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Inhomogeneity in gelation and nonuniversality of sol-to-gel transitions studied by a computer simulation model

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Effects of the quality of a solvent on the sol-to-gel transition are studied by a computer simulation model. A nearest neighbor interaction of strength J between the polymeric units is introduced to control the quality of the solvent. The Metropolis algorithm is used to move the monomers and microgels that react with their neighboring units with a rate of reaction. The critical exponents for the sol-to-gel transition are found to depend on the nature of solvent, i.e., the exponent β for the gel fraction and the exponent γ for the weight average degree polymerization vary with the values of J. The dynamic evolution of the structure of gel networks is analyzed by collective structure factors. Due to the competition between the effect of dilution and the coagulation of clusters, a phase-separated gel network seems to emerge, leading to inhomogeneities. We also find that the interplay between the rate of the reaction and the energy parameters that represent the quality of solvents determines the final morphology of gel networks. [S1063-651X(96)08212-8]

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I. INTRODUCTION

Sol-to-gel transitions have been a subject of extensive studies for a long time with early approaches, such as classic descriptions by Flory and Stockmayer [1], to the contemporary percolation theory [2]. The Flory-Stockmayer model is equivalent to the random bond percolation theory in which the effect of solvents and the correlation between molecules are not considered. It is assumed in both theories that the interactions between polymer units are screened by an intervening cluster and all states of the system consisting of a fraction of occupied bonds are equally probable. However, in real polymeric systems, monomers and solvent are in thermal equilibrium, that is, their movements are controlled by interaction forces.

The behaviors of gels in the presence of a solvent have been studied theoretically [3,4] and experimentally [5]. It is found that the critical properties, such as fractal dimension and critical exponents, are quite different from the values predicted by the classical theory and the percolation theory [4,5]. Real solvents are also selective, i.e., the thermodynamic properties and phase behaviors of gels such as gel time, gel structure, and gel modules are different for different interactions between polymers and solvents. The presence of a solvent gives rise to motion of the species in the reaction bath, and due to this diffusion the reactivity of functional groups are no longer equal. When polymers are diluted by a solvent, the interaction between the clusters may not be screened out. Due to the excluded-volume interaction, the solvent would change the nature and magnitude of electrostatic and hydrogen bonding interactions in the system. These interactions, in turn, greatly affect the sol-gel reaction and hence the structure of the resulting gel by phase separation [6–8].

In a good solvent, the phase-separation effects are usually suppressed and the system is assumed to be homogeneous. However, in a poor solvent, the competition between the dilution effects and the effective attraction induced by chemical cross-linking can often produce concentration inhomogeneities in gel networks [9]. These inhomogeneities have been observed by scattering experiments in various polymer systems [10–16]. In fact, even in a very good solvent, the evolving polymer network will tend to segregate. However, the phase separation is prevented by cross-linking. As a result, only a microscopic separation takes place, leading to localized inhomogeneity in the gel structure. The microphase separation in irreversible gels is explained as a reaction-induced phase separation since there is no temperature quenching involved in the irreversible gelation [17–20].

Several computer simulation models have been proposed to include the mobility of polymers in the gelation process in recent years [21–29]. The solvent effect, however, is ignored in most of these models. Coniglio *et al.* [30] developed a site-bond correlated percolation model to include the solvent effects. In their model, the monomers are no longer distributed randomly but are distributed according to a distribution at thermal equilibrium at a temperature T via a nearest-neighbor interaction. They considered two types of interactions: the usual van der Waals interaction and a directional interaction that leads to chemical bonds. This analytical model can be solved only on simple structure such as a Cayley tree due to the counting problem. Moreover, the mobility of a monomer or polymer is neglected in the model. Very recently, we have also investigated the effects of temperature on the structural properties of gel in a thermodynamic model [31], in which monomers and microgels are mobile; we reported some interesting results on the critical gel points and melting points. Nevertheless, the effect of solvents is not considered.

In this paper, we use the Monte Carlo simulation method to study the effects of a solvent on the sol-gel transition and gel structure. We consider interactions between monomers and polymers in this model and investigate the sol-gel phase behaviors of irreversible gels in different solvents.

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II. METHODS AND SIMULATION TECHNIQUES

We consider a simple cubic lattice of size $L \times L \times L$ with a periodic boundary. The system starts with randomly distributed unreacted monomers. Each monomer carries a number (f) of reactive groups (functionality) capable of forming bonds in pairs. A fraction C_2 of the lattice sites is randomly occupied by bifunctional monomers, a fraction C_4 by tetrafunctional units, leaving the remaining fraction $1-C_2-C_4$ of lattice sites empty. A lattice site cannot be occupied by more than one unit at a time.

We consider the interactions between nonbonded neighboring monomers. This potential is expressed through the reduced energy ϵ/k_BT. The polymer-solvent interactions are not explicitly included. Then the energy parameter $J=\epsilon/k_BT$ describes the solvent quality. When $J>0$, the interaction between polymers is repulsive. If $J<0$, then the interaction is attractive. For the polymer clusters formed by aggregations, we consider only the surface interactions with neighboring monomers of the other clusters. The interior units of a cluster have no interaction with each other. The energy associated with monomers will affect the molecular jump probability, i.e., the motion of the molecules and thus the formation of a bond (cross-link). The Metropolis algorithm is used to accept and reject the hopping of monomers or microgels, i.e., the ratio of moving probability depends on the energy change in the system via $e^{-\Delta E}$, where ΔE is the difference in the energy between the new and old configurations. The only link with thermodynamics is through the probability of $W=e^{-\Delta E}$.

