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Computer Simulation of Irreversible Kinetic Gelation: Crossover between Random and Kinetic Growth, Radical Conservation, Poisons, and Chain-Preferred Reactions

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A Monte-Carlo study is presented for irreversible kinetic gelation in binary polymers in three dimensions. Using a growth scheme where attempts are made to form bonds with the help of radicals with probability $k/(1+k)$ and without the help of radicals with probability $1/(1+k)$, where $k = 0, 1, 2, \ldots, \infty$, we have studied the crossover from one universality class of critical phenomena in kinetic gelation to another universality class of random percolation. In the radical assisted gelation, several features are incorporated to make the model more realistic, for example, the conservation of the number of radicals during the growth (more suited for living anionic polymerization), the introduction of poisons and chain-preferring reactions are considered. Conserving the radicals delays gelation as well as trapping. The trapping can also be delayed by increasing the functionality of the monomers. The effect of the poison is rather severe; even a small concentration of poison ($c_p > 2\%$) terminates the reaction well before the gel point in a mixture of binary and ternary monomers, and it seems to affect the critical phenomena in the sol–gel phase transitions. In our growth mechanism, where reactions prefer to grow L length steps each in a random direction, the critical phenomena remain unaffected by the length scale, but the flexibility of varying the chain step L allows us to study the changeover between the phase transition in different gel structures.

KEY WORDS: Kinetic gelation; radical polymerization; universality; crossover; percolation.

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1. INTRODUCTION

The problem of kinetic gelation has been an area of continued interest(1-6) ever since the beginning of the quantitative treatments by Flory(1) and Stockmayer(2) to study the problem of sol–gel phase transitions in the complex systems of branched polymers. In this early approach, the reactions are grown along the geometry of Cayley trees to form branched molecules. The sol to gel transition, characterized by the formation of the molecule, practically infinite in size, in this way was later known(7,8) as the percolation phase transition on Bethe lattices. Because of its simplicity these percolation theories, now known as classical theories, are still a valuable tool in deriving the rigorous results(6) in particular for the molecular weights in the pregel state and the position of the gel point, but they are limited only to the idealized trees. Since the classical theory of Flory and Stockmayer is identical to the percolation on a Cayley tree, de Gennes(4) and Stauffer(5) suggested that the percolation on a three-dimensional lattice is a good model for the critical phenomena in gelation. The main criticism(4,5) of the classical theory of Flory and Stockmayer for the sol-gel phase transitions came from the poor comparison of their critical exponents with that of the percolation in three dimensions (3D), for example

$$\nu_{\text{classical}} = 1/2, \qquad \beta_{\text{classical}} = 1, \qquad t_{\text{classical}} = 3$$

$$\nu_{d=3} \simeq 0.9, \qquad \beta_{d=3} \simeq 0.4, \qquad t_{d=3} \simeq 2$$

where ν, β, and t refer to the exponents of the percolation correlation length, volume fraction, and elastic modulus, respectively. It is argued that the tree approximation suffers from its oversimplification in that one assumes no closed cycles and no steric hindrances, the tree branches freely in space without being limited in its growth by the existence of the other branches in the same or in another cluster (or tree), neglecting altogether the excluded volume effects. The problems of percolation have been extensively studied during the last decade. Lubensky and Isaacson(9) presented a field theory for the statistics of the linear chains and branched polymers in dilute and semidilute athermal solvent and showed that the critical exponents for the sol–gel transition will still be of the same type, but no predictions for the position of the gel point could be obtained.

This widely accepted notion of gelation as standard percolation(4) was soon at stake when it was realized(5,10) that both the percolation theory on a 3D lattice and the original classical theory of Flory and Stockmayer describe an uniform static growth process in which the chemical bonds are formed randomly, while in a real irreversible kinetic gelation bonds are formed as a result of a kinetic process(10) which contains both deterministic and random elements. Manneville and de Seze(10) have modeled a reaction growth simulation incorporating the kinetics and suggested that a kinetic gelation model might not even be in the same universality class of the standard percolation. (A universality class is a group of materials or models having, among other properties, the same critical exponents.) Using nearly the same model, Herrmann *et al.*(11) have presented detailed Monte-Carlo simulation data for the kinetic gelation on the simple cubic lattice. Comparing the ratios of the critical amplitudes of the "susceptibility" (the second moment of the cluster size distribution which is a measure of the weight average degree of polymerization) both below and above the gel point, they have shown that this model of kinetic gelation is neither in the universality class of standard percolation nor in that of the classical (Flory–Stockmayer) theory but in a new universality class of its own. In this model all the monomers are randomly distributed on the lattice sites and they are fixed at their positions once for all. It is assumed that the dissociation process is fast enough to produce all the radicals at the beginning of the reaction, and the mobility of the macromolecule, because of its heavy weight, is so low that it can be treated as immobile for all practical purposes. Bansil *et al.*(12) have further extended this model incorporating the solvent (zero functional monomers) and the mobility by exchanging the unreacted monomers with the solvents randomly during the growth. Although these two effects did not change the universality class, they make the computer model more realistic for comparison with laboratory work. The data for the trapping and growth terminations were interpreted in a more transparent picture of loop formation and its shielding.

Recently Jan *et al.*(13) have studied the kinetic gelation in the same system of binary mixtures of bifunctional (2*f*) and tetra functional (4*f*) monomers (without the solvent and mobility) on a triangular lattice by growing the bonds with and without the help of radicals. Their observation on the cluster distribution confirms the conclusions of Herrmann *et al.*(11) that this model is indeed different from the random restricted valence percolation. But in contrast to 3D systems they find that the gel point decreases by increasing the concentration of bifunctional monomers, a phenomenon well known in polymer science.(13a) A study of the critical properties of the radical initiated gelation in the same binary mixture on the square lattice is reported by Rushton *et al.*(14)

In the kinetic gelation, a macromolecule represents a trail of the nearly random movements of the radicals. Here the bonds are grown through a small fraction of the randomly selected sites (active centers). This process results in a growth with memory which incorporates the kinetics of the reaction growth. More uniform randomness can be introduced either by increasing the concentration of the active centers or by allowing the formation of bonds even without the help of radicals as in standard percolations. This possibility was first introduced in Ref. 13. How does the sol–gel phase diagram depend on the extent of deterministic growth? A brief study of this question is recently reported by Pandey and Stauffer.(15) In the present paper we ask: how are the critical properties affected by introducing a small fraction of bond formation other than through radicals in addition to that with radicals (a typical example would be the formation of associates due to hydrogen bonds or crystallization of strands(13a); how does the crossover take place from the static growth (as in percolation) to the kinetic growth (as in gelation)?

As the kinetic reaction grows, the total number of the radicals decreases due to their annihilation which may cause an early termination of the reaction. It is therefore expected that conserving the number of radicals throughout the reaction may delay termination. Perhaps this may bring us closer to the experiments(12) where the extent of trapping is believed to be considerably lower than in the earlier gelation models. However, the trapping can also be delayed(15) in some systems by introducing higher functional monomers in the lattice. This would hopefully permit one to investigate systems otherwise not accessible in their postgel regime. A detailed study of these effects on the sol–gel phase diagram and related critical phenomena is presented here. Further, it is suggested in Ref. 12 to incorporate another feature which entails the termination of the chain growth other than the radical recombinations. Here we do this by including a small fraction of unifunctional monomers which act like poisons preventing the growth on the points of the chains with which they react. Finally, as an extension of all the above models we introduce a new parameter which controls features like the extent of loop formation, cross-linking, branches etc. In earlier models the reaction was grown randomly in all directions through randomly selected active centers; this would perhaps result in a uniform (homogeneous) distribution of loops and dangling ends. In reality, reactions possibly prefer to grow in chains. Inclusion of our new parameter allows us to study in detail the change from the growth with a preference of long chains to the one with no preference. The effect of chain growth on the critical phenomena is also discussed.

