

Kinetics of gelation growth in a sol-gel transition by a computer-simulation model

Yehan Liu, R. Pandey

► **To cite this version:**

Yehan Liu, R. Pandey. Kinetics of gelation growth in a sol-gel transition by a computer-simulation model. *Journal de Physique II*, EDP Sciences, 1994, 4 (5), pp.865-872. <10.1051/jp2:1994170>. <jpa-00248007>

HAL Id: jpa-00248007

<https://hal.archives-ouvertes.fr/jpa-00248007>

Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

64.60A — 61.40K — 82.20W

Kinetics of gelation growth in a sol-gel transition by a computer-simulation model

Y. Liu ^(1,2) and R. B. Pandey ^(1,3)

⁽¹⁾ The Program in Scientific Computing, University of Southern Mississippi, Hattiesburg, MS 39406, U.S.A.

⁽²⁾ Department of Computer Science and Statistics, University of Southern Mississippi, Hattiesburg, MS 39406, U.S.A.

⁽³⁾ Department of Physics and Astronomy, University of Southern Mississippi, Hattiesburg, MS 39406, U.S.A.

(Received 15 January 1994, accepted 31 January)

Abstract. — A computer simulation model is used to study the kinetics of gelation of a low concentration of bifunctional (C_2) and tetrafunctional (C_4) monomers on a simple cubic lattice. The mobilities of the monomers and the microgel particles are considered. Monomers react with their neighbors with a certain probability after hopping with a fixed number of steps. Growth of the concentration of saturated bonds, weight average degree polymerization, and the volume fraction of the gel are studied as a function of reaction time. We find that the critical gel time (i.e. the gel point) depends nonlinearly on the mobility steps of hopping.

Understanding the growth process in gelation has attracted a considerable interest for a long time dating back to Flory [1] and Stockmayer [2] when the percolation on the Cayley tree was used to describe the sol-gel transition. In order to incorporate loop formation and the effects of excluded volume, de Gennes [3] and Stauffer [4] proposed random percolation on a real lattice as a model for the sol-gel transition [5]. The kinetics was then considered in a computer simulation model [6, 7] for irreversible gelation which spurred a lot of interest about a decade ago [8] on the universality of the sol-gel transitions. Since then, a considerable progress has been made in understanding the universality of sol-gel phase transition in irreversible gelation as well as various growth processes involving aggregations [9, 10]. However, in most of the previous studies of irreversible kinetic gelation [9, 10], effects of solvent were not considered while there is a considerable interest in sol-gel transition in good solvent in recent years [12-14]. Furthermore, to our knowledge, there is no study on the effect of the mobility of the monomers and microgel particles on the sol-gel transition and the temporal evolution of the growth of the concentration of bonds and the size and number of the microgel particles ; we use a computer simulation model here to address these issues. We would like to mention that Bansil *et al.* [8] have considered the mobility of only unreacted monomers (i.e. single particle

mobility) in their studies of sol-gel transition. There have been several investigations on aggregation studies involving the cluster of clustering [15, 16] where the mobility of clusters are considered. But unlike the work presented here, a limited functionality of the particles is not considered and most of these studies emphasize on the fractal dimensionality of the aggregate rather than sol-gel transition.

We consider a simple cubic lattice of size $L \times L \times L$. A fraction C_2 of the lattice sites is then randomly occupied by bifunctional monomers and a fraction C_4 , by tetrafunctional units leaving the remaining fraction $(1 - C_2 - C_4)$ of lattice sites empty. The empty sites can be considered to be occupied by solvents with only a hardcore interaction between the solvent and monomers. A lattice site cannot be occupied more than one monomer at a time. On reaction, a bifunctional monomer can be connected to its two neighboring monomers at the most by single bonds and to one neighboring monomer at the most by a double bond. Similarly, a tetrafunctional monomer can be connected to its four neighboring monomers at the most by a single bond, to one monomers at the most by four bonds, or to its neighboring monomers by various bonding with multiplicity between one and four. The kinetics of the reaction is implemented by the following procedure.