We assume that each of the units in the system has an equal reactivity. 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 monomer at the most by four bonds, or to its neighboring monomers by various bonding with multiplicity between one and four.

Monomers and microgel particles (a finite cluster resulting from the reaction) can move a distance of one lattice unit in a randomly selected direction (one of six simple cubic directions) in one attempt if the excluded-volume criterion and energetic conditions (see below) are met. We focus here on the rigid network. During the move, all bonds must be preserved and the conformation of the polymer is unchanged during this movement. The diffusion coefficient D_n for a free cluster with n monomers is given by $D_n \sim 1/n$, i.e., the hopping rate of a cluster is inversely proportional to its mass. To evolve the system, we select a monomer or cluster randomly and attempt to diffuse it by a lattice unit distance in a randomly chosen direction with its hopping rate. The acceptance of a move is checked with the energetic criterion. After each hopping, the monomer attempts to react with one of its randomly selected neighbors. If both monomers have at least one unsaturated bond (i.e., unreacted functional unit), then a bond is formed between the two monomers with a certain bonding probability p_b. An attempt to form a bond fails if the randomly selected neighboring site is not occupied by a polymer unit or if either of the units is saturated. A unit becomes saturated as soon as it bonds with all of its functional groups. This process of hopping each particle by one step and attempting to form bonds is repeated again and again until the reaction is nearly complete, i.e., all monomers are nearly saturated. The time is measured in units of Monte Carlo steps (MCS). A unit of MCS is defined as an attempt to move all the monomers and clusters and to let them react with their nearest neighbors. One MCS may be divided into m intervals, i.e., in each m interval, only $1/m$ of the total species in the system can be selected randomly to move and react.

In the course of polymerization and kinetic growth, the concentration of reacted monomers increases. The extent of the reaction or the extent of cross-linking p, which is defined as the fraction of bonds formed, increases accordingly. At the sol-gel transition thresholds, where an incipient infinite gel network appears, $p_c=p(t_c)$, with p_c and t_c the critical bond concentration and critical gelation time. In this model, the time evolution of a given configuration is based on the fact that the monomers or microgel particles tend to move close to the other units and form a bond when attractive potentials exist between polymer units (in a poor solvent). On the other hand, they tend to move away from each other in a good solvent where the repulsive interactions dominate. Thus the collision probability of reactive groups and thus the rate of reaction are controlled by the diffusivity of monomers and clusters.

The sol-to-gel transition is related to the connectivity property of the system. As the reaction proceeds the clusters (microgels) grow. When a cluster spans the system, a sol-to-gel transition occurs. This geometrical transition can be studied as a function of time (t) and fraction of bonds (p). We choose the gel fraction as the order parameter of the system. The volume fractions of the two components (gel cluster and clusters in a sol) are ϕ_G and ϕ_S, which are defined as $\phi_G=n_G/(n_S+n_G)$ and $\phi_S=n_S/(n_S+n_G)$, respectively. n_G and n_S are the number of monomers in the gel and in the sol phases, respectively. $N=n_G+n_S$ is the total number of monomers in the system. The gel fraction is defined as

$$G=\frac{\phi_G}{\phi_S+\phi_G}=\frac{n_G}{N}. \tag{1}$$

In the simulations, we also keep track of the following quantities besides the order parameter G: (i) the weight average degree polymerization M_W, characterized by the mean size of the cluster, which is the ratio of the second moment to the first moment of the mass distribution, i.e.,

$$M_W=\frac{\sum_s n_s s^2}{\sum_s n_s s}, \tag{2}$$

where n_s is the number of clusters containing s monomers per site; and (ii) the correlation length ξ (or z average of the radius), which is the measure of the spatial extension of the connectivity, is given by

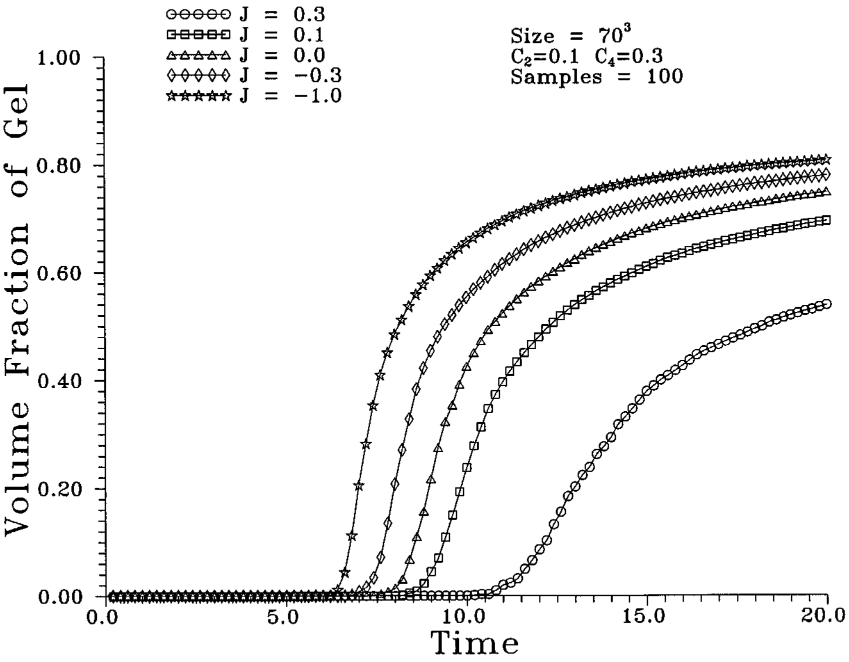

FIG. 1. Gel fraction vs time for various solvent conditions ($J =$ 0.3,0.1,0.0,−0.3,−1.0) with $C_2 = 0.1$ and $C_4 = 0.3$ on the lattice of size 70^3.