In the following section we describe the models, and we clarify the definitions in Section 3. The results are presented in Section 4 in which the subsection 4.1 contains the results of the growth with and without the help of radicals, 4.2 deals with the universality and crossover, 4.3 with the effects of conserving the number of radicals, functionality, and poison on gelation, and 4.4 the chain preferred reactions. Section 5 closes with our conclusions.

2. MODELS

As in the earlier studies,(11,12) we have modeled the reactions on a simple cubic lattice. It is believed(11) that restriction to discrete lattice model, though unrealistic, does not affect the qualitative nature of the kinetic gelation. Using the lattice as a tool, the loop formation (cyclization) and the excluded volume effects are automatically taken into account, which were neglected in the Flory–Stockmayer theory. The effect of the solvent is not considered explicitly.

As a first step of the model, we randomly distribute the m-functional (mf) and n-functional monomers on the sites of a simple cubic lattice with concentrations c_m and $1 - c_m$, respectively. We assume that the mf and nf monomers have the same volume. No two monomers are allowed to occupy the same site simultaneously. In the reaction growth the site occupied by the mf monomers can be connected to the neighboring sites at the most by m bonds and those occupied by the nf monomers at the most by n bonds. For example, a site occupied by a bifunctional monomer can be connected at the most by two bonds with one or two of its six nearest neighbors. Thus monomers up to a maximum functionality six can be simulated on the simple cubic lattice. Again, a mf monomer can be connected by multiple of bonds (m) with one of its neighbors.

Instead of considering the reaction between initiators [e.g., ammonium persulfate and TEMED (tetra methyl ethylene diamine)] to produce a radical(17) we start from distributing the radicals (called initiators) on a small fraction c_I of the lattice sites in addition to the monomers already present. The sites occupied by the radicals are called active centers and are also occupied by the monomers. Now one of these active centers and one of its nearest-neighbor sites are selected randomly, then a bond is formed between the two sites if the monomers at the two sites each have at least one bond left unsaturated. The radical is then shifted to the neighboring site if there is no radical already present at that site, otherwise the two radicals will annihilate each other but the bond will still be formed. If all the bonds of the original or of the neighboring site are saturated then no bond will be formed between the two sites and the radical stays at its place and a new active center with a new neighbor is tried. A site is saturated if all m bonds of the mf monomer at that site are already connected. A radical is trapped if the radical site itself or all its neighboring sites are saturated. The process of randomly selecting an active center, attempting a move to its randomly chosen nearest-neighbor site (called one Monte-Carlo step) and connecting the two sites for a successful move is repeated again and again. The number of occupied bonds increases with time (Monte-Carlo steps) while the number of active centers decreases in time due to their annihilation. The reaction stops when all the active centers are trapped (or annihilated). The bonds grown this way establish permanent links among the constituent monomers and make the reaction irreversible; we do not allow breaking of any connected bond throughout the reaction. The clusters formed by connecting the sites in this process represent the trail of the motion of the radicals (active centers); these clusters are called macromolecules. By studying the statistics of these macromolecules and their growth in time one can study the kinetics of the gelation, sol–gel phase diagram and the associated critical phenomena (see the next section).

So far we have discussed the model already studied in most of the literature mentioned above. Now we describe how to develop it further to cover a wide range of reactions and how to study the basic problems of universality and crossover.

2.1. Random and Kinetic Bond Growth

In kinetic gelation the bonds are grown only through a small fraction of the lattice sites (the active centers) by randomly selecting them and making attempts to form bonds with their nearest neighbor monomers using the procedure of preceding paragraphs. Thus the system has a strong memory. On the other hand, in random (restricted valence) percolation(18) we randomly choose any of the percolating lattice sites and by selecting one of its nearest-neighbor sites randomly we connect them if both sites are not yet connected.

To combine the two growth procedures, the kinetic gelation by initiators and the random bond growth by percolation, we modify our growth algorithm such that after every k attempts made by radicals to form bonds one attempt is made to form a bond without the help of the radicals. Thus the probabilities of an attempt to form a bond with and without the help of radicals are

$$P(k) = k/(1 + k), \qquad Q(k) = 1/(1 + k) \tag{1}$$

where $k = 1, 2, \ldots, \infty$ in our program. Thus the total number of bonds in the system added by radicals divided by the total number of bonds formed without radicals is equal to $P(k)/Q(k) = k$. (For simplicity we take the number of bond formation attempts equal to the number of bonds formed, which is valid for small p, the fraction of occupied bonds.) But if we look only at the unsaturated bonds attached to a monomer with a radical on it, then the probability for one of these bonds to be formed by the radical, divided by the probability for one of these bonds to be formed without the radical, equals k/c_I since only the fraction $c_I \ll 1$ of all bonds formed without a radical happen to be a radical site.

The limit $P(k) \to 1$ $(k \to \infty)$ corresponds to the radical initiated gelation while the limit $P(k) \to 0$ $(k \to 0)$ corresponds to a restricted valence percolation process.(18) One must note that the latter limit is not identical to the percolation procedure, since in our case the two neighboring sites can be multiply connected (as in gelation), which is not permitted in standard percolation. However, since the probability of the multiply connected neighboring sites is small, the critical concentration p_c above which the largest (infinite) cluster appears (and only finite cluster below), is increased by only a small amount over that of the standard percolation threshold p_{perc}, i.e.,

$$p_{\mathrm{perc}} = f(p, p^2, \ldots) = p + ap^2 + O(p^3) \tag{2}$$

Thus we expect p_{perc} to be an analytic function of p. Therefore the critical behavior described by the leading singularities in $|p - p_c|$ should remain the same as the percolation behavior. We will therefore refer to this limit $P(k) \to 0$ $(k \to 0)$ as restricted valence percolation.

Thus by varying $P(k)$ or k one can study the crossover from one class of kinetic growth (gelation) to another class of random growth (percolation). We employ this method to discuss various features governing the phase diagram and critical phenomena. In the rest of this paper we frequently use the parameter k to characterize different cases. We should also mention that the parameter k here is equivalent to m in Ref. 15 and to $1/n$ in Ref. 13.

2.2. Conservation of Radicals

Trapping of the radicals is often a problem in studying the complete growth reaction in radical initiated gelation. If the radicals are trapped before the gel point is reached, one cannot study the sol–gel phase transitions. Sometimes even if trapping is not a problem in studying the pregel reactions, it is not possible to estimate the extent of reaction in the gel due to trapping of the radicals soon after gelation. Also, as the reaction grows the number of radicals decreases due to annihilation; this results in an early trapping. The number of radicals can be conserved by avoiding the annihilation or by creating a pair of radicals in the system whenever the two radicals annihilate each other. Here we adopt the former; whenever a radical would be annihilated in its subsequent move, we move this radical, prior to its annihilation, to a randomly selected site (not occupied by the radical). Now this radical attempts growing the macromolecule to which this random site belongs, in the usual procedure described above.

2.3. Poison

In real gelation(12) there is always a finite chance that the growth of the chain terminates due to poison. In our model of radical initiated gelation, this would be the case at the end of a chain, where the radical is trapped or annihilated apart from the usual trapping inherent in the model. This effect of poison can be taken into account by adding a small concentration of unifunctional ($1f$) monomers in the system. Since the site occupied by the $1f$ monomer can be connected only by one bond with the other molecule, whenever a radical moves on to a $1f$ monomer it has to stay there forever as no chemical bond is left to leave that site.