The mobility is set by assigning a fixed number of steps, ISTEP, for the hopping of each particles (monomer and microgel) before allowing them to react ; a microgel particle is defined as a finite cluster resulting from the reaction. The hopping rate of a particle is inversely proportional to its mass. Initially, we also set the reaction or bonding probability P_B which is unity for this study. We select a particle randomly and attempt to move it with its hopping probability by a lattice constant in a randomly chosen direction, subject to hardcore interaction (i.e. without the overlap). An attempt to move each particle once is defined as unit time step. After each ISTEP time steps of hopping, each monomer attempts to react with one of its randomly selected neighbor. A bond is formed between the two neighboring monomers by the following rule. We select one of the monomers, and one of its neighboring sites randomly. If the neighboring site is occupied by a monomer and both monomers have at least one unsaturated bond (i.e. unreacted functional unit), then a bond is formed between the two monomers. An attempt to form bond fails if the randomly selected neighboring site is empty or if either of the monomers is saturated. A monomer becomes saturated as soon as it bonds with all of its functional units. This process of hopping each particle by ISTEP time steps and attempt to form bonds is repeated again and again until most of our attempts to form bonds fail i.e. when the reaction is nearly complete. During this process we keep track of several quantities such as fraction of bonds formed, the number and size of clusters formed from the bonded monomers, second moment of the cluster size distribution (i.e. the average weight degree polymerization), the critical gel time, and the volume fraction of the gel (the infinite cluster of bonded monomers). Further, we repeat this process for a number of independent runs to find an average estimate of these quantities for a reliable estimate.

Figure 1 shows the growth of the volume fraction of the gel as a function of time for various hopping steps at the concentrations $C_2 = C_4 = 0.20$. Note that the monomer concentration is very low and with relatively low mobility i.e. with ISTEP = 1 and 2, we do not even reach the gel point in many samples. On increasing the mobility we have always seen the onset of gelation with well defined gel point with a continuous growth of the mass of the gel. The gel point seems to depend on the mobility of the monomers. The kinetics of the growth is also observed for the weight average degree polymerization (χ) as shown in figure 2. We do not see as sharp peak in χ with ISTEP = 1 and 2 as with the higher steps of mobility i.e. with ISTEP = 5, 10 and 50. The broad peaks in χ at low mobilities (ISTEP = 1 and 2) support the idea that the kinetic reaction does not reach the post-gel regime in many samples which remain in sol phase ; this leads to smearing of the sol-gel transition with low mobilities. However, the

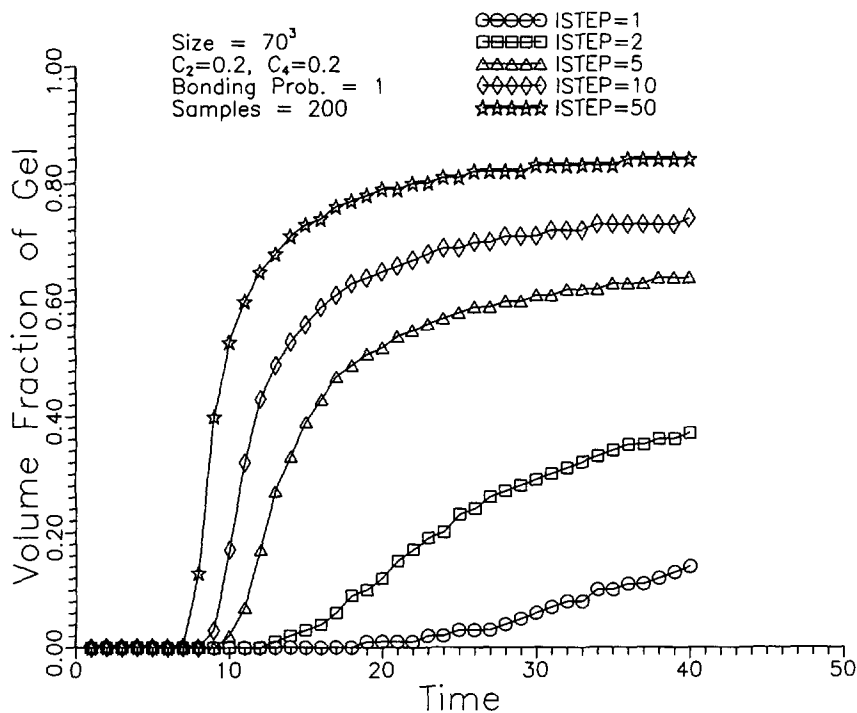


Fig. 1. — Volume fraction of gel versus time with various time steps of mobility. $70 \times 70 \times 70$ lattice was used with 200 samples.