$$\xi^2 = \frac{\sum s^2 n_s R_s^2}{\sum s^2 n_s}, \tag{3}$$

where R_s is the radius of gyration

$$R_s^2 = \frac{1}{s}\left\langle \sum_{i=1}^{s} (\mathbf{r}_i - \mathbf{r}_0)^2 \right\rangle, \tag{4}$$

where $\mathbf{r}_0 = \Sigma_{i=1}{}^{s} \mathbf{r}_i / s$ and $\mathbf{r}_i$ denotes the position of the ith connected site. In the next section, we will discuss the behavior of some of these quantities.

III. RESULTS AND DISCUSSION

A. Solvent effects on the gelation process

The monomer-solvent interactions are characterized by a Flory parameter χ [3]. $\chi = 1/2$ corresponds to a cancellation between the steric repulsion and attraction between monomers. At lower χ values, i.e., in the good solvent regimes, steric repulsion dominates. While $\chi > 1/2$ corresponds to a poor solvent, χ can be related to the energy parameter ϵ as [32]

$$\chi = z\epsilon / k_B T, \tag{5}$$

where z is the effective coordination number. In this section, we study the critical properties of gelations in a solvent of various qualities (J = 0.3,0.1,0.0,−0.1,−1.0). The simulations are carried out on a lattice of size 70×70×70. The bonding probability is 0.8. The concentrations of monomers are $C_2 = 0.1$ and $C_4 = 0.3$ throughout this paper. The evolution of the gel fraction with time (MCS) is shown in Fig. 1. The effects of the solvent on the gel time are evident. The gel time is longer in a good solvent. This is because when the repulsive potential ($J > 0$) become larger, the monomers need more energy to overcome the repulsive force and hence have less of a chance of moving close to other polymers to form a bond. For $J < 0$ (in a poor solvent), on the other hand, the attractive interactions facilitate the formation of clusters.

At a low concentration of monomers, the probability of forming a gel becomes very small in the limit $J \rightarrow \infty$, when the probability of forming even a finite cluster is small. We can see this effect more clearly in Fig. 2, which is the plot of the gel time t_c versus the parameter J. The variation of the mean gel size with the extent of the reaction is presented in Fig. 3. We know that the mean gel size shows a maximum divergence in the infinite system at the gel point (p_c). We see that the gel point (p_c) depends strongly on the quality of the solvents (see Fig. 4). In a poor solvent, a gel network forms in a relatively short time, so the extent of reaction is lower at the gel point than that in a good solvent. This seems to be consistent with our previous observation of the gel fraction. However, the attractions between polymer units bring monomers and clusters closer to each other. This enhances the reaction probability, resulting in a more compact network, i.e., the gel fraction (Fig. 1) has greater value at the saturated stage in a poor solvent.

It is generally believed that continuous phase transitions have certain universal properties, e.g., the critical exponents that characterize the phase transitions are independent of the microscopic details of the systems [2]. Near the critical point, the mean gel size M_W diverges with a critical exponent γ, while the evolution of the gel fraction (G) is characterized by a critical exponent β,

$$M_W \sim |1 - p_c/p|^{-\gamma}, \tag{6}$$

$$G \sim |1 - p_c/p|^{\beta}. \tag{7}$$

We have attempted to estimate the critical exponents using the finite-size scaling analysis method [33,34]. Since the correlation length (ξ) is limited by the linear size of the

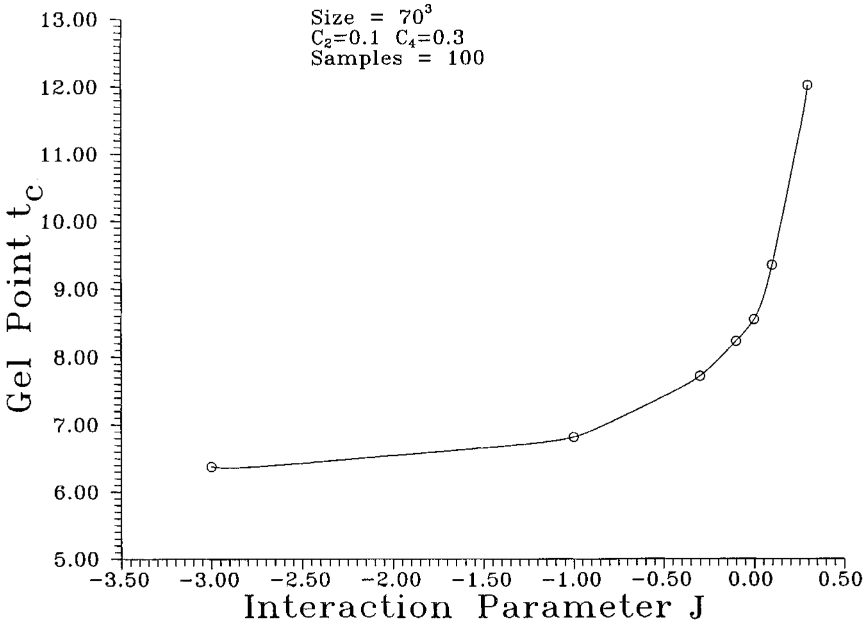

FIG. 2. Plot of gel point (t_c) vs the value of J, with $C_2=0.1$ and $C_4=0.3$ on the lattice of size 70^3.