2.4. Chain-Preferred Reaction

Until now we have applied no constraint on the formation of loops, branches, cross-links etc. in the growth models discussed above. The reactions are grown in a completely random process in which all the active centers are chosen with equal weight to form bonds randomly in any direction with equal probability. The loops, branches, and cross-links formed this way are distributed uniformly. It is, however, possible that in actual gelation the reactions prefer to grow in chains; then it is more likely to form branches and cross-links than loops. To model this situation we grow the reaction in a random direction with a preferred length of L steps, where $L = 1, 2, \ldots,$ in one direction. Thus we randomly choose an active center, say i, and one of its nearest-neighbor sites j, then we connect the sites i and j if both the sites are unsaturated and shift the radical to the site j if there is no radical already present on it; otherwise the two will annihilate each other. This radical now attempts to move the remaining $L - 1$ steps in the same direction $(i \to j)$ if allowed and then—or if it was not allowed earlier to continue moving in one direction—it forgets its directional history. The last site of the series of L moves is a new site for this radical to start its next move in a random direction again of L steps. This process is repeated again and again by selecting the active centers and following the prescribed moves. The limit $L \to 1$ corresponds to our radical initiated uniform gelation while for a large value of L it gives a gelation with more chains and some cross-links. Thus by varying the parameter L one can study the kinetic gelation and the changeover between the two topologically different gels.

3. DEFINITIONS

The basic idea behind defining the various physical quantities in studying the kinetic gelation is the same in all the models described in the preceding section, and the numerical evaluation of them is similar to percolation problems. These methods have already been discussed in the earlier literature(11,12); however, we will briefly recapitulate them here for the sake of completeness.

In the growth process we have seen that the number of occupied bonds (i.e., the connected bonds) increases as the reaction proceeds. A cluster formed by joining the nearest-neighbor sites in the growth attempts is ramified in geometry and is recognized as a branched macromolecule. At a particular instant of the reaction there exist clusters (macromolecules) of various sizes; the distribution of the cluster sizes depends on the reaction mechanism adopted. As the time increases (i.e., as the reaction grows) the probability of finding the larger macromolecules increases and so does the fraction of occupied bonds. An infinite macromolecule appears at a critical concentration p_c of the occupied bonds, known as a gel point, above which the probability of a monomer belonging to this macromolecule increases towards unity as $p \rightarrow 1$. The large molecules are highly ramified consisting of branches, loops, and crosslinks. The topology of the form of a large molecule is believed to change in the course of the reaction growth. Because of the heavy weight, these large molecules are usually assumed(12) to be immobile, although we have assumed even the smaller molecules to be immobile in our growth scheme. From the statistics of the molecules during the kinetic reactions we study the gelation through the various quantities defined below.

In the radical assisted reactions the time of growth at any stage of the reaction is defined in analogy with the standard Monte Carlo practice, and is equal to the sum of all the attempts (including both successful and unsuccessful attempts) made by radicals to form bonds until that stage of reactions normalized by the number of the active centers. In other growth procedures where we allow the formation of bonds even without the help of the radicals, we may analogously define the time as the total number of attempts to form bonds with and without the help of the radicals, normalized by the total number of bonds in the lattice.

The fraction of the occupied bonds $p(t)$ is equal to the total number of carbon bonds (C–C) grown until time t divided by the total number of available bonds in the lattice. Since $p(t)$ increases smoothly with time t all along through the gel point as noted by Herrmann *et al.*,(11) and also supported by our data, one can study the kinetic growth as a function of p rather than t. Note, however, that higher orders of nonanalyticity in $p(t)$ cannot be ruled out.(11)

The weight average degree of polymerization can be expressed in terms of the number of finite macromolecules and their moments. Let n_s be the number of finite clusters (macromolecules) consisting each of s monomers per site. If we assume that mf and nf units have the same weight, then s is proportional to the molecular weight of the molecule of size s; otherwise s is regarded as the degree of polymerization. The weight average degree of polymerization is then defined as

$$\chi_w = \sum_s s^2 n_s \Big/ \sum_s s n_s$$

where the sum is over all clusters of size s, including the isolated monomers ($s = 1$) but excluding the largest cluster. The first moment in the denominator sometimes creates difficulties in the Monte Carlo simulation of finite systems due to strong influence of boundaries; its value deviates appreciably from unity at the gel point. Therefore we focus our attention only on the numerator, the second moment of the cluster size distribution (analogous to susceptibility in thermal phase transitions)

$$\chi = \sum_{s=1}^{\infty} s^2 n_s$$

In the infinitely large system, where the first moment is unity in the sol χ is equal to the weight average degree of polymerization.

The probability $G(t)$ that a monomer is a part of the largest macromolecule is equal to the number of monomers belonging to the "infinite" cluster divided by the total number of monomers. And the probability that a monomer has participated in the reaction is equal to the fraction v, the number of monomers that have at least one bond occupied, divided by the total number of monomers.

We keep track of the data, calculating all the physical quantities described above, throughout the simulation. The initial concentration of the initiators c_I is usually small; a typical value is $c_I = 0.01$, which we choose in all of our simulation here. In real gelation, however, the concentration c_I can be much smaller. As we mentioned earlier, if we allow annihilation of the active centers (whenever the two happen to join together), then the number of initiators decreases smoothly with time. During the growth, all the relevant information (including the physical quantities defined above) are printed in equal intervals of increasing concentration of the occupied bonds. The reaction stops when all the radicals are trapped. The gel point p_c is characterized by the onset of the largest molecule, where χ shows a maximum. We use the numerical estimate of χ to discuss the critical phenomena (see Section 4.2). For a reliable estimate of the quantities in most of the studies here we average over 30 runs on samples $30 \times 30 \times 30$ and $50 \times 50 \times 50$. In all these studies presented here we have used a CDC Cyber 76 machine where we use the efficient subroutine RANF for generating the random numbers. For the large samples the execution time roughly varies between 5 to 15 minutes for 30 runs.

4. RESULTS

Using the above definitions we now discuss our results of simulating the models of Section 2. For studying the critical phenomena we use the largest sample (50 × 50 × 50) and except for extrapolating the results to obtain estimates in the statistical limit of size infinity, we use only the sample 30 × 30 × 30 for the rest of our analysis. The initial concentration of the radicals c_I is kept 0.01 in all our detailed studies here. The effect of varying the concentration c_I on the ratio of the critical amplitude of weight average degree polymerization R (see part 4.2 of this section) has already been discussed by Herrmann *et al.*(11) and we will discuss its effect on the nature of growth in 4.1. A considerable change in the critical concentration p_c on changing the c_I for small c_I observed by us is in agreement with earlier findings.(11,12)

4.1. Random and Kinetic Growth

As discussed in Section 2 of reactions models, after every k attempts made by radicals to form bonds, one attempt is made to form a bond without the help of radicals as in percolation. This process is repeated again and again until all the radicals are trapped or annihilated. The concentration of initiators decreases and the concentration p of the occupied bonds increases with time. As p approaches the critical concentration p_c (the gel point) the largest macromolecule appears. This is a general growth scheme which incorporates both the random and bond growth as in percolation as well as the kinetic bond growth by radicals with attempts probabilities $Q(k)$ and $P(k)$ [see Eq. (1)], respectively. In the limit $k \to \infty$ we get an exclusively radical assisted gelation while in the limit $k \to 0$, a growth as in random percolation.

We should mention here an alternate way to go from the kinetic growth limit to the static growth limit and vice versa. We know that, in gelation, the formation of bonds through a restricted number of sites (the active centers) with concentration c_I results in a deterministic growth process. Increasing the concentration c_I reduces the deterministic growth because the number of the restricted sites increases, and in the limit $c_I \to 1$ when there is no restriction at all, the bonds are formed through any lattice site as in percolation. Therefore, by changing the concentrations of initiators c_I one may study the crossover from kinetic gelation (small c_I) to the percolation (large c_I).(11) The two methods, of changing k and changing c_I may not be similar in their effects on the critical phenomena. Here we will limit to study the effect of varying the k on the sol–gel phase diagram.