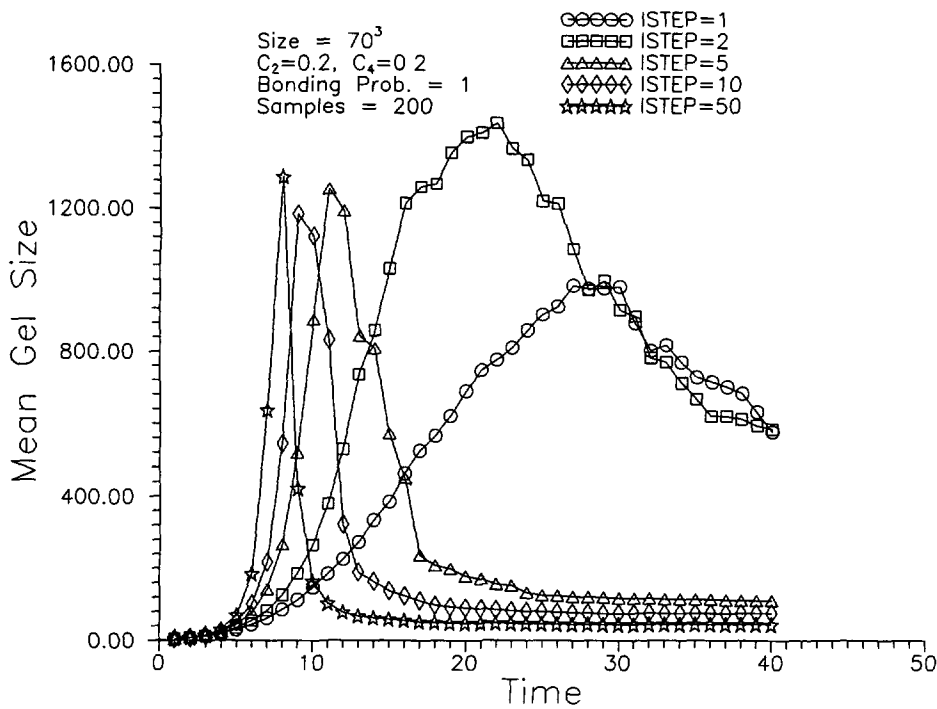


Fig. 2. — Weight average degree polymerization versus time with the same statistics as figure 1.

decay of the gel point on increasing the ISTEP is clearly seen in this figure 2. A plot of the critical gel point *versus* hopping steps is shown in figure 3 which does not seem to exhibit a power-law decay with the mobility steps. However, the existence of different power-laws at low and high mobility regimes cannot be ruled out.