lattice L as $p \rightarrow p_c$, i.e., $\xi \sim |1-p_c/p|^{-\nu} \sim L$, the gel fraction G and the mean gel size M_W can be expressed in terms of scaling function $\widetilde{G}$ and $\widetilde{M}_W$,

$$GL^{\beta/\nu}=\widetilde{G}[(1-p_c/p)L^{1/\nu}], \tag{8}$$

$$M_W L^{-\gamma/\nu}=\widetilde{M}_W[(1-p/p_c)L^{1/\nu}]. \tag{9}$$

To use the finite-size scaling, we have carried out our simulations with various lattice sizes (50^3-80^3) with $J=-3.0$. Figures 5 and 6 are the finite-size scaling plots of G and M_W, which show that the family of curves G and M_W nearly collapse on a single function $\widetilde{G}$ and $\widetilde{M}_W$ with the choice of $\beta=0.58$, $\gamma=1.42$, and $\nu=0.73$. In Table I, we list the estimates of the critical exponents we found in various solvent conditions. We found that the value of β seems relatively less sensitive to the quality of solvent, while the values of γ and ν increase by varying the quality of the solvent from good to poor.

The cluster structure can be described by the radius of gyration R_s. The fractal dimension of the gel at gel point can be evaluated from the power law

$$s \propto R_s^D (p=p_c, s \rightarrow \infty), \tag{10}$$

where D is the fractal dimension. Figure 7 shows that the variation of s with R_s on a log-log scale at the gel point in different solvents. We find that the slope (D) is almost invariant with solvent qualities with $D \simeq 2.05$. This value is in good agreement with the result from theoretical prediction [4] and experimental result [35].

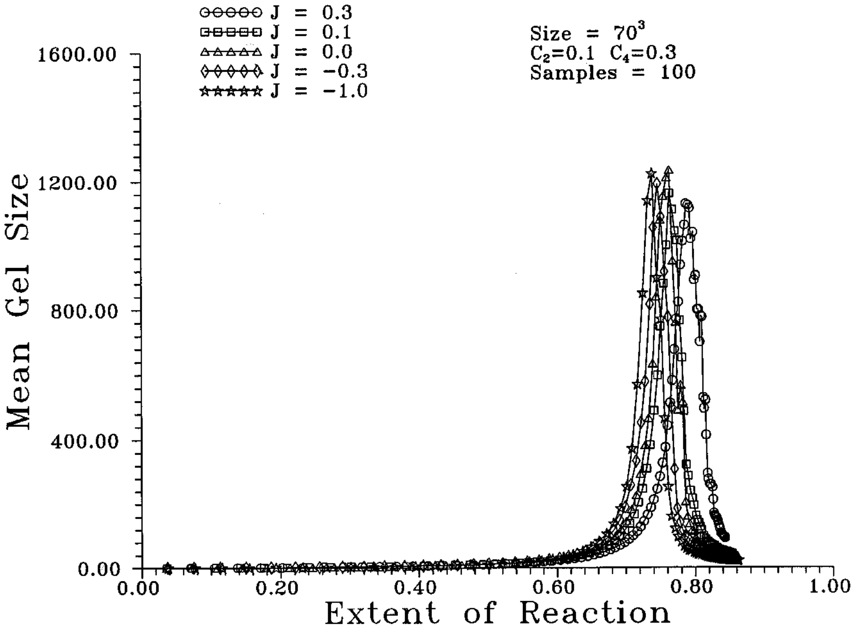

FIG. 3. Mean gel size vs extent of the reaction for various solvent conditions ($J=$ 0.3,0.1,0.0, $-0.3,-1.0$) with $C_2=0.1$ and $C_4=0.3$ on the lattice of size 70^3.

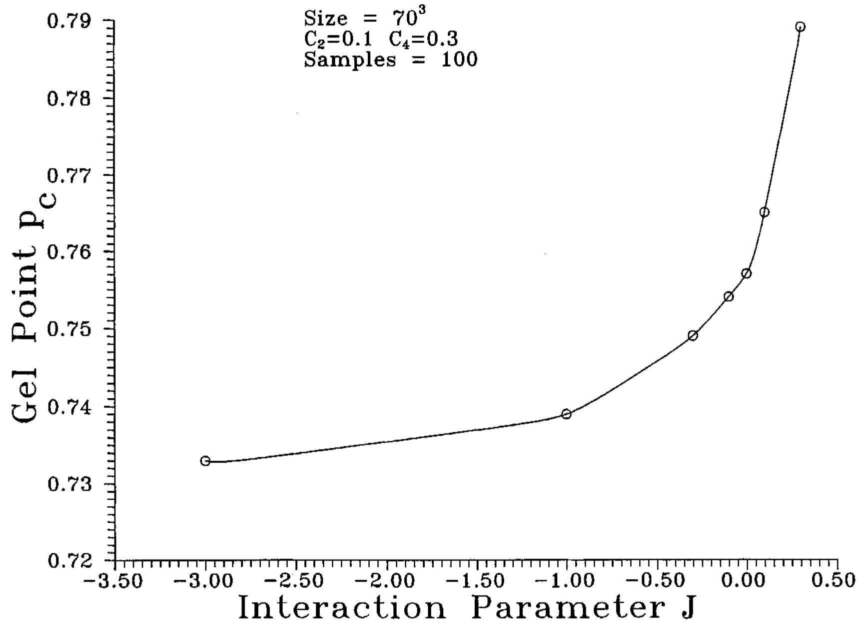

FIG. 4. Plot of gel point (p_c) vs the value of J, with $C_2=0.1$ and $C_4=0.3$ on the lattice of size 70^3.