The reactions are grown on a 30 × 30 × 30 simple cubic lattice for a set of binary mixtures $2f$–$4f$ with concentration of bifunctional monomers between 0.0 and 0.95 each for several values of k. All critical and trapping concentrations, p_c and p_t, are determined by averaging over 50 runs. The corresponding critical curves (the variation of the critical concentration p_c with c_2) and the trapping curves (the variation of the trapping concentration p_t with c_2) are presented in Fig. 1. Let us first consider the case $k = 1$, when there is equal probability of attempts to form bonds with and without the help of radicals. Then the trapping occurs well before the gel point even at $c_2 = 0$. In the growth process, where $0 < k < \infty$, a fraction of the monomers act like poison, which prevents the growth of the molecule. This can be understood as follows: suppose a bond is formed between two

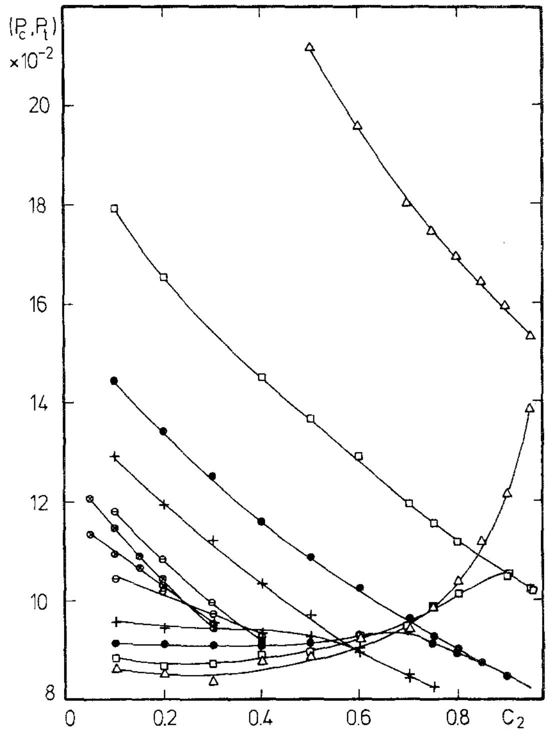


Fig. 1. Plots of the critical concentration (the gel point) p_c (lower points) and the trapping concentration p_t, the concentration of occupied bonds when all the radicals are trapped (upper points) versus c_2, the concentration of bifunctional monomers, in a $2f$–$4f$ binary mixture. Sample size $30 \times 30 \times 30$, number of runs = 50, initial concentration of radicals $c_I = 0.01$. The critical and trapping points, for different values of k (the growth process where, after every k attempts made by radicals to form bonds, one attempt is made to form a bond without the radicals) are shown with different symbols: $k = 2, 3, 6, 10, 24$, and ∞ correspond to ⊗, ⊖, +, ●, □, and △.

bifunctional monomers without any previous bonds. Then these two monomers are left with one unsaturated bond each. Now, if a radical moves into one of these one functional monomers, it will be trapped at the site to which it reacts. This may be the case with any monomer of even functionality (say $4f$) when an odd number of bonds (say 1 or 3) are grown without the help of radicals and if the rest of the bonds are grown with the help of radicals. Then it may act as a poison sooner (when three bonds of a $4f$ monomer are formed without radical) or later (when one bond of the $4f$ monomer is formed without radical). Thus there is a finite probability that some of the even functional monomers may act as a poison (slow or fast) whenever k is finite. For higher values of k the effect of growth termination by such poisoning is expected to be more pronounced at later stages of the reaction. However, the termination due to such poisoning can be delayed by increasing the concentration c_I of radicals.

At the lower values of k (2, 3), both the gel point and the trapping point decrease with increasing concentration of bifunctional monomers, which is in accord with the mechanism discussed above. At slightly higher values of k (6), the gel point p_c remains constant for a fairly large range of c_2 and then it decreases with increasing c_2. In the regime where p decreases, the trapping concentration p_t is quite close to p_c. The fall of p_c with increasing c_2 may be spurious; the data are more fluctuating in this regime. However, the poisoning may also result in such trend. For still higher values of k (10, 24), the gel point remains constant for a larger range of c_2 and then it increases (more pronounced with $k = 24$) and finally it starts decreasing (pronounced with $k = 10$) with increasing concentration c_2. In the limit $k \to \infty$, the gel point first remains constant and then increases with increasing concentration c_2. For the unexpected increase of the gel point p_c with increasing c_2 or decrease of p_c with increasing concentration of tetra functional monomers c_4 may be indicative of some shielding of the tetra functional monomers as is speculated by Bansil *et al.*(12) The trapping concentration decreases all the time with increasing concentration of bifunctional monomers as is expected. The critical-trapping concentration (the concentration of $2f$ monomers at which the critical curve is expected to cross the trapping curve) increases with increasing value of k; this is again in accord with our above arguments.

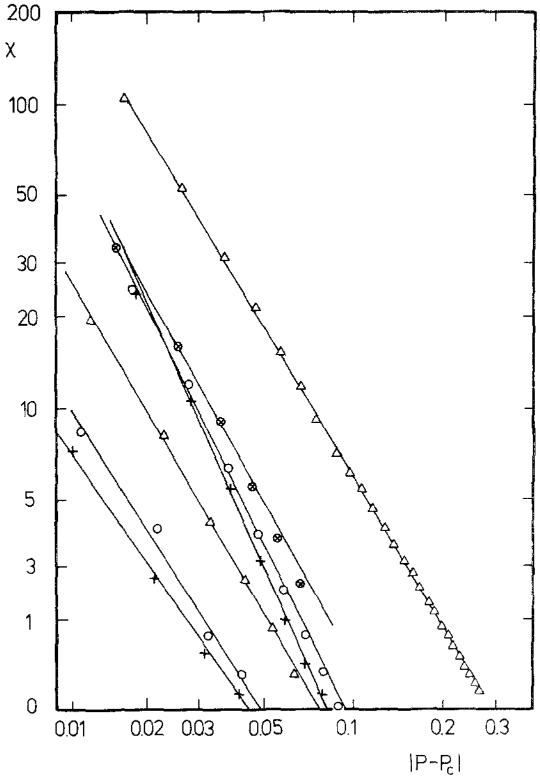
4.2. Universality and Crossover

Here we study the questions regarding the universality class of the sol–gel phase transition and related crossover. We have already discussed that by changing the probability of growth attempts by radicals $P(k)$ (or k) one can make a crossover from one kind of critical behavior of radical assisted kinetic gelation with $P(k)\to 1$ $(k\to\infty)$ to another kind, of percolation with $P(k)\to 0$ $(k\to 0)$. To study the critical phenomena we calculate the degree of polymerization

$$\chi = C_-(p_c - p)^{-\gamma}, \qquad p < p_c$$

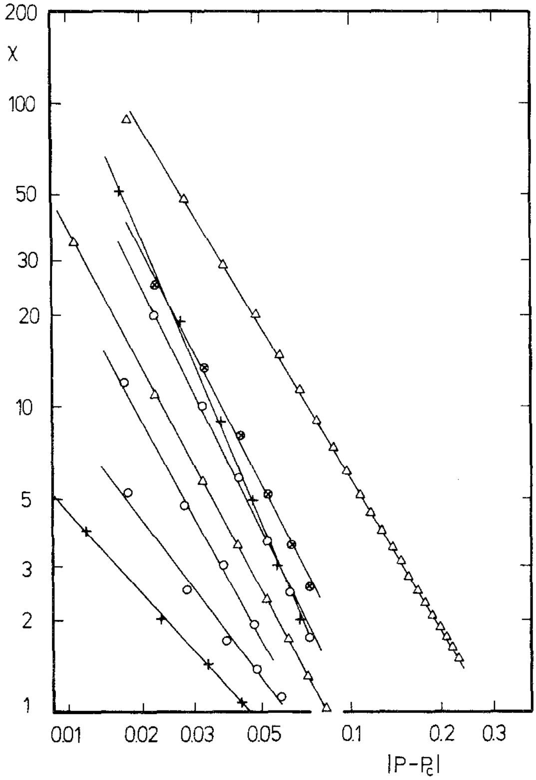
$$\chi = C_+(p - p_c)^{-\gamma'}, \qquad p > p_c$$

where p is the fraction of occupied bonds, p_c is its critical value (the gel point) as we have already mentioned, C_+ and C_- are the critical amplitudes for $p > p_c$ and $p < p_c$, respectively, and γ' and γ are the corresponding exponents. Usually $\gamma' = \gamma$ in most of the second-order phase transitions



(a)

Fig. 2. Log–log plots of the average degree of polymerization, χ versus $|p - p_c|$ for various values k. Symbols △, ⊗, ○, and + denote values for $k = 0$, 3, 6, and ∞, respectively; the fitted lines are shown. Upper points denote data for $p < p_c$ and the lower points for $p > p_c$. Sample size $50 \times 50 \times 50$, number of runs = 30, $c_l = 0.01$. Plots (a) show data for the binary system $2f$–$4f$ with $c_2 = 0.0$ and plots (b) show data for the binary system $2f$–$6f$ with $c_1 = 0.1$.



