Computer simulation of a model for irreversible gelation

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Abstract. A random mixture of bifunctional and tetrafunctional units is placed on a simple cubic lattice. Permanent bonds between these units are then formed by the random motion of active centres (radicals) resulting in a model for the gelation of polyacrylamide and similar processes. The largest of the clusters formed by this kinetic percolation process is identified with the gel fraction, the 'mean cluster size' with the weight-average degree of polymerisation. The critical exponent γ of the mean cluster size is roughly the same as for random percolation, that is, different from that of the 'classical' theory of Flory and Stockmayer, but the corresponding amplitude ratio, that is, the ratio of average molecular weight on both sides of the gel point, differs strongly from its value in random percolation. Thus, this kinetic gelation model seems to belong to a universality class of its own, different from both that of random percolation and that of classical gelation theories.

1. Introduction

The phase transition (gelation) from the sol to the gel for branching molecules was investigated several decades ago by Flory (1941, 1953) and by Stockmayer (1943) by what became later (Fisher and Essam 1961, Frisch and Hammersley 1963) known as percolation theory on a Bethe lattice. In contrast to other phase transitions like Curie points, little attention has been paid until quite recently (de Gennes 1976, Stauffer 1976) to critical phenomena in this polymerisation process. As a recent review indicates (Stauffer *et al* 1982), it is at present unclear, both theoretically and experimentally, to which 'universality class' gelation belongs. This means we do not yet know reliably if the critical exponents of the sol–gel transition have the 'classical' values obtained from the Flory–Stockmayer theory and similar methods (Stauffer *et al* 1982), if they agree with the exponents of random three-dimensional percolation theory¶ (de Gennes 1976, Stauffer 1976, Stauffer *et al* 1982), or if they differ from both.

An important drawback of many theories, in particular of both random percolation theory on a three-dimensional lattice and of the original Flory–Stockmayer theory, is their assumption that chemical bonds are formed randomly. In reality, for irreversible gelation the bonds are formed as a result of a kinetic process which contains both deterministic and random elements. There is no *a priori* reason to believe that the results of this growth process are the same, or at least belong to the same universality

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¶ We use the expression 'random percolation' for what is often simply called percolation to underline that the bonds are not created according to a thermal equilibrium distribution (Coniglio *et al* 1982).

class, as random percolation on a Cayley tree (Flory–Stockmayer theory) or on a simple cubic lattice (random percolation theory).

The aim of the present paper is to shed more light on the question of how a kinetic gelation process differs from random theories. For this purpose we perform computer simulations of a lattice model for gelation that to our knowledge is the most realistic model investigated so far. It is a generalisation of an earlier study of Manneville and de Seze (1981). In the language of Billmeyer (1962), our model describes an addition polymerisation and not a condensation and was motivated by radical-initiated gelation studies, for example of polyacrylamide. It consists of bifunctional units (corresponding in this analogy to monoacrylamide), tetrafunctional units (corresponding to bisacrylamide) and active centres ('radicals', 'initiators', corresponding to ammonium persulphate) which trigger the polymerisation of the acrylamide. All these units are put into a chemically inert solvent where they can move.

The next section describes this model in greater detail. Section 3 gives the methods, and § 4 the results of our computer simulation. The discussion compares our results with those of other kinetic percolation theories. A short account of our work was given earlier (Herrmann et al 1982); the effects of the solvent with mobility are investigated separately by Bansil et al (1982); therefore, the present results refer mostly to fixed molecules without a solvent.

2. The model

To clarify our radical addition polymerisation model we will first present the example of polyacrylamide gelation (Bansil et al 1982, Tanaka 1981). Monoacrylamide (figure 1(a)) and bisacrylamide (figure 1(b)) are put into an inert solvent. Monoacrylamide has one and bisacrylamide two outer carbon double bonds which can be opened. As each opened double bond gives two new bonds the monoacrylamide is bifunctional and the bisacrylamide tetrafunctional. In our computer model we also denote these molecules as 'units'. An initiator I_2 (e.g. ammonium persulphate: $(NH_4)_2(SO_4)_2$) is included in the sol which dissociates into two radicals: $I_2 \rightarrow 2I^*$ (e.g. two $NH_4SO_4^*$ radicals). Each radical can saturate by breaking up a carbon double bond but leaving the other bond unsaturated (figure (2a)). This free bond acts as new radical opening up another double bond, and thus in a series of reactions a chain is created (figure 2(b)). Chains can crosslink in the tetrafunctional molecules, thus forming branched

Figure 1. (a) Monoacrylamide and (b) bisacrylamide where —R— is an abbreviation for
$$O = \overset{|}{\underset{|}{C}} - N - H;$$
inset: schematic representation.