B. Inhomogeneities in gels

The gel network is highly ramified and heterogeneous particularly at the gel point. It is rather difficult to characterize the inhomogeneities in such a heterogeneous system [36]. The inhomogeneities of gel networks can, however, be thought of as some regions of high cross-link density embedded in the network with low cross-link density. In a gelation in the presence of a solvent, the solvent condition has great effects on the mobility of the components of the mixture as we saw above. Depending on the quality of the solvent, i.e., the value of J and the rate of polymerization, a network with different structures and properties can be grown.

To get a qualitative analysis of the microphase structure, we compute the static structure factors of the system. It is known that the scattered intensity is the result of local variations of the cross-linking density. The structure factor $S(q,t)$ of an L^3 lattice is the Fourier transformation of the spatial correlation function that measures the difference between the local concentrations of two components: ϕ_p, the fraction of polymers, and ϕ_s, the fraction of solvents:

$$S(\mathbf{q},t)=\frac{1}{L^3}\left\langle\left\{\sum_{\mathbf{r}} e^{i\mathbf{q}\cdot\mathbf{r}}[(\phi_p-\phi_s)-\langle\phi_p-\phi_s\rangle]\right\}^2\right\rangle, \tag{11}$$

where $\mathbf{r}$ runs over all lattice sites and $\mathbf{q}=(2\pi/L)\boldsymbol{\mu}=(2\pi/L)(u_x,u_y,u_z)$, $u_x,u_y,u_z=0,\ldots,L$. A local concentration variable ϕ_p^j is equal to 1 if the lattice site j is occupied by a polymer unit and otherwise 0. ϕ_s^j is set to zero in this simulation.

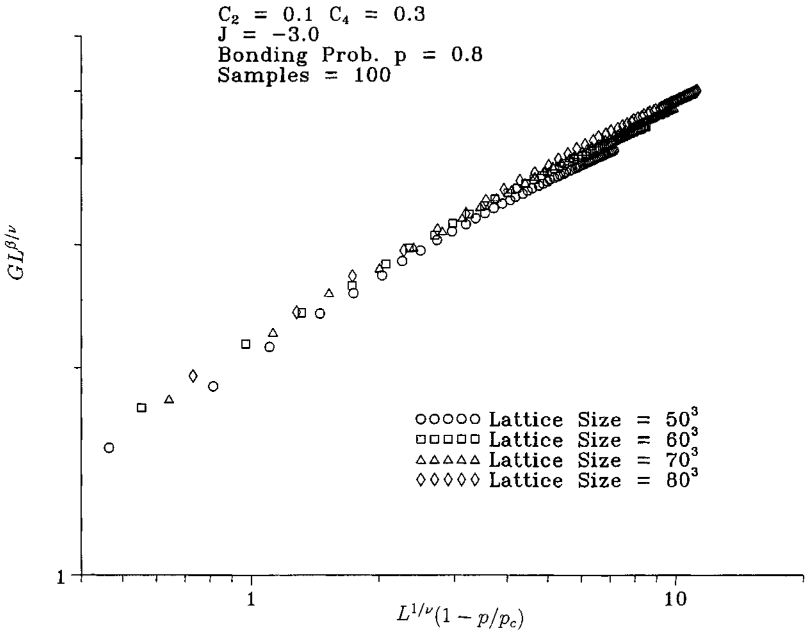

FIG. 5. log-log plot of $GL^{\beta/\nu}$ vs $|1-p/p_c|L^{1/\nu}$, with $J=-3.0$, assuming that $\beta=0.58$, $\nu=0.92$, and p_c = 0.77.