(b)

Fig. 2. Continued.

according to the scaling theories. However, let us look into the data as such and then we follow our analysis in the framework of scaling hypothesis. This is merely to show how much one has to shift these Monte Carlo data (for χ here) by changing p_c, to obtain the exponent $\gamma = \gamma'$ as in scaling theory.

To calculate the degree of polymerization χ we simulate the data on a $50 \times 50 \times 50$ simple cubic lattice and take 30 runs for each χ to get an average estimate. For $2f$–$4f$ and $2f$–$6f$ binary mixtures the log–log plots of χ versus $(p - P_c)$ are presented in Figs. 2a and 2b, respectively, for various values of k $(= 0, 1, 2, 6, \infty)$. Clearly, these data give very good fits to straight lines (perhaps due to systematic errors) the slope of which vary with k; the deviation in their slopes is clear from these figures. For the $2f$–$6f$ binary mixture we have calculated the slopes γ' and γ and their ratios γ'/γ from the plots; these are collected in Table I. Evidently, for different k

Table I.

k	p_c	γ	γ'	γ'/γ
0	0.288	1.823	1.569	0.875
2	0.123	1.806	1.907	1.056
6	0.102	1.303	1.843	1.408
∞	0.091	1.083	2.385	2.202

values from a systematic change of γ'/γ from 0.87 to 2.20 as k is varied from 0 to ∞, one may be led to believe that the crossover from kinetic gelation to static percolation may be characterized by the change in the value of γ'/γ. Then the question arises how to characterize the universality class where the exponents are supposed to have the same value in one class.

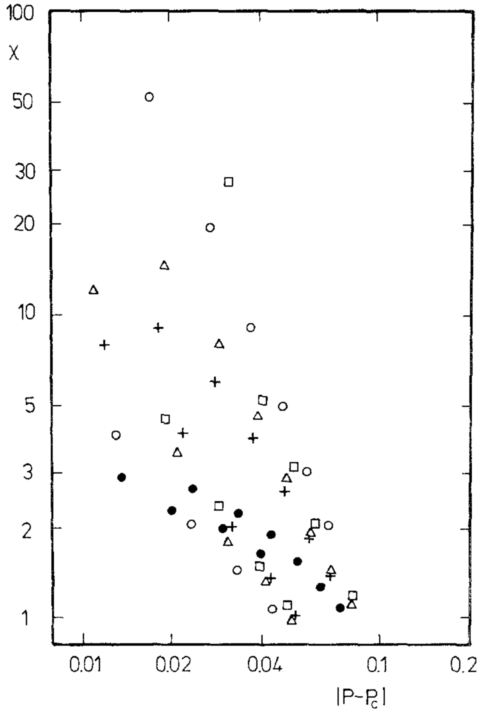
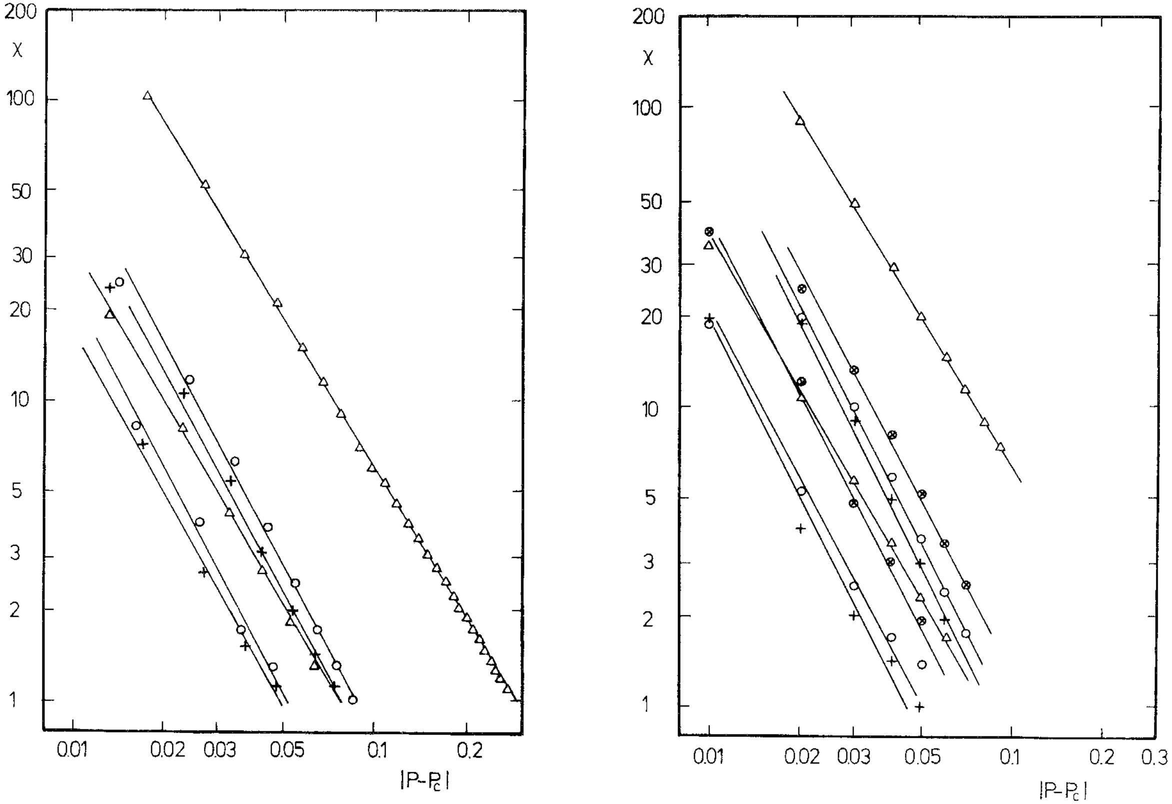


Fig. 3. Log-log plots of χ versus $|p-p_c|$ for the radical initiated growth ($k=\infty$) in a $2f$–$6f$ binary mixture with $c_1=0.1$. From 80 runs on each sample $10\times10\times10$ (●), $20\times20\times20$ (+), $30\times30\times30$ (△) along the data on $50\times50\times50$ (⊗) for $k=\infty$ for Fig. 2b, the extrapolated data for the infinite-size sample are shown by □. Upper points are for $p<p_c$ and lower for $p>p_c$.



(a)

(b)

Fig. 4. Log–log plots of χ versus $|p - p_c|$ of the data obtained after fitting (by varying p_c to make $\gamma = \gamma'$) from the data presented in Fig. 2. Accordingly, (a) and (b) here denote data in $2f$–$4f$ and $2f$–$6f$ binary mixtures, respectively.

One may think that the systematic error due to finite size effect appears both in p_c as well as in the prefactors of the degree of polymerization which causes different values of γ and γ' for different values of k. To resolve this doubt we generated data on various samples $10 \times 10 \times 10$, $20 \times 20 \times 20$, $30 \times 30 \times 30$ for $k = \infty$, and took 80 runs for each to calculate average χ. From these data including our average value of χ and p_c for $50 \times 50 \times 50$ sample we extrapolated the values of χ and p_c to infinite sample. The log–log plots of χ versus $|p - p_c|$ of these extrapolated data along with their original values are shown in Fig. 3. The extrapolated curves give $p_c = 0.91$, $\gamma = 2.24$, and $\gamma' = 1.53$. Although the result supports $\gamma' \neq \gamma$, it should not be regarded as conclusive because of the poor fits in the extrapolated data for $p > p_c$; secondly, the slope is calculated from the data which are not close to p_c, and a slight change in p_c gives considerable change in γ and γ'.