Figure 2. (a) Initiated monoacrylamide molecule and (b) chain of three molecules; the central one is a bisacrylamide. I is the initiator and * the unsaturated bond; inset: schematic representation.

macromolecules. The gel point is reached when for the first time an infinite macromolecule appears forming the gel which has a finite shear modulus, etc. If two unsaturated carbon atoms encounter each other they can form a bond, thus annihilating their radical character. This is a characteristic of radical activation and would not be possible in the case of anionic or cationic activation. We will not take into account in our model disproportionation, where annihilating unsaturated molecules form two separate polymers, nor processes with poison, which could inactivate the radical, nor degradation, that is the possibility that chemical bonds may break up again. We will also not allow for the possibility that acrylamide molecules react even without the help of radicals. Billmeyer (1962) discusses these effects in detail.

In our simulation we put the molecules on the sites of a simple cubic lattice. Clearly, a lattice is not realistic for a polymer solution; but computer simulations (Vicsek and Kertész 1981, Gawlinski and Redner 1983, Haan and Zwanzig 1977, Gawlinski and Stanley 1981) of continuum random percolation without a lattice gave no qualitative change compared with random percolation on a lattice. We use the lattice as a tool to take into account automatically the excluded volume effects (no two molecules at the same place) and to allow for loop formation, two effects neglected in simple Flory–Stockmayer theory (Flory 1941, 1953, Stockmayer 1943). We do not believe that this lattice approximation changes the universality class of critical phenomena in this model.

Each site of the simple cubic lattice is initially occupied randomly by one of three types of molecules: tetrafunctional units with probability c_t, bifunctional units with probability c_b and zero-functional solvent molecules with probability c_s. Obviously,

$$c_t + c_b + c_s = 1.$$

Chemical bonds can only be made between nearest neighbours on the lattice. The functionality of each molecule or unit gives the maximum number of chemical bonds which it can form with its neighbours; thus the zero-functional solvent is chemically inert and the bifunctional units alone would only form chains without crosslinks and without a transition to a gel (infinite network). Gelation is made possible by the presence of tetrafunctional units which allow for chain intersections and for the formation of large networks of chemically bonded molecules. In our lattice each site has six nearest neighbours; since four is the maximum functionality of any site in our model we have taken into account, to some extent, the steric hindrances which may prevent all functionalities of a molecule from being used simultaneously. We call the bi- and tetrafunctional units 'polymerisable' to distinguish them from the inert solvent.

The growth process is governed by the radicals which we call active centres. In our model, only polymerisable units may carry an active centre which is regarded as part of that polymerisable unit and does not occupy a separate lattice site.

Usually the active centres are produced by the dissociation of more complex molecules, as in our example of the ammonium persulphate molecule that splits into two ammonium sulphate molecules. If this dissociation is relatively slow then new active centres may be formed during the gelation process; if it is relatively fast, all active centres are produced at the beginning of the reaction. This second 'fast' limit is adopted in our model. In the special case of no solvent and no mobility of condensable units, all active centres in the beginning of the simulation are assumed to occur in pairs since they did not have enough time to physically separate after their chemical dissociation. Thus initially a fraction c_I of the links connecting nearest neighbours in our lattice is assumed to be 'occupied' randomly; and an occupied bond

means that the two units connected by that link each carry an active centre and are permanently bound together. Since the number of bonds is three times the number of sites in a simple cubic lattice, and since each initiator (initially occupied bond) contributes two active centres, the total number of active centres is $6c_1L^3$ in a lattice with L^3 sites at an initiator concentration c_1. When the polymerisable units are mobile in a solution (Bansil *et al* 1982) $(c_s \neq 0)$ we take the active centres as highly mobile and thus distribute them randomly at the beginning, no longer pairwise, with the only restriction that no unit carries more than one radical. (We keep, however, the definition of c_1 as above with the factor 6.)