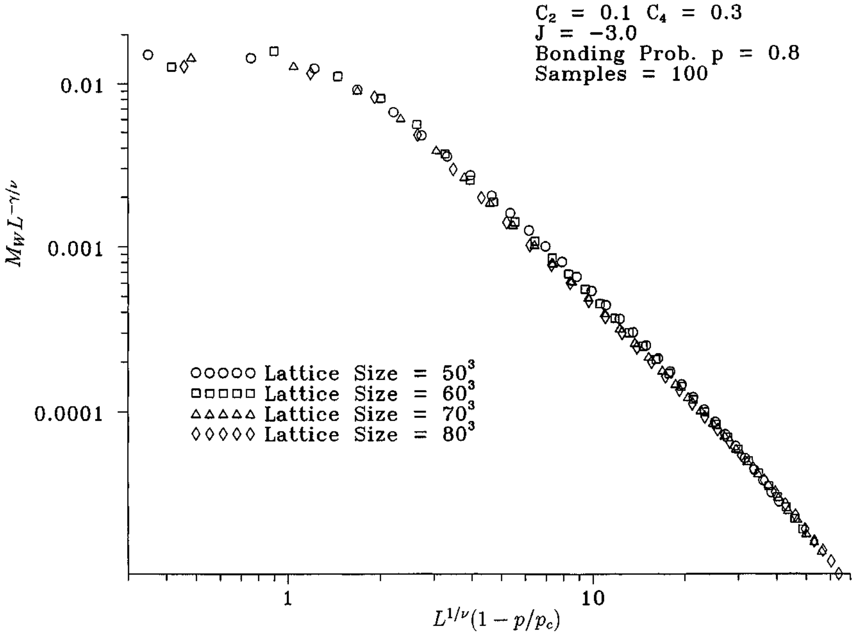

FIG. 6. log-log plot of $M_W L^{-\gamma/\nu}$ vs $|1-p/p_c|L^{1/\nu}$, with $J=-3.0$, assuming that $\gamma=2.08$, $\nu=0.92$, and p_c = 0.77.

In order to investigate the time evolution of the structure, we compute the collective structure factor of the system, which is the average of $S(\mathbf{q},t)$ in a spherical shell of radius q with one lattice unit [37–40],

$$S(q,t)=\sum_q S(\mathbf{q},t) \Bigg/ \sum_q 1, \tag{12}$$

for $q=(2\pi/L)n$. The sum Σ_q goes over all values of $\mathbf{q}$ such that

$$\frac{2\pi}{L}n \leqslant |\mathbf{q}| < \frac{2\pi}{L}(n+1). \tag{13}$$

We use $n=1,2,\ldots,20$ in the calculation.

To see the correlation of the formation property of the gel, we prepared gels at different solvent conditions by varying the values of interaction parameters J. The size of the lattice is 60×60×60 in this section. Figure 8 is a plot of the structure factor $S(q,t)$ as a function of $q'=qL/2\pi$ at various times after the reaction begins with (a) $J=0.1$, (b) $J=-0.1$, and (c) $J=-1.0$. These profiles of the static structure factors of the evolving gel network show the rate of phase separation in various solvent conditions. The growth in the scattered intensity indicates the evolution of inhomogeneities. As the aggregation proceeds, a large cluster forms from smaller ones, which gives rise to depletion zones in the system. This leads to an inhomogeneity in the density of cross-links. But the position of the peak of $S(q,t)$ seems to show no shifts. This indicates that some structures grow after the onset of gelation due to the increase in the extent of the reaction in the network formation. Notice that the bonding probability in these figures is 0.4. To show the effect of the rate of the reaction on the inhomogeneities, we conduct the simulations with $J=-1.0$ and the bonding probability p_b = 0.8, 0.2, and 0.1 (see Fig. 9). In the case of higher bonding probability [Fig. 9(a)], the formation of the large cluster due to the cross-linking reaction is comparatively fast. The phase-separation process is arrested and the growth of the intensity tends to cease faster than in the case of a lower bonding probability [see Fig. 8(c), where p_b = 0.8]. In Figs. 9(b) and 9(c), the bonding probabilities are even lower (p_b = 0.2 and 0.1). The intensities increase and the position of the peaks shifts from a large angle to a small angle because

TABLE I. Critical exponents for the sol-to-gel transition for various solvent conditions. The statistical uncertainty in the estimate of these exponents is around ±0.10.

J	β	γ	ν
0.3	0.64	1.24	0.48
0.1	0.49	1.69	0.91
0.0	0.39	1.92	0.77
−0.1	0.57	1.85	0.82
−0.3	0.58	2.08	0.92
−1.0	0.65	2.21	0.74

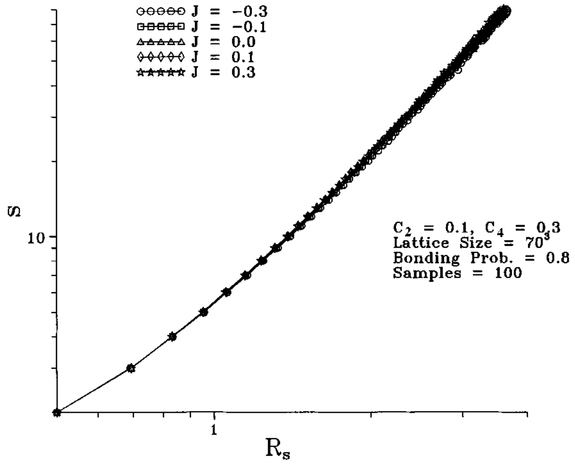

FIG. 7. log-log plot of s vs R_s, with $C_2=0.1$ and $C_4=0.3$ on the lattice of size 70^3.