Now we resort to our analysis in context to the scaling hypothesis $\gamma = \gamma'$, which is adopted by Herrmann *et al.*(11) Here we choose the value of p_c to fit our data such that $\gamma \simeq \gamma'$. Log–log plots of these fits for $2f$–$4f$ and $2f$–$6f$ binary mixtures (of the preceding section) are shown in Figs. 4a and 4b for various values of k (0 to ∞). The continuous shifts of the curves give a feeling for the change of the critical behavior as k changes. The crucial quantity for the test of the universality here is the ratio $R = C_-/C_+$ of the critical amplitudes of χ for $p < p_c$ to $p > p_c$. The fitted values of p_c, γ, and R are presented in Table II for various values of k. For the lower values of k we are not able to get sufficient data to calculate γ (for $p > p_c$) because of the early trapping possibly due to poisoning effects. However, the different values of R (~ 9) for $k = 0$ (standard percolation) and R (~ 2) for $k = \infty$ (kinetic gelation) lead one to conclude that the kinetic gelation belongs to a different universality class than that of the standard percolation. Note that various $2f$–$4f$ and $2f$–$6f$ mixtures with $0 < c_2 < 1$ which may correspond to percolation ($c_2 = 0$), restricted valence percolation ($c_2 = c_6 = 0$), and random restricted valence percolation ($c_2 \neq 0$), are believed to be in the same universality class with $R \simeq 8$–10.

How does the universality class change from kinetic gelation to standard percolation—i.e. what is the nature of the crossover? Table II tries to answer these questions. Here the universality class is characterized by the

Table II.

k	p_c	$\gamma \simeq \gamma'$	R
0	0.290	1.7	8.4
2	0.120	1.8	2.7
6	0.100	1.6	3.6
∞	0.090	1.8	3.8

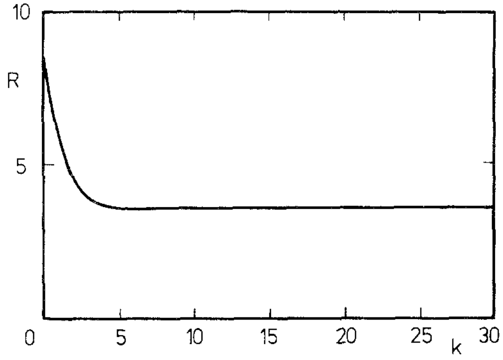


Fig. 5. A qualitative variation of R, the ratio of the critical amplitudes of χ (from $p < p_c$ to $p > p_c$), versus k, from the data on the sample $50 \times 50 \times 50$ of $2f$–$6f$ binary mixture of Fig. 4b.

amplitude ratio R which varies with k. A qualitative nature of the variation of R with k is shown in Fig. 5 for the $2f$–$6f$ binary mixture. The value of $R = 8$ at $k = 0$ drops to almost half of its value at $k = 2$ and then it remains almost constant fluctuating around $R = 3$, throughout the range of k. The variation of R with k leads one to speculate that the point ($p = 0$, $k = 0$ ($P(k) = 0$)) may be a multicritical point where the static percolation and kinetic gelation phase transitions meet. Then there may be a sharp crossover from a percolationlike growth to a gelationlike one at the multicritical point. However, the possibility of a continuous variation of R with k for $k < 2$ cannot be ruled out especially if we look at the variation with $P(k)$ rather than k. We hope further work in this range will clarify our speculations.

4.3. Effect of Conserving the Radicals, the Functionality of the Monomers, and the Poison

Let us now turn our attention to the practical side of the kinetic reactions. Trapping is often a problem since it terminates the reaction preventing the complete growth. Sometimes the reaction terminates before the gel point is reached, making it difficult to study even the pregel regime. Of the various effects in real gelation, here in our simulation we consider mainly three effects: (i) trapping of a radical due to saturated neighbors, (ii) the annihilation of the radicals whenever the two radicals happening to meet, and (iii) the generation of poisons in reactions where k is finite. However, in the radical initiated reactions ($k \to \infty$) in a mixture of monomers of even functionalities, no poisons are generated during the growth, and the reaction terminates only due to annihilation of the active centers and the saturations of the monomers surrounding the radicals. In such cases, the effect of poisons as expected in real gelation may be compensated, to some extent, by annihilation of the active centers.(12) In the following we analyze the data by avoiding annihilation and including the poisons separately in our growth reactions.

We conserve the number of radicals throughout the reaction by avoiding the annihilation. In the growth procedure, whenever a radical would be annihilated with another radical in its subsequent move, we shift this radical instead to a randomly selected other site avoiding the active centers. For the $2f$–$4f$ binary mixtures we simulate the reaction on a $30 \times 30 \times 30$ simple cubic lattice. We take 15 runs for each concentration to find the average value of degree of polymerization χ, gel point p_c, and trapping concentration p_t. The variations of the gel point p_c and the trapping concentration p_t as a function of the concentration of the bifunctional monomers c_2 are plotted in Fig. 6. For comparison we have also shown the corresponding critical and the trapping curves without conserving the radicals. Figure 6 clearly demonstrated that both the gelation as well as trapping are delayed by conserving the radicals. A close observation of the data shows that trapping is delayed more than the gel point, extending the postgel regime. Thus conserving the radicals in our growth mechanism could be helpful in studying the kinetics of the system otherwise inaccessible to their postgel regime.

In the phase diagram of the radical initiated gelation in a $2f$–$4f$ binary mixture we saw that on increasing the concentration of the $2f$ monomers, the gel point first remains constant and then increases as long as gelation occurs. The decrease of the critical concentration p_c on increasing the concentration of the tetra functional monomers was speculated(12) to be due to some shielding of the $4f$ monomers. Is such shielding effect more dominant in higher functional monomers, as is the case in $2f$–$4f$ binary mixtures? To address this question, we performed simulation for the radical initiated kinetic gelation in $2f$–$6f$ binary mixtures, on a $30 \times 30 \times 30$ simple cubic lattice. We took 15 runs to find the average values of the critical concentration p_c and the trapping concentration p_t. The corresponding critical and trapping curves are shown in Fig. 7; for comparison we have shown the same curves for the $2f$–$4f$ binary mixtures. In the critical curve we do not observe significant change except for a little shift which is within the statistical errors. This implies that the probability of shielding the $6f$ monomers is the same as that for the $4f$ monomers. There is, however, a considerable change in the trapping curve; it falls more steeply with increasing concentration of $2f$ monomers. Thus by increasing the functionality the trapping can be delayed as is expected.

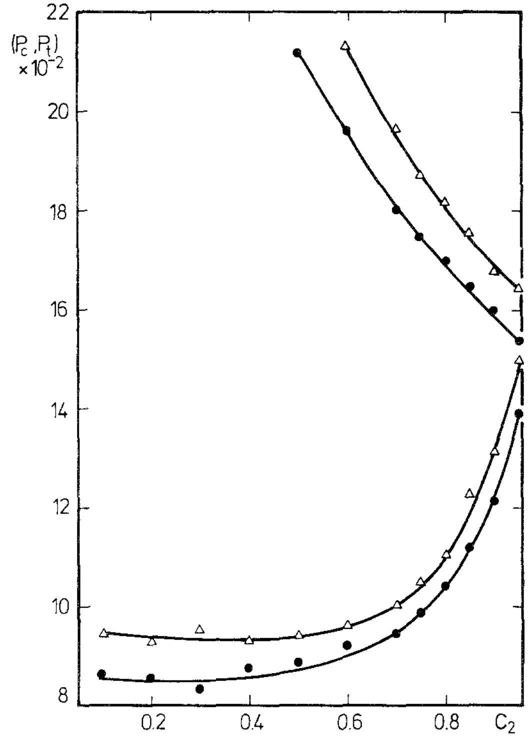


Fig. 6. Plots of the critical concentration (the gel point) p_c (lower points) and the trapping concentration p_t (upper points) versus c_2 the concentration of bifunctional monomers in 2*f*–4*f* binary mixtures. Sample size 30 × 30 × 30, number of runs = 15, $c_I = 0.01$. The points denoted by △ are the data obtained by conserving the number of radicals in the radical initiated reaction ($k = \infty$). For comparison the corresponding data obtained without conserving the radicals are also shown by ●.