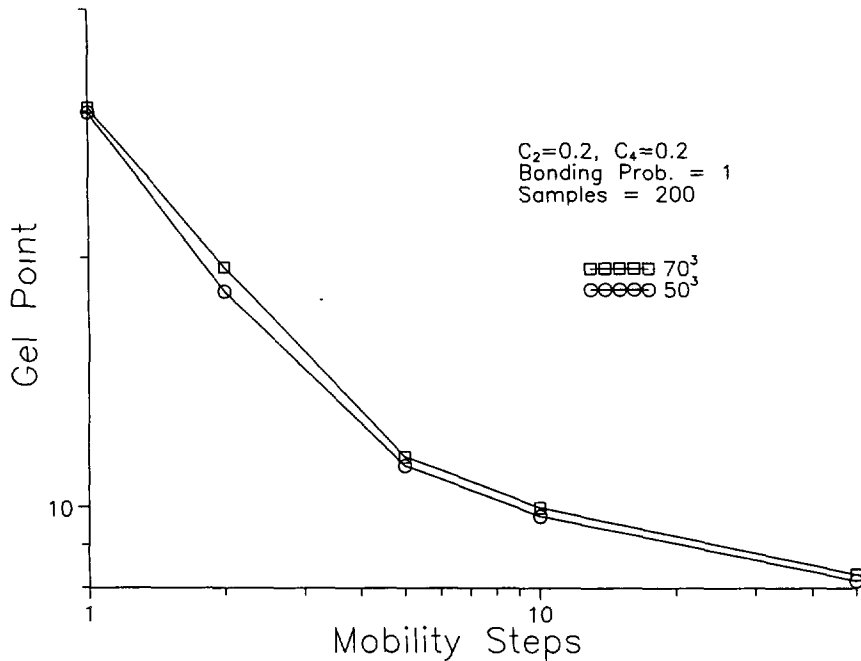


Fig. 3. — Gel point (i.e. the critical gel time) *versus* the steps of mobility on a log-log scale for the data of figures 1 and 2.

Figure 4 shows the plots of the gel volume fraction and weight average degree polymerization *versus* time for various sample sizes. We do observe a finite size effect — the larger the sample, the sharper is the sol-gel transition. Such finite size effects are expected in geometrical phase transitions like sol-gel here.

Sol to gel transition at the critical point is usually described by a second order geometrical phase transition [1-5] as a function of the concentration of bonds formed. However, if we assume that the reaction time is equivalent to the concentration of bonds then the volume fraction of the gel should be described by an exponent β ,

$$P_G \sim (t - t_c)^\beta \quad (1)$$

while the weight average degree polymerization χ by the exponent γ ,

$$\chi \sim |t - t_c|^{-\gamma} \quad (2)$$

Plots of P_G and χ *versus* $t - t_c$ is shown in figure 5. It is rather difficult to conclude if there is any power-law dependence in our log-log plot ; lack of a good power-law dependence may be due to low concentration of monomers, mobility, and small sample size. However, the variation in the plots with the mobility steps suggests that the nature of the sol-gel transition