So far we have only explained the initial distribution of the various molecules which then undergo a polymerisation process. This gelation process is defined by the motion of active centres: each active centre can move from its present site to a nearest-neighbour site, and then the bond between its old site and the new site is called occupied (permanent chemical bond). Groups of polymerisable units connected by occupied bonds are called clusters and correspond to macromolecules. (Unattached monomers are not called clusters.)

The motion of an active centre to its nearest-neighbour site is random except that the new site must have at least one free functionality. That means at most three (one) of the four (two) possible bonds emanating from the tetrafunctional (bifunctional) neighbour are allowed to be occupied before the active centre jumps to that neighbour. Solvent molecules never carry an active centre and are never connected by occupied bonds. Should the active centre jump to a site carrying another active centre, the two radicals annihilate each other and the bond between the two sites becomes occupied. Thus the number of occupied bonds increases with time, and these bonds trace the motion of active centres, the number of which decreases in time due to annihilation. Active centres can also become trapped even if they are not annihilated, if all their neighbours are chemically saturated, that is, have all their possible two or four bonds occupied. Entrapment can eventually stop the whole growth process.

No bonds can become occupied in our model except by the above process of initial distribution and later motion of active centres. Since the active centres can jump rather freely from one polymerisable unit to another, we arrive at chemical bonds between different tetrafunctional units, between different bifunctional units and between tetra- and bifunctional units. No direct links are possible between the functionalities of one unit (which would transform a tetrafunctional into a bifunctional unit). Loop formation is not restricted and excluded volume effects are taken into account automatically by the lattice structure.

Since the occupied bonds describe the path of motion of an active centre they are spatially correlated, in contrast to random percolation. But since at every moment the motion of the active centres is random, and since their initial (pairwise) distribution is also random, we have taken into account fluctuations in our model and avoid the completely deterministic approach of some other theories (Schulthess *et al* 1980, Ziff 1980, Leyvraz and Tschudi 1981, Ziff *et al* 1982, 1983) where kinetic equations involving the *average* concentrations of units and macromolecules determine the changes with time. We think that this deterministic averaging approach is valid in the limit of extremely high mobility where a molecule can react with equal probability with every molecule in the whole system independent of their separation. Our model deals mainly with the opposite limit of zero mobility of polymerisable units. We now describe how the intermediate and more realistic case of finite mobility can be simulated.

A finite mobility is allowed in the model with help of the solvent molecules (zero-functional units). Each solvent site may exchange place with a neighbour, be it another solvent molecule or a polymerisable monomer. (Monomers are units which have not yet reacted at all.) The problem is how to treat the mobility of macromolecules, that is, what to do if the solvent molecule wants to exchange its position with a neighbouring polymerisable unit which is connected by permanent chemical bonds to other polymerisable units and thus forms part of a macromolecule or cluster. A complete treatment would have to include the motion of the macromolecule as a whole (Gould and Holl 1981) as well as conformational changes where only parts of the cluster move. Entanglement between different macromolecules will hinder these motions and make a computer simulation quite difficult. For simplicity we thus allow a unit to move only if it is connected by at most one occupied bond to another unit. The bond length is then changed to the new distance. (In the study by Bansil *et al* (1982) only unattached monomers were allowed to exchange sites with solvent molecules.) We vary the mobility by changing the ratio of the rate of exchange attempts for solvent molecules to the rate of jump attempts (reaction rate) for the active centres.

Our model is similar to that of an earlier study of Manneville and de Seze (1981), the main differences being that we allow for bonds between nearest neighbours only (whereas Manneville and de Seze also take into account jumps of the active centres to next-nearest neighbours) and that our initial distribution of initiators has a constraint. We also look at different and experimentally more relevant quantities, use larger lattices to obtain better statistics and smaller boundary effects, and differ in some conclusions from Manneville and de Seze (1981) (see below). Finally, Manneville and de Seze had no solvent and no monomer mobility in their computer simulation. Thus our model is a continuation, generalisation and improvement of that studied by Manneville and de Seze (1981).

Our work was suggested in part by polyacrylamide experiments (Bansil *et al* 1982). This model may work even better for divinylbenzene-styrene, methyl methacrylate or other experimental examples. The main aim here is not to reproduce one given experiment but to investigate deviations from randomness due to the growth process.