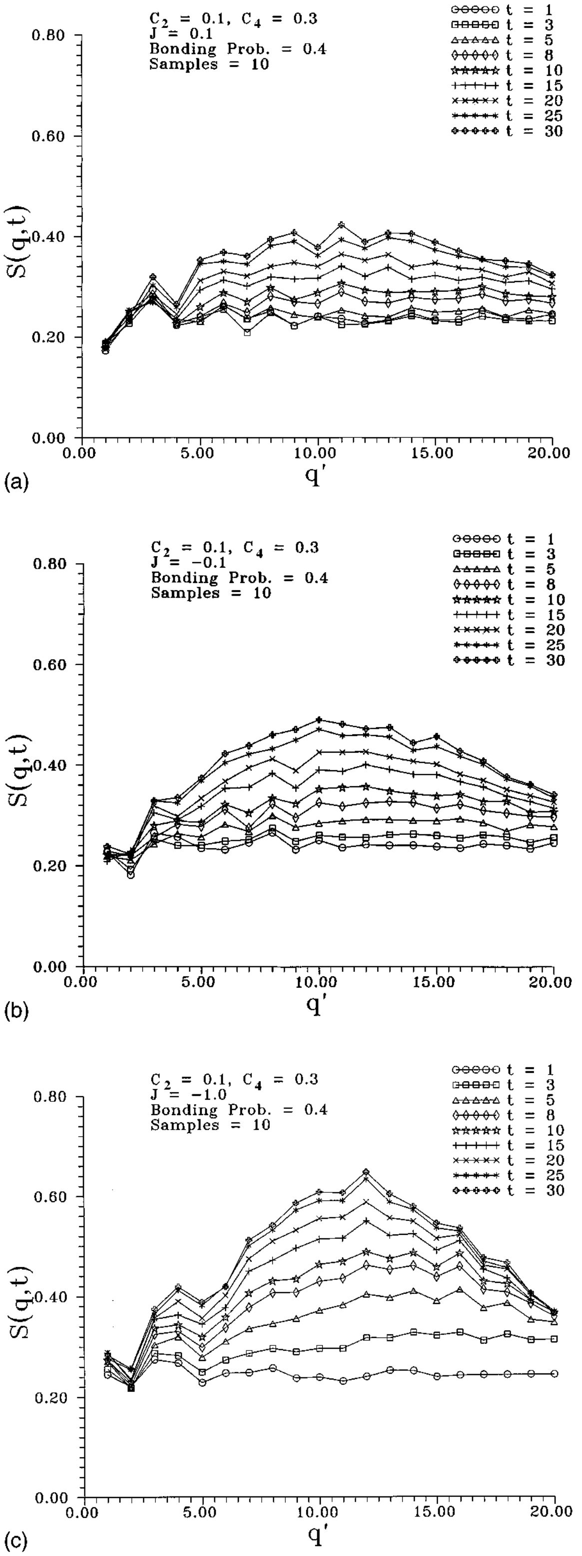

FIG. 8. Structure factors $S(q,t)$ plotted vs $q' = qL/2\pi$ at various times (MC steps), for various solvent conditions (a) $J = 0.1$, (b) $J = -0.1$, and (c) $J = -1.0$ after the reaction with the bonding probability $p_b = 0.4$.

the rate of growth is quite slow compared to the rate of diffusion. These shapes of the structure factor are in good agreement with those observed in experiments [17–20].

The microstructured inhomogeneities in gel can be seen in Fig. 10, which shows the structure factor $S(q,t)$ as a function of $q' = Lq/2\pi$ with various solvent qualities after reacting for $t = 80$ (MCS). It is evident that the final structure depends on the solvent conditions in the formation of gel networks. The inhomogeneities increase with the changing of the value of the interaction parameter J from a good to a