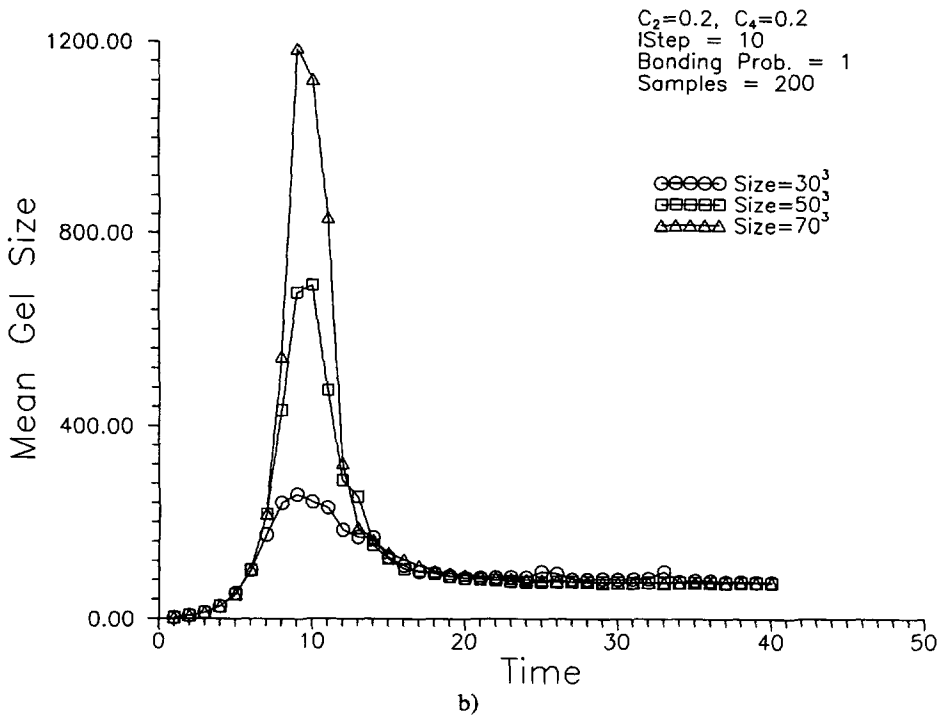
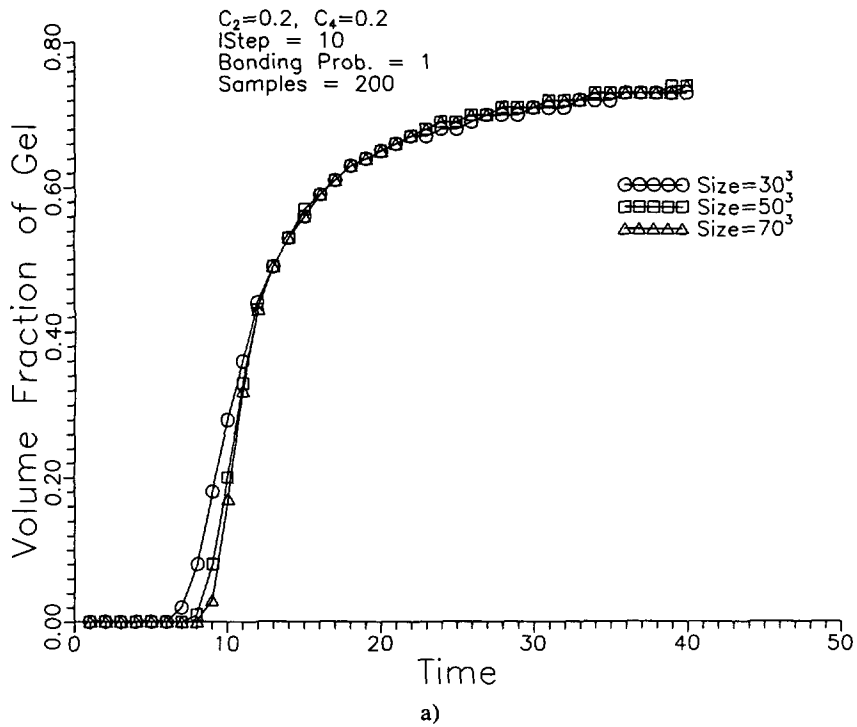


Fig. 4. — Gel fraction (a) and weight average degree polymerization *versus* time with samples of sizes $30 \times 30 \times 30$, $50 \times 50 \times 50$, and $70 \times 70 \times 70$.