The presence of poison is expected to affect the sol–gel phase transition. To investigate this effect, we should remember that even in the radical initiated reactions, the presence of the monomers with odd functionalities acts like poison, since they prevent the growth increasing the possibility of trapping. The higher the order of this odd functionality, the later is their effect as poison. Therefore, we call the higher odd functional monomers "slow" poisons whereas the one functional monomers are called "fast" poisons. Whenever a unifunctional monomer reacts with any molecule, it immediately terminates the growth of the molecule in the direction in which it is attached.

First we consider the sol of 4*f* monomers with a small concentration of poison (the 1*f* monomers) and grow the reaction by radicals allowing the

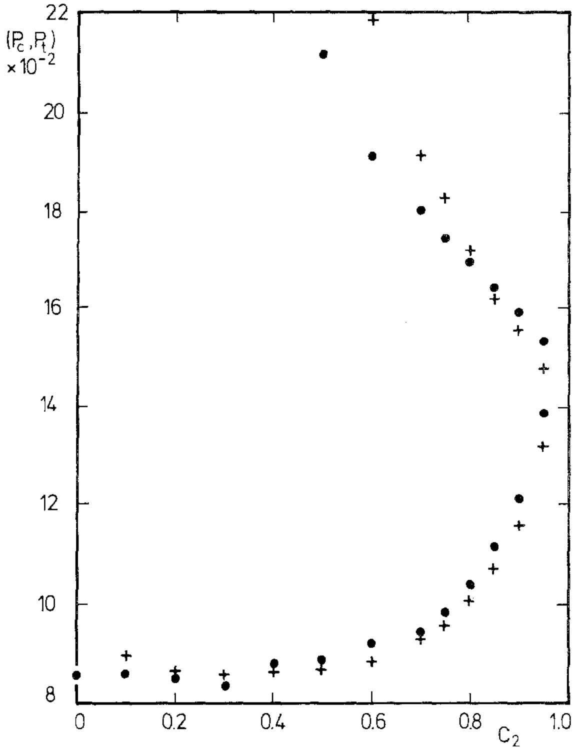


Fig. 7. Critical curves (lower points) and trapping curves (upper points) for 2*f*–4*f* and 2*f*–6*f* binary mixtures for the radical initiated growth are shown by ● and +, respectively. Sample size was 30 × 30 × 30 for both the systems with 15 runs for averaging.

annihilation of the active centers, i.e., we study the radical initiated gelation in a random binary mixture of 1*f*–4*f* monomers. From our simulation on a 30 × 30 × 30 simple cubic lattice (averaging over 15 to 30 runs) we find that the poison with concentration $c_p \geqslant 0.02$ terminates the reaction very fast well before the gel point. We may say that the system will never gel(12) in the presence of poison with concentration more than 2%. At $c_p = 0.01$, which is equal to the initial concentration of the radicals, we do get a gel point but the reaction does not continue very long in the postgel regime. If we conserve the number of radicals, then the gelation can be achieved for the concentration of poison c_p up to 3%: at $c = 0.04$ trapping occurs well before the gel point. By going to 1*f*–6*f* binary mixtures we get the gelation for concentration of poison c_p up to 4%, irrespective of whether we conserve the radicals or allow the annihilation of the active centers. In the latter case trapping occurs soon after the gel point. Introducing a small amount of 2*f* monomers $c_2 = 0.1$, in no case ($1f$–$2f$–$4f$ or $1f$–$2f$–$6f$) we get gelation even at $c_p = 0.01$. This behavior is quite expected, since the $2f$ monomers, after reacting with poisons ($1f$ monomer) immediately become poisons terminating the reaction faster.

How does poison affect the critical behavior in the sol–gel phase transitions and the related crossover? We explore this question by studying the kinetic growth in a $1f$–$4f$ binary mixture with $c_4 = 0.99$ and $c_1 = c_p = 0.01$ and initial concentration of the radicals $c_I = 0.01$ without conserving them. The sample size is $50 \times 50 \times 50$ and we take 30 runs to find out average degree of polymerization χ, critical concentration p_c, and trapping concentration p_t. We carried out this study scanning the entire range of growth processes with $k = 0$ to $k = \infty$. Using the method outlined in

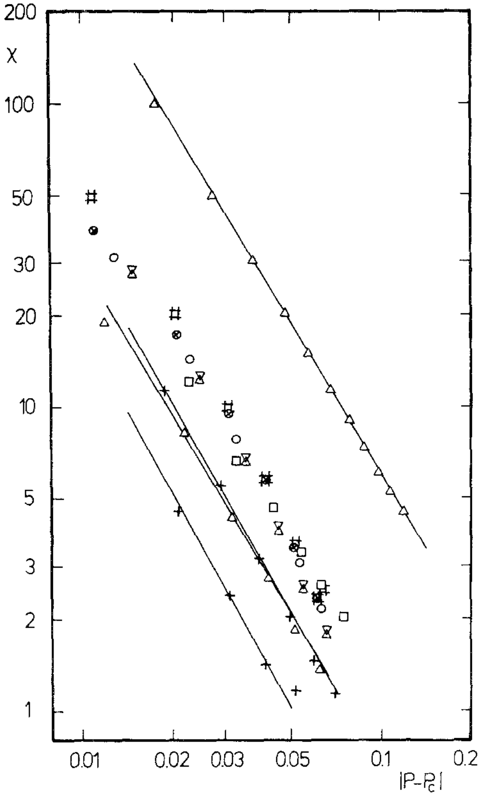


Fig. 8. Log–log plots of the fitted data (by varying p_c to obtain $\gamma = \gamma'$ for χ versus $|p - p_c|$ for $1f$–$4f$ binary mixture with $c_1 = c_p = 0.01$. Sample size $50 \times 50 \times 50$, number of runs = 30, $c_I = 0.01$. Symbols △, □, ○, ⊗, #, ⧗, and + denote the data for the reactions with $k = 0$, 1, 2, 3, 4, 6, and ∞.

Section 2.2, i.e., by shifting the value of p_c until the critical exponents γ (for $p < p_c$) and γ' (for $p > p_c$) become equal, we found the resulting log–log plot presented in Fig. 8. In the two extreme limits we find

$p_c = 0.079$, $\gamma \simeq \gamma' \simeq 1.52$, R 2.0, $k \to \infty$ gelation

$p_c = 0.288$, $\gamma \simeq \gamma' \simeq 1.65$, R 9.3, $k \to 0$ percolation

There are some deviations in the ratios of the critical amplitudes R from those without poison, but the deviations are too small to be regarded as numerically reliable. To analyze the crossover we show the data for $k = 1, 2, \ldots, 6$. Here we do not get sufficient data for the postgel regime, therefore we cannot fit them as in the two extreme cases above. Note the difference in the early trapping from those studied in part 4.2 of this section, where trapping was not much of a problem at least in getting the data for $k = 6$ in $2f$–$4f$ or even for $k = 2$ in $2f$–$6f$ mixtures. However, from the data presented here there is a clear evidence of a drastic change in the value of R as one goes from the $k \to 0$ case to the $k \to \infty$ case; this will make the variation of R with k more steep in the qualitative sense shown in Fig. 5. This may then support that the point ($p = p_c$, $k = 0$) is a multicritical point, and there may be a dramatic change in the critical behavior if we allow the formation of bonds both with and without radicals with equal attempt probability. The presence of "fast" poisons make the crossover sharper.