3. Methods

Our method of investigation is a computer simulation of the model described in § 2. This method is a Monte Carlo simulation, since it involves the use of random numbers. Our method differs from Monte Carlo simulation of thermal phase transitions in that no thermal equilibrium, described by Boltzmann factors, is assumed anywhere: we look at a growth model for irreversible gelation, not an equilibrium model for reversible gelation. Therefore our simulation has more similarity with Monte Carlo studies of random percolation than with Monte Carlo simulation of lattice gases. (See Binder (1979) for a collection of review articles on both Monte Carlo methods.) In particular, our method is closely connected, though with different results, to the single-cluster percolation studies of Leath (1976), Alexandrowicz (1980), Pike and Stanley (1981) and Grassberger (1982).

At the beginning of each simulation we randomly distribute tetrafunctional units with probability c_t on a simple cubic lattice of $L \times L \times L$ sites, with L up to 60. All other sites are occupied by bifunctional units with a concentration c_b or by solvent

units with a concentration c_s. The positions of bi- and tetrafunctional units are fixed throughout the simulation, with the exception of some runs (to be described in the next section) where some mobility is allowed due to the presence of zero-functional units ('solvent molecules'). In the case $c_t = 1$ all sites are occupied by tetrafunctional units but even then the system does not correspond to random percolation. One reason is that in random percolation on this simple cubic lattice each site has functionality six, whereas our sites are only tetrafunctional. The other reason is that we look at a growth process whose results differ from those of random percolation, where bonds are formed randomly instead of our process of gradual initiation of neighbouring bonds.

In the previous section we explained the meaning of an occupied bond. To simplify the computation we assume that initially no unit can have more than one occupied bond, in other words, the initiators are not allowed to be nearest neighbours; apart from that restriction, the spatial distribution of initiators is taken as random. According to Kertész *et al* (1982), for $c_t = 1$, the initiators would form an infinite network of neighbouring bonds if c_I is larger than about $\frac{1}{3}$, if they are allowed to be nearest neighbours (restricted valence percolation). For c_I much smaller than this percolation threshold for tetrafunctional units, most initially occupied bonds are automatically isolated from other initially occupied bonds even if our neighbour avoiding restriction is not imposed. Thus for $c_I \ll \frac{1}{3}$ our assumption should not change the results, and therefore we only worked with rather small c_I. If one wants to study effects from larger c_I, however, it would be useful, and possibly more realistic, to allow occupied bonds to touch each other already at the beginning; the necessary changes in the computer program may increase the computation time by about 10%. (In the simulation following the initial distribution of occupied bonds, our restriction is no longer used and occupied bonds may touch.) While c_I is low, the number $3c_I L^3$ of initially occupied bonds (or $6c_I L^3$ radicals) is always much larger than unity ensuring that our model differs from the growth of a single cluster (Leath 1976, Alexandrowicz 1980).

The kinetic process following the initial distribution of radicals is defined as follows: each initially occupied bond is regarded to connect a pair of free radicals (see figure 3(a)). At each time unit of our model, that means at each Monte Carlo step per radical, a radical randomly selects one of the six bonds emanating from this radical
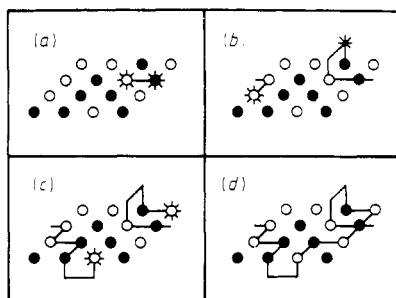

Figure 3. Schematic growth process for $L = 4$, $c_t = 0.5$, $c_s = 0$ and $c_I = 0.021$. Full circles are tetrafunctional units, open circles bifunctional units and stars are radicals. (*a*) Initial state; (*b*) and (*c*) after 4 and 11 successful attempts to occupy a bond; (*d*) the two radicals annihilate and a closed loop is formed. We show one plane only but allow bonds to go to planes above and below. Note our periodic boundary conditions for the motion of the radicals.