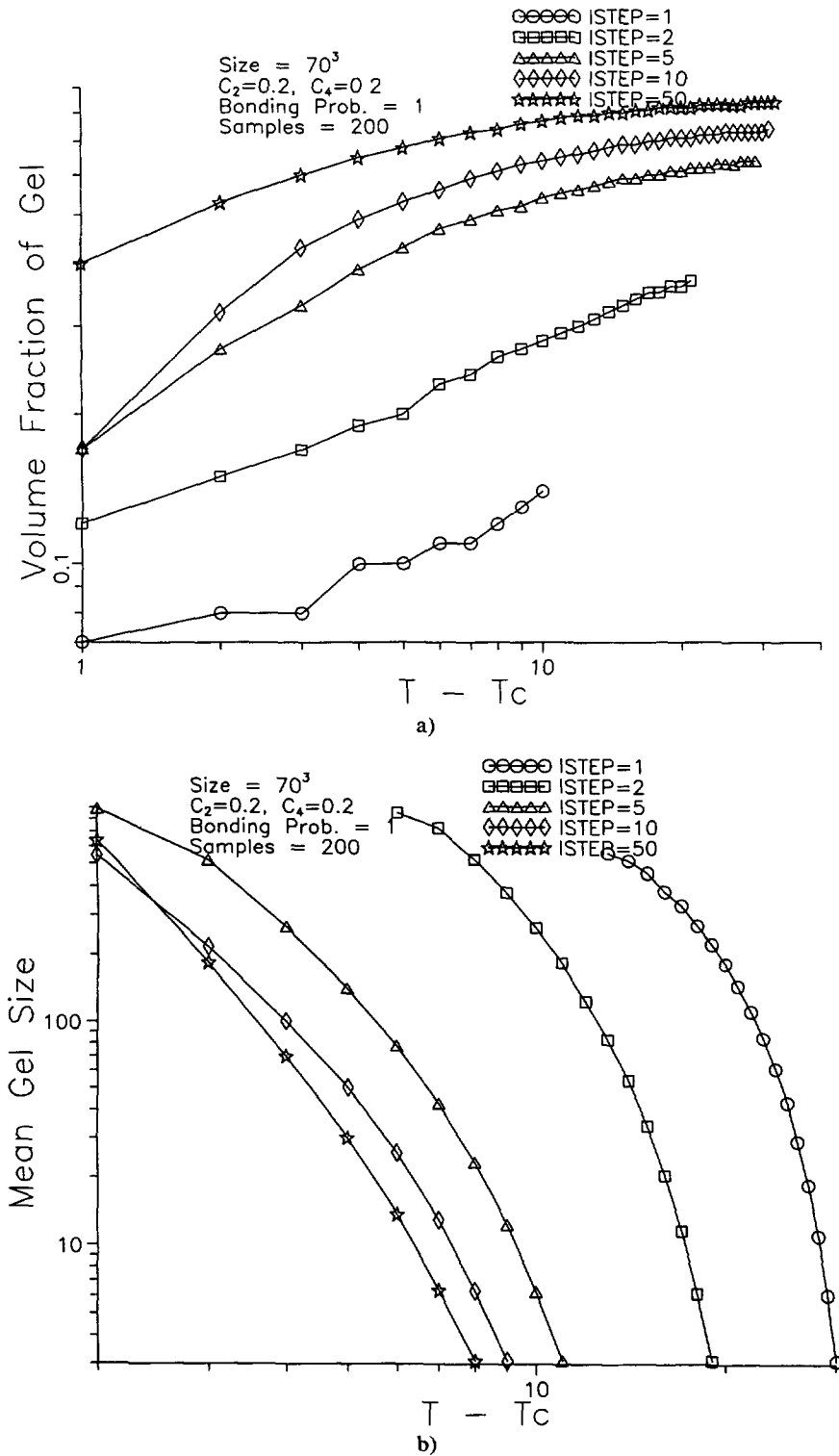


Fig. 5. — Gel fraction (a) and weight average degree polymerization (b) versus $(t - t_c)$ with the same statistics as that of figures 1 and 2.

may depend on the mobility. We are unable to evaluate these exponents more accurately or to estimate the ratio of the critical amplitudes of χ to a good precision to comment on the universality of the phase transition more definitely as has been done in the past [9].

We have also studied the growth of the concentration of the saturated bonds. Figure 6 shows plot of the fraction of the saturated bonds *versus* time on a semilog scale. Initially, the mobility does not seem to effect the concentration of the saturated bonds. In the asymptotic limit in the post-gel regime, the concentration of the saturated bonds seem to increase on increasing the mobility.

