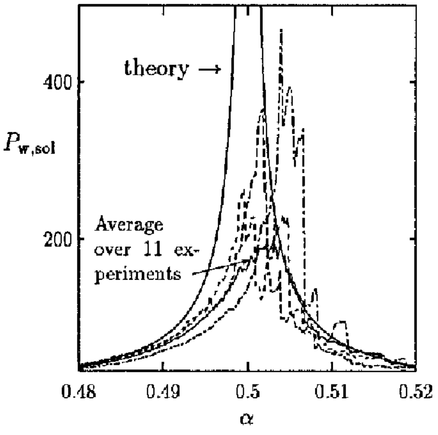

Figure 4: $P_{w,sol}$ for different experiments using different starting numbers of generator with $N = 10^6$.

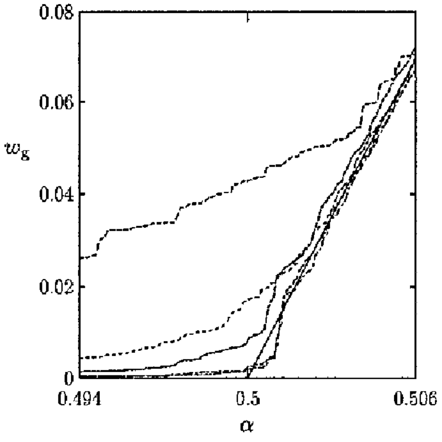

Figure 5a

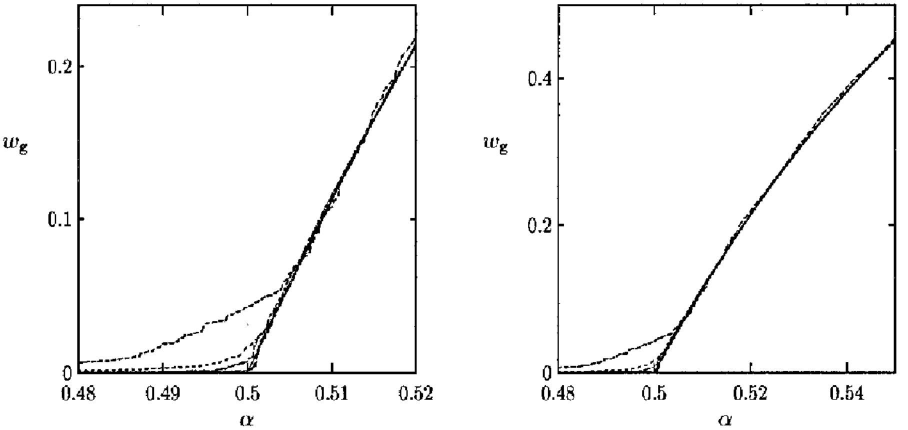

Figure 5b

Figure 5c

Figure 5: The weight fraction of the largest molecule, w_g, as a function of α for $N = 10^5$ —, 10^6 ---, 10^7 —, 3×10^7 --, 5×10^7 -- compared with theoretical dependence (—), with varying conversion scales in Figs. 5a, 5b, 5c.

The agreement of P_w (before the gel point) and $P_{w,sol}$ (beyond the gel point) is somewhat worse partly because of the steepness of the P_w or $P_{w,sol}$ vs. α dependences near the critical point, in an infinite system.

The log – log plots of P_w and $P_{w,sol}$ vs. $|\alpha_g - \alpha|$ (Figs. 6a, b) show that a reasonable agreement between the simulated and exact values can be reached for P_w up to about 2×10^2 – 10^3 for N changing from 10^5 to 5×10^7. The $P_{w,sol}$ values seem to be lower to a farther distance from the gel point than the P_w values. Note that the scaling relation