lattice site. This newly selected bond leads to another neighbouring lattice site. Now one of two possibilities occurs: in the first case this neighbouring lattice site has all its two or four bonds occupied, for bi- and tetrafunctional lattice sites, respectively. (For example, if the neighbour is bifunctional and sits on top of the original radical lattice site, then it may have occupied bonds with its left and right neighbour, whereas its four other bonds pointing up, down, back and forward are still empty.) In this case no additional bond can be occupied for this neighbour, and the original radical stays at its old place without creating any new occupied bond; we simply go over to some other radical. In the other case, the number of occupied bonds emanating from this neighbour is smaller than the functionality (two or four) of their neighbour. Then the bond connecting the original radical and its selected neighbour is regarded as occupied (figures 3(b) and (c)). If in this case of a successful attempt to create a new bond the neighbour happened to be another radical, the two radicals are regarded as annihilating each other (figure 3(d)); otherwise the neighbour is now a radical whereas the original radical site is not now a radical.

In one Monte Carlo attempt a radical site was selected randomly. If all its six neighbours are already saturated, that is, have all their functionalities occupied, then the radical is called trapped. If all radicals in the system are trapped, then no changes at all will occur even if we make an infinite number of attempts. We therefore stopped the calculation if a predefined number of attempts to find a new bond to be occupied were unsuccessful; then a message was printed out informing us about this entrapment. Otherwise we stopped the calculation after a time when we were sure that gelation (i.e. formation of an infinite network) had already occurred.

Initially, besides isolated monomers we have only clusters of size two, that is, macromolecules containing two lattice sites connected by the initially occupied bonds (no neighbouring bonds were allowed). During the growth process described above the clusters can grow by the addition of one previously isolated site, or by coalescence of two clusters. Thus during the simulation it is rather easy to keep track of the number n_s of clusters (per lattice site) containing s monomers each. s is proportional to the molecular weight if the bifunctional and tetrafunctional units have the same weight; otherwise s should be called the degree of polymerisation for that particular macromolecule. For light scattering studies it is of particular interest to know the weight-average degree of polymerisation defined as $\Sigma_s s^2 n_s / \Sigma_s s n_s$ where the sum runs over all finite cluster sizes s (including $s = 1$ for isolated monomers). In Monte Carlo simulations of finite systems, the denominator in this definition is known to present some difficulties since it is strongly influenced by the boundaries of the system and deviates appreciably from the value of unity it should have at the gel point (and in the sol) (Hoshen *et al* 1979). Therefore we looked at the second moment of the cluster size distribution, that is, at the numerator in the definition of the average molecular weight:

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

This second moment is represented by the symbol normally used for the susceptibility in ferromagnets, for in the analogy between gelation and ferromagnet-to-paramagnet transitions this second moment corresponds to the zero-field susceptibility (Stauffer *et al* 1982). For infinitely large systems at the gel point, the difference between χ and the weight-average degree of polymerisation becomes negligible. We also determined G, the size of the largest cluster divided by the total number of lattice sites;

this G is the gel fraction in our model and corresponds to the spontaneous magnetisation in the magnetic analogy.

Originally we stored in the computer information on which bonds are occupied and which are empty; however, execution time was reduced by nearly one order of magnitude if we restricted ourselves to keep in the memory only the number of occupied bonds emanating from each site. With this method one necessarily allows for up to three bonds to be occupied between neighbouring sites if both sites were initially tetrafunctional radicals. One allows up to two bonds to be occupied between neighbouring sites if the sites were initially radicals and one or both bifunctional or if the sites are both tetrafunctional but the bond was not initially occupied.

On the IBM computer 370/158 the random numbers were determined by a mixture of two random-number generators (Ambegaokar *et al* 1973): with one we filled a table of a hundred random numbers while with the other we selected which of these random numbers should be used now and which should be replaced by a fresh random number. We used one random number to determine several random variables. On the CDC Cyber 170/730 computer, we used the better random number generator RANF available there.

The whole procedure of distributing bi- and tetrafunctional units, initialising and growing was performed N times and the statistical average was taken. N was chosen between 50 and 500 depending on the fluctuations observed.

In summary, we simulated a growth process where many free radicals in our lattice wander around rather randomly and leave occupied bonds in their path which connect chemically the neighbouring bi- and tetrafunctional units. For an initial concentration $c_I = 0.003$ of occupied bonds, an attempt of a radical to move took about 0.3 ms on the IBM at the University of Georgia. The program was about 30% faster on the CDC.