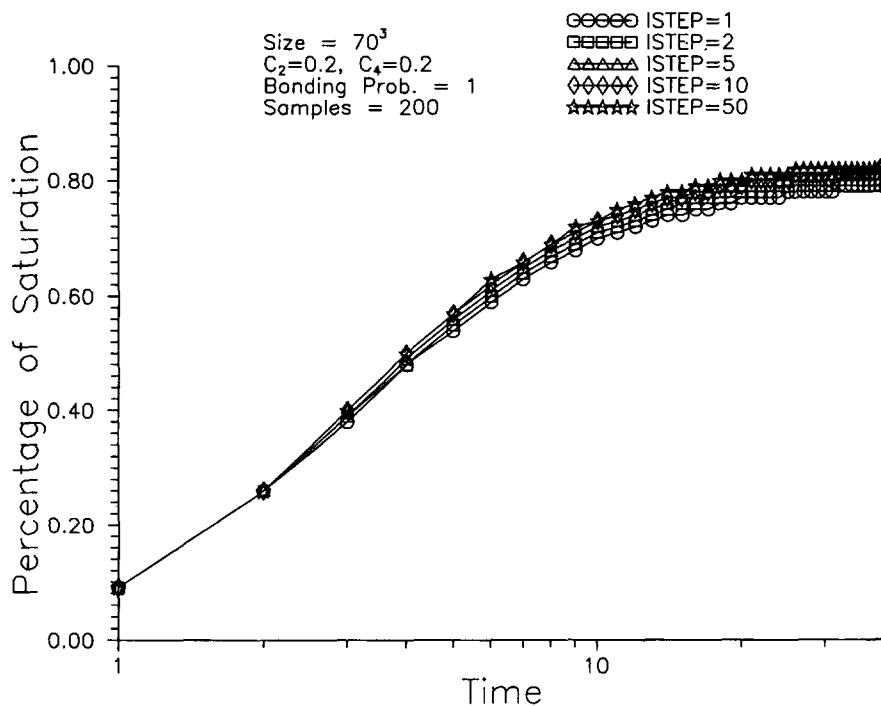


Fig. 6. — Fraction of saturated bonds *versus* time.

In summary, we have presented a computer simulation for studying the kinetics of gelation where the mobility of the monomers, the microgel particles and the solvents are considered. Low concentrations of bifunctional and tetrafunctional monomers are used to study the onset of gelation. We find that the mobility affects the gel point and the nature of the sol-gel transition : the higher the mobility, the lower is the gel point and sharper is the transition. The sol-gel transition seems to be smeared with the low mobilities. A detail study of the model with the effect of the concentration of the monomers, functionality, bonding probability, etc. will be published elsewhere.

Acknowledgments.

Authors would like to thank Dietrich Stauffer for comments and suggestions on the manuscript. Computer simulations were performed on IBM RISC 6000 machines at USM and on Cray XMP at the Mississippi Center for Supercomputing Research. A partial support from NSF-EPSCoR grant is also acknowledged by RBP.

References

- [1] Flory P. J., *J. Am. Chem. Soc.* **63** (1941) 3083, 3091, 3096 ; Principle of Polymer Chemistry (Cornell University Press, 1953).
- [2] Stockmayer W. H., *J. Chem. Phys.* **11** (1943) 45 ; **12** (1944) 125.
- [3] de Gennes P. G., *J. Phys. France Lett.* **37** (1976) L1.
- [4] Stauffer D., *J. Chem. Soc. Faraday Trans. II* **72** (1976) 1354.
- [5] Stauffer D., Coniglio A. and Adam M., *Adv. Polym. Sci.* **44** (1982) 103.
- [6] Manneville P. and de Seze L., in Numerical Methods in the Study of Critical Phenomena, I. Della Dora, J. Demongeot and B. Lacolle Eds. (Springer Verlag, Berlin, 1981).
- [7] Herrmann H. J., Landau D. P. and Stauffer D., *Phys. Rev. Lett.* **49** (1982) 412.
- [8] Bansil R., Herrmann H. J. and Stauffer D., *J. Polym. Sci.* **17** (1984) 998 ;
Jan N., Lookman T. and Stauffer D., *J. Phys. A* **16** (1983) L117 ;
Pandey R. B., *J. Stat. Phys.* **34** (1983) 191.
- [9] Herrmann H. J., *Phys. Rep.* **136** (1986) 153.
- [10] Kinetics of Aggregation and Gelation, F. Family and D. P. Landau Eds. (North Holland, 1984).
- [11] Random Fluctuations and Pattern Growth, H. E. Stanley and N. Ostrowsky Eds. (Kluwer Acad. Pub., 1988).
- [12] Geissler E., Hecht A., Horkay F. and Zrinyi M., *Macromolecules* **21** (1988) 2594.
- [13] Cohen Y., Ramon O., Kopelman I. J. and Mizrahi S., *J. Polym. Sci. B* **30** (1992) 1055.
- [14] Hu Z. and Li C., *J. Chem. Phys.* **99** (1993) 7108 ;
Li Y., Hu Z. and Li C., *J. Appl. Polym. Sci.* **50** (1993) 1107.
- [15] Meakin P., in reference [11], p. 174.
- [16] Kolb M. and Herrmann H. J., *J. Phys. A* **18** (1985) L435.