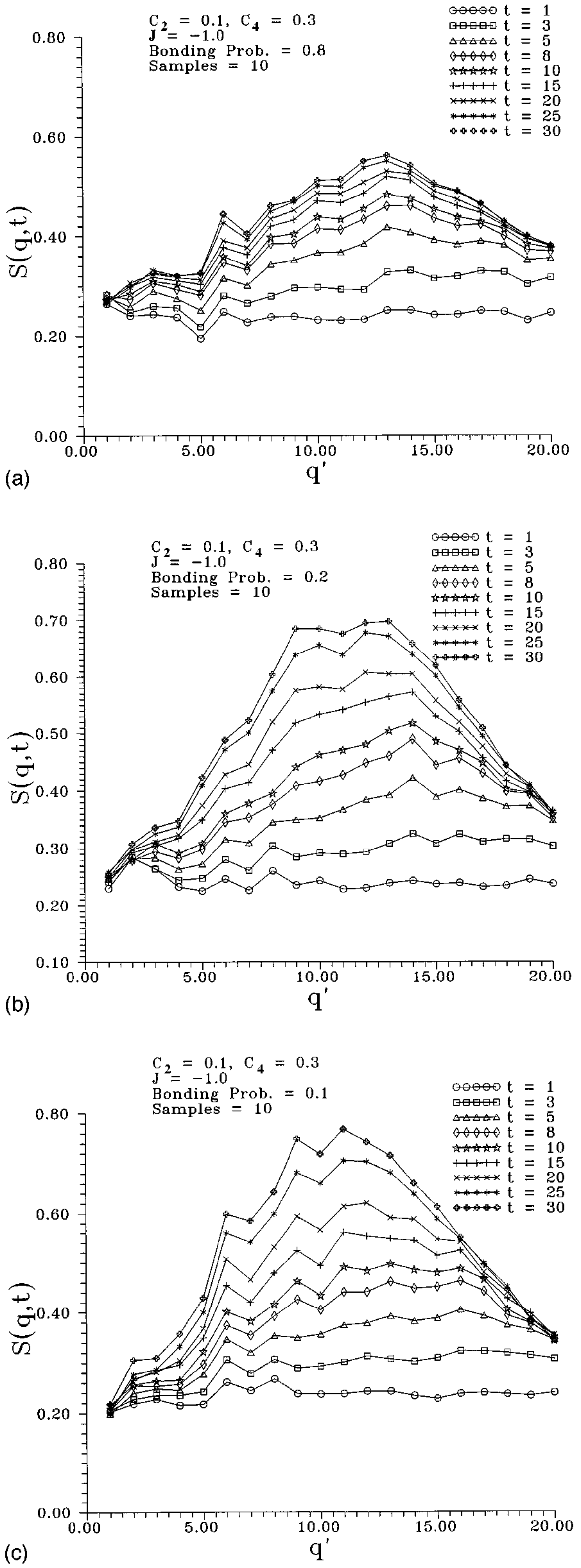

FIG. 9. Structure factors $S(q,t)$ plotted vs $q' = qL/2\pi$ at various times (MC steps), for various bonding probabilities (a) $p_b = 0.8$, (b) $p_b = 0.2$, and (c) $p_b = 0.1$ after the reaction with $J = -1.0$.

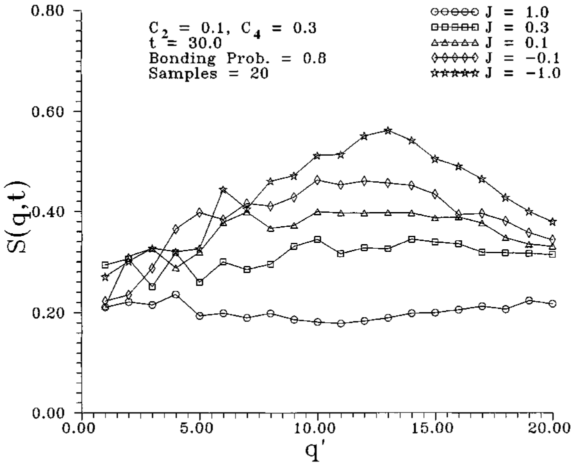

FIG. 10. Structure factors $S(q,t)$ plotted vs $q'=qL/2\pi$ at a time equal to 80 MCS, for various solvent conditions $J = 0.1,0.3,0.1,-0.1,-1.0$, with bonding probability $p_b = 0.8$.

poor solvent range. Notice that when $J\rightarrow\infty$ (a good solvent), the system contains no structural inhomogeneity and the phase separation effects are suppressed. Since the attraction is not as strong as in a poor solvent, the growth of clusters is sufficiently slow and the polymer units are more mobile. So the rate of phase separation is slower than that of gelation. This miscibility of gel networks is affected greatly by the inhomogeneities of cross-link distribution. Our structural data suggest that in a good solvent, the coagulates of polymer segments were less developed (lower gel fraction), forming a loosely packed cluster compared to the gel and microgels in a poor solvent. The polymer thus shows soluble characteristics in a good solvent.

The inhomogeneities were also observed in kinetic gelation models for free-radical polymerization [36]. In the kinetic gelation model, the bonds are formed via the process of a radical (initiator) moving from one site to neighboring sites. Thus the bonding probability depends on the concentration of initiators. To avoid the trapping of initiators (a radical has no site to jump), the concentration of the initiators is usually very low. Therefore, the unequal reactivity of reactive groups due to the very low concentration of initiators is the origin of the inhomogeneity of gel networks. While in our model, the inhomogeneities are caused by the competitions of the unfavorable interactions between polymer units and cross-linking reactions.

IV. CONCLUSION

A computer simulation model is used to study the sol-to-gel transitions in an irreversible gel. A nearest-neighbor interaction of strength $J(\epsilon/k_BT)$ is considered and a Metropolis algorithm is used to move the monomers and microgel particles. In addition to mobility, the rate of reaction is also governed by the bonding probability. The value of the interaction strength J determines the quality of the solvent, i.e., positive J corresponds to a good solvent, while negative J to a poor solvent. The evolution of a gel and sol-to-gel transition is studied as a function of the quality of the solvent. Several interesting observations are made. We find that the gelation process can be affected strongly by the solvent conditions. The critical exponents for the sol-to-gel transition, particularly for the volume fraction of the gel and the mean gel size, vary with the energy parameter J. For example, the magnitude of the gel fraction exponent β decreases from 0.64 to 0.39 on reducing J from 0.3 to 0.0 in a good solvent, while it increases ($\beta=0.57$–0.65) on increasing J from -0.1 to -1.0 in a poor solvent. The exponent γ for the weight average degree of polymerization shows a systematic increase in changing the quality of the solvent from good ($J=0.3$) to poor ($J=-1.0$) (see Table I). This suggests that the universality of the sol-to-gel transition depends on the quality of the solvent. However, the fractal dimension of the gel at the gelation threshold seems insensitive to the solvent conditions. We have also investigated the dynamic development of phase separation and gelation under various cross-linking rates and solvent conditions. The final morphology of the macroscopic gel structure resulting from the interplay between gelation and phase-separation processes can be determined from the analysis of the static structure factors. The structure factor is a good quantity to estimate the inhomogeneities in such heterogeneous gels. We find that the inhomogeneities grow on varying the quality of the solvent from good to poor: the degree of inhomogeneity increases on reducing the solvent quality. The inhomogeneity also depends on the rate of the reaction: the lower the rate of reaction, the higher the probability to develop an inhomogeneity. The qualitative features of these structure factors are in good agreement with the scattering experiments in different polymer systems. From this study of the inhomogeneities in the irreversible gelation, it seems that the evolution of the inhomogeneities near the transition threshold plays an active role in the sol-to-gel transition.

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