4. Results

Since the kinetic model presented in the previous sections is expected to describe a time-dependent behaviour, we wish to clarify what the time is in our model. Let us set $t = 0$ for the time when the growth begins. Then we define our time t to be equal to the number of attempts (successful and unsuccessful) to grow a bond on the lattice, normalised by the initial number of active centres $n_0 = 6c_I L^3$. Naturally this definition is arbitrary but we believe it coincides more or less with reality.

To establish the relationship to percolation we will look at quantities depending on p instead of t, where p is the number of occupied bonds at a certain time divided by the total number of bonds in the lattice ($3L^3$). In figure 4 we show the dependence of p/n_0 against $t/3L^3$ and see that the behaviour is smooth also at the gel point p_c for $c_I = 0.003$, $c_s = 0$ and two values of c_t. Certainly higher-order non-analyticities cannot be ruled out by a plot of this kind but they are very improbable.

In experiments the measurable quantity is not p but the fraction v, which is defined as the number of units that have at least one occupied bond per total number of polymerisable units. In figure 5(a) we plot v against time. As expected we see a monotonic increase of v and note a smooth behaviour of v at the gel point p_c. Experimentally v shows a saturation at large times at a value v_0 that may be smaller than 1. In our case we also see a saturation, but at some time t_t all our active centres are trapped and the growth stops. This early trapping is certainly an artifact of the lack of mobility and takes place at a v of about 0.6. Fortunately the gelation usually
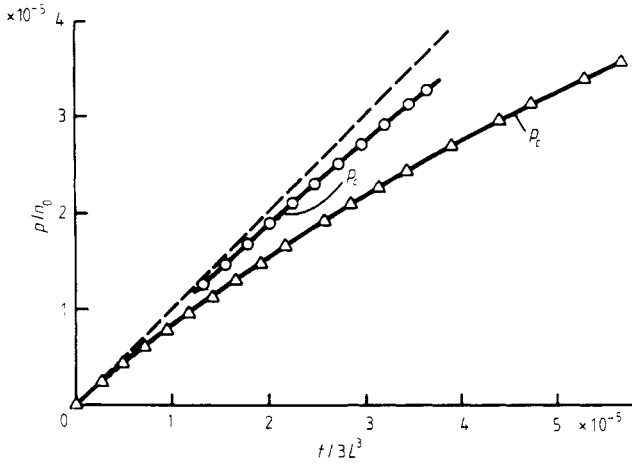
Figure 4. p divided by the initial number of active centres n_0 against the time t divided by the number of bonds for $c_1 = 0.003$, $c_s = 0$ and $L = 60$. The open circles stand for $c_t = 1$ and the open triangles for $c_t = 0.1$. The gel point is marked by p_c.

occurs well before the trapping so that trapping does not perturb the investigation of the critical properties of the gel point.

Another quantity of interest is the number of active centres as a function of time (or of p). Obviously the annihilation process will make this number decrease as shown in figure 5(b). The decrease is monotonic and smooth at the gel point but stops again at the trapping point. n_0 is the initial number of active centres and n_t the number of trapped active centres. $(n_0 - n_t)/n_t$, the ratio of the annihilated to trapped active centres, is usually between one and three at the trapping point.
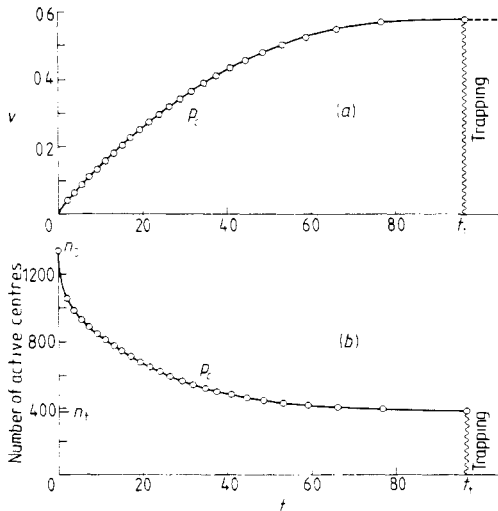
Figure 5. (a) v against t for $c_1 = 0.003$, $c_t = 0.1$, $c_s = 0$ and $L = 42$. (b) Number of active centres against time for $c_1 = 0.003$, $c_t = 0.1$, $c_s = 0$ and $L = 42$. The gel point is marked by p_c.