4.4. Chain-Preferring Reactions

Now we discuss the results of our model of gelation (Section 2.4) where reactions prefer to grow in chains of L-length steps. First, we study the kinetics in a $2f$–$4f$ binary mixture by radical initiated growth on a $30 \times 30 \times 30$ simple cubic lattice. To estimate the gel point p_c, the trapping point p_t, and other physical quantities (χ, G, molecular size distributions, etc.) we simulate 30 runs each for the entire concentration regime of c_2 (0.0 to 0.95) and for several values of L ($= 1, 2, 3, 10, 50$). The calculated critical and trapping curves are presented in Fig. 9, where the critical curves shift downward as L increases. As we have already discussed, $L = 1$ corresponds to the usual kinetic gelation in which the reaction grows randomly in all directions with equal probability through the randomly distributed active centers; this results possibly in a uniform random distribution of cross-links, loops, and branches. As L increases, the reactions still grow through the randomly selected active centers but now the radicals prefer to add monomers (or bonds) in random direction each of L length steps; therefore, the probability of the loop formation is reduced, which brings down the gel

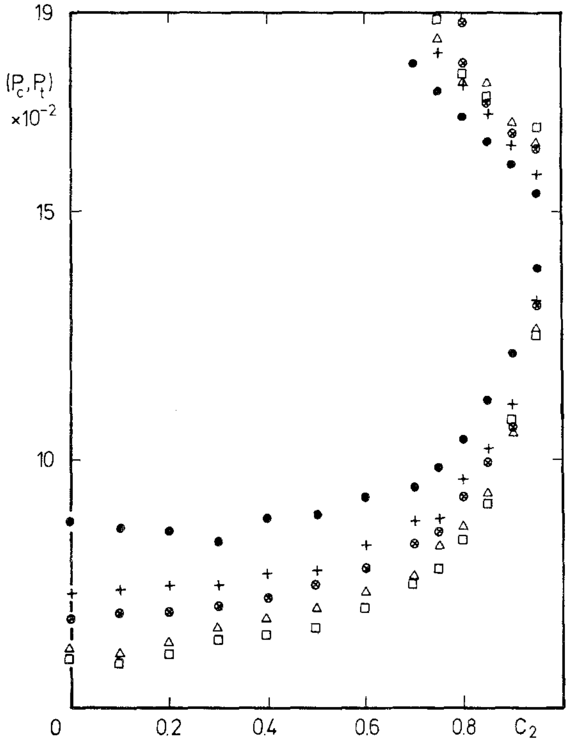


Fig. 9. Plots of the critical concentration (gel point) p_c and trapping concentration p_t versus c_2 the concentration of bifunctional monomers in a $2f$–$4f$ binary mixture of radical initiated chain-preferred reactions with length steps L. $L = 1$ (●), $L = 2$ (+), $L = 3$ (○), $L = 10$ (△), $L = 50$ (□). Sample size 30 × 30 × 30, number of runs = 30, $c_I = 0.01$.

point. When L is large, it is most probable that the gel consists of more branches and cross-links and few loops; on further increasing the value of L, eventually there is no significant reduction in the number of loops and therefore there is a little change in the gel point. This may explain the observed phase diagram in Fig. 9. For varying length steps, there are large fluctuations in the trapping concentration which prevent us from observing a regular trend in the trapping curves.

To study the critical phenomena, we simulate the data on a 50 × 50 × 50 simple cubic lattice and take 30 runs for each value of L. The log–log plots of the averaged susceptibility versus $|p - p_c|$ are shown in Fig. 10. Here also we use the method of comparing the critical amplitude ratio R, to see the effect of L on the critical behavior. Fitting the data by shifting the

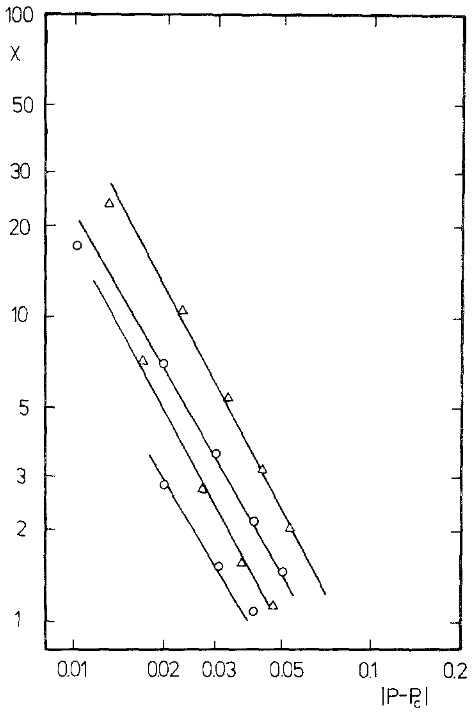


Fig. 10. Log–log plots of χ versus $|p - p_c|$ for the radical initiated chain-preferred reactions in a $2f$–$4f$ binary mixture with $c_2 = 0.0$. Sample size $50 \times 50 \times 50$, number of runs = 30, $c_l = 0.01$. Symbol △ denotes fitted data for the chain length $L = 1$ (where $\gamma = \gamma' = 1.8$, $p_c = 0.083$, $R = 2.55$) and symbol ○ denotes fitted data for $L = 10$ (where $\gamma = \gamma' = 1.5$, $p_c = 0.070$).

critical concentration p_c to obtain $\gamma \simeq \gamma'$, we get

$$p_c = 0.083, \quad \gamma \simeq \gamma' \simeq 1.80, \quad R \simeq 2.6 \quad \text{for} \quad L = 1$$

$$p_c = 0.070, \quad \gamma \simeq \gamma' \simeq 1.55, \quad R \simeq 2.3 \quad \text{for} \quad L = 10$$

These data apparently show that, allowing the reactions to grow with preference of L steps each in a random direction does not change the nature of the critical phenomena.

5. CONCLUSIONS

Using the computer simulation as a tool, we have attempted to look into the basic questions of the kinetics of growth reaction in gelation, how and when it deviates from the random growth processes. We incorporate the two schemes of static and kinetic growth in a model where the attempts are made to form bonds with the help of radicals as in kinetic gelation with probability $P(k)$ and without the radicals as in static percolations with probability $Q(k) = 1 - P(k)$. Varying the probability $P(k)$, we have studied the crossover between the two different universality classes, from percolation $[P(k) \rightarrow 0]$ to gelation $[P(k) \rightarrow 1]$. It appears that the possibility of slow poisoning, which is inherent in our model, makes the crossover sharper; the point $(p = p_c, P(k) = 0)$ may be a multicritical point where the critical behavior changes from static geometrically driven fluctuations to kinetic fluctuations. However, on the basis of our discussions in Section 4.2, the possibility of a set of universality classes resulting in a continuous changeover cannot be ruled out. Clearly, more detailed analysis is needed to shed more light in the precise nature of the crossover in the absence of poison or any other interventions.

We have explored several possibilities to bring the computer models closer to the actual reaction growth. For example, we have studied the reaction by conserving the number of radicals throughout the growth and found this delays both gelation as well as trapping—this could be a valuable tool to study the kinetics where trapping is a problem. The existence of slow poisons and fast (strong) poisons causing an early trapping is discussed. We find that even a small concentration of strong poisons ($c_p \geqslant 2\%$) is sufficient to terminate the reaction preventing the formation of gel. In the case where a gelation is achieved in the presence of poison with very small concentration ($c_p \leqslant 1\%$), the critical behavior seems to be affected by the poison.

For the kinetic gelation in polymers we have studied a new model in which the reactions prefer to grow in linear chains of L-length steps. It appears that by varying the length scale L, the distribution of loops, branching, and cross-links can be changed; this allows us a flexibility for studying the topologically different polymer gels. We find that the critical behavior of the sol–gel phase transitions remains unchanged by changing L; nevertheless, we observe a changeover in the sol–gel phase diagram from a uniform gelation (corresponds to $L = 1$) to a chainlike (with cross-links) gelation as L is changed to a large value.

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