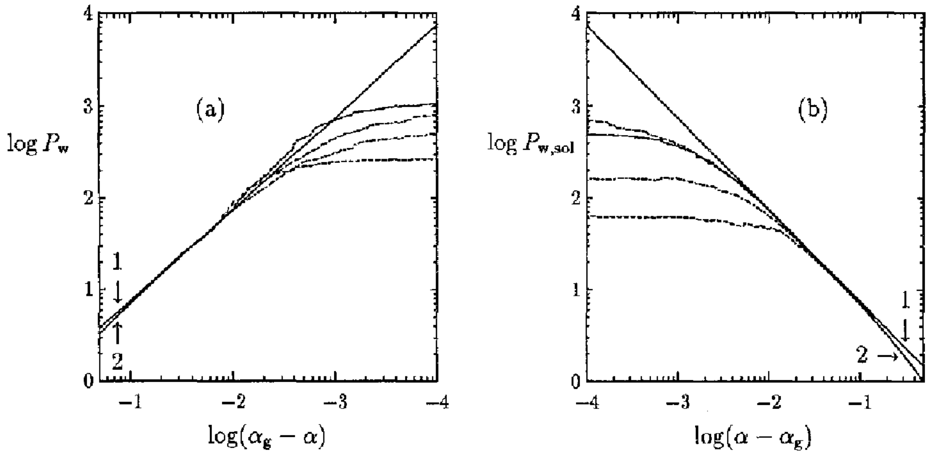

Figure 6: Theoretical and simulation dependences of P_w before and $P_{w,sol}$ beyond the critical conversion ($\alpha_g = 0.5$) compared with exponential (scaling) approximation $\frac{f}{2}\frac{\alpha_g}{|\alpha - \alpha_g|}$ (line 1) and theory (line 2) for $N = 10^5$ ---, 10^6 ---, 10^7 — and 5×10^7 --.

$\log P_w = -\log|\alpha - \alpha_g| + \log(f\alpha_g/2)$ (line 1) fits the exact dependence $\log P_w = -\log|\alpha - \alpha_g| + \log(f\alpha_g/2 - \alpha_g|\alpha - \alpha_g|)$ in a wide range of $|\alpha - \alpha_g|$.

The simulated values of cycle rank show a good agreement with the exact values for an infinite system for $N \gtrsim 10^6$. The simulation behaviour is similar to that of w_g.

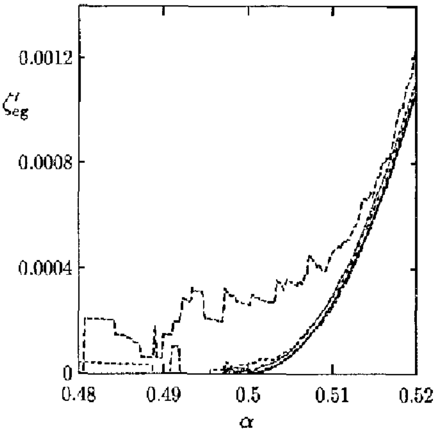

Figure 7: Effective cycle rank per monomeric unit of the largest molecule as a function of α for $N = 10^5$ ---, 10^6 ---, 10^7 —, 3×10^7 ---, 5×10^7 --- and theory —.

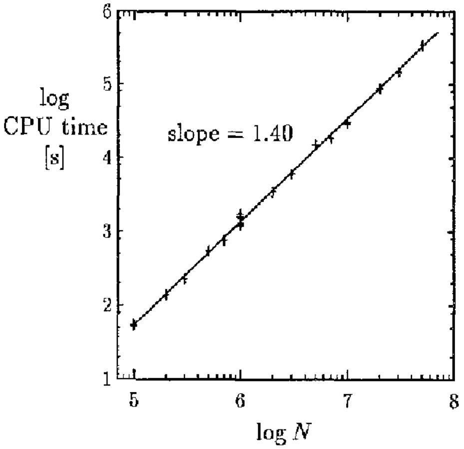

Figure 8: Computer (CPU) time as a function of N for Silicon Graphics computer with processor MIPS R4000.

Conclusions

The Monte-Carlo simulation of network growth described here gives a reasonable approximation for values expected for infinite systems for numbers of monomeric units $N = 10^6 - 10^7$; for the sol fraction, even $N = 10^5$ is still reasonable. The best method for determination of the gel point conversion is the extrapolation of the gel fraction to zero. The weight-average degrees of polymerization are more sensitive to N and fluctuations of computer experiments. A method for location of the critical point suggested in the literature [4] is based on the assumption of the same critical exponents of P_w and $P_{w,sol}$. The method consists in the log – log plot of these quantities against $|\alpha - \alpha_g[$ and shifting α_g, so that the slopes are equal. We consider this method less reliable because: (a) the assumption of symmetry has not been generally proved, (b) the exponents (slopes) depend more on N and conversion range than w_g.

In increasing the reliability of the prediction, the increase in system size and increasing number of computer experiments at the same size are competitive. Figure 8 shows the dependence of computer CPU time in dependence on N and may serve as a guideline for selection. The increase in N by a factor of 10 corresponds to an increase in CPU time by a factor of 25. This means that, for instance, 10 experiments each with N units are less time-consuming than one experiment with $10N$ units.

The application and testing of this Monte-Carlo simulation is by far not limited by this simple case. As will be reported later, it works also well with complex reactions involving a number of elementary reaction steps like free-radical crosslinking copolymerization.

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