At this place it should be mentioned that in order to avoid prohibitively large computer times and at the same time not to bias the 'time' interpretation, we choose to use a more lenient definition of trapping; whenever the number of unsuccessful growth attempts is two or more times larger than the number of successful attempts, we will stop the growth and call the system trapped. A more extensive discussion on trapping is given by Bansil *et al* (1982).

The quantities discussed above showed no peculiarities at the gel point and are therefore not suitable for describing the critical behaviour. The order parameter of gelation is the gel fraction G_1 which is the number of sites that are in the largest cluster divided by the number of sites that are in any cluster. In figure 6 we show G_1 against p for different lattice sizes at $c_1 = 0.003$, $c_t = 1$ and $c_s = 0$. Increasing the lattice size L reduces G_1 below the gel point p_c and it should go to zero for $L \to \infty$. Particularly the inflection point of $G_1(L)$ should behave as $G_1^{\text{infl}}(L) \sim L^{-\beta/\nu}$ (Fisher 1971) but unfortunately it is very difficult to determine the inflection point accurately. The broken curve shows the expected behaviour for infinite lattice sizes but clearly this is not a very accurate way to determine p_c. Above p_c the gel fraction is finite and tends to unity if we increase p. Thus, there is clearly only one infinite cluster far above p_c.
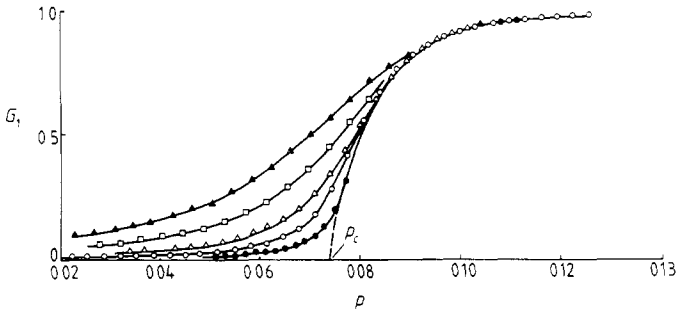
Figure 6. Gel fraction G_1 against p for $c_1 = 0.003$, $c_t = 1$, $c_s = 0$ and different lattice sizes: ▲, 15^3; □, 20^3; △, 30^3; ○, 43^3; ●, 60^3. The broken curve is an extrapolation to the infinite lattice.

We expect G_1 to behave near p_c as

$$G_1 \propto (p - p_c)^{\beta} \qquad \text{for } p \to p_c^{+}. \tag{2}$$

In order to determine β we use finite size scaling (Fisher 1971, Landau 1976):

$$G_1(L, p) = L^{-\beta/\nu} \mathscr{S}[(p - p_c)L^{1/\nu}] \tag{3}$$

where $\mathscr{S}$ is the scaling function. In the asymptotic limit $L \to \infty$ and $p \to p_c$ we regain equation (2). In figure 7 we thus plot $G_1 L^{\beta/\nu}$ against $L^{1/\nu}|p - p_c|/p_c$ adjusting β/ν and $1/\nu$ so that the points of different lattice sizes lie on the same curve. p_c was chosen to be 0.0835 for $c_1 = 0.003$, $c_t = 0.4$ and $c_s = 0$. (Later we explain how this p_c was determined.) The fitting is done best by $\nu = 0.82 \pm 0.10$ and $\beta/\nu = 0.45 \pm 0.05$, thus yielding $\beta = 0.37 \pm 0.09$. The slope of the curve for $p > p_c$ should be β as (2) should hold for infinite lattice size. Figure 7 gives a slope $\beta = 0.4$ consistent with our previous estimate. This β is also consistent with the β of three-dimensional random percolation. For $p < p_c$ different lattice sizes also scale according to (3); the asymptotic slope indicates that G_1 decreases faster than $L^{-1/\nu}$.
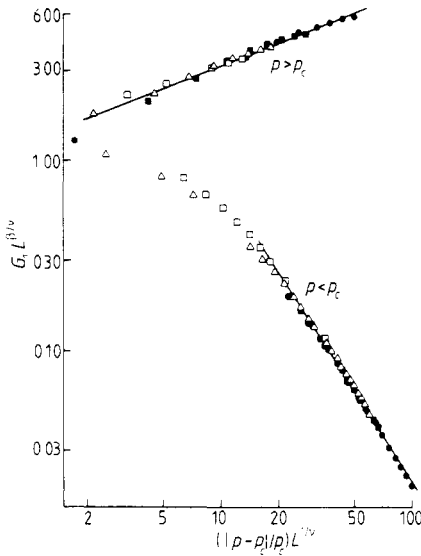
Figure 7. Finite size scaling of G_1 for $c_I = 0.003$, $c_t = 0.4$, $c_s = 0$ with $\beta/\nu = 0.45$ and $1/\nu = 1.22$. The straight line for $p > p_c$ has a slope of 0.4. Lattice size: $\square$, 20^3; $\triangle$, 30^3; $\blacksquare$, 40^3; $\bullet$, 60^3.

Manneville and de Seze (1981) had raised the possibility of more than one infinite cluster near p_c. Although for static percolation a finite number of infinite clusters greater than one cannot exist (Newman and Schulman 1981), a kinetic approach like ours cannot exclude this possibility from the beginning. Thus we plot the fraction G_2 of the second largest cluster, in an analogous definition to that of G_1, against p in figure 8 for $c_I = 0.003$, $c_t = 0.9$ and $c_s = 0.1$. We clearly see that for larger lattice sizes the effect of the second largest cluster becomes less important. A finite size scaling of the maximum of the curves (Margolina *et al* 1982)

$$G_2^{\max}(L) \sim L^{-0.5}$$

supports this quantitatively yielding an exponent of $\beta/\nu = 0.5 \pm 0.1$ which agrees in its error bars with the values we got from G_1 and the value of random percolation ($\beta/\nu \leqslant 0.5$). The region in $p > p_c$ for which G_2 is large shrinks to zero for $L \to \infty$, in contrast to G_1. Thus we have clear evidence that the gelation model has only one infinite cluster.

More pronounced effects at the gel points are shown by the average molecular weight χ defined in (1) as seen in figure 9, where the data for $c_I = 0.003$, $c_t = 0.4$ and $c_s = 0$ are shown for different lattice sizes. The gel point can be localised at $p_c = 0.085 \pm 0.002$. The singularity at p_c is expected to behave as

$$\chi = C_+(p - p_c)^{-\gamma} \qquad \text{for } p \to p_c^+$$
$$\chi = C_-(p_c - p)^{-\gamma} \qquad \text{for } p \to p_c^-. \tag{4}$$

The ratio

$$R = C_-/C_+ \tag{5}$$

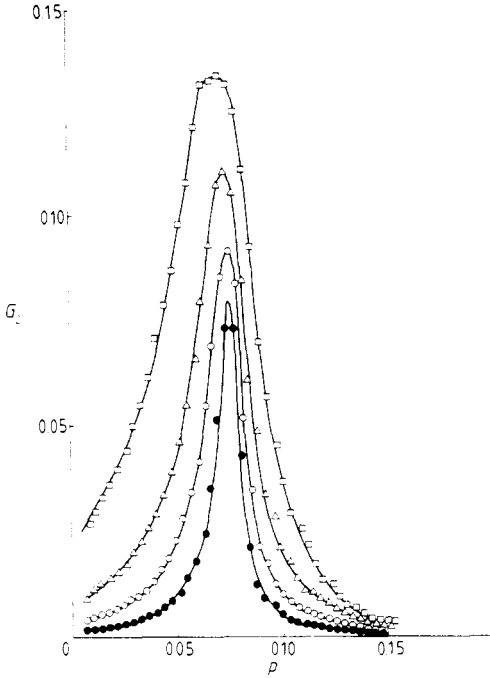will play a major role in the forthcoming discussion. The behaviour (4) of χ can be

Figure 8. Fraction of the second largest cluster G_2 against p for $c_I = 0.003$, $c_t = 0.9$ and $c_s = 0.1$ for different lattice sizes: $\square$, 20^3; $\triangle$, 30^3; $\bigcirc$, 40^3; $\bullet$, 60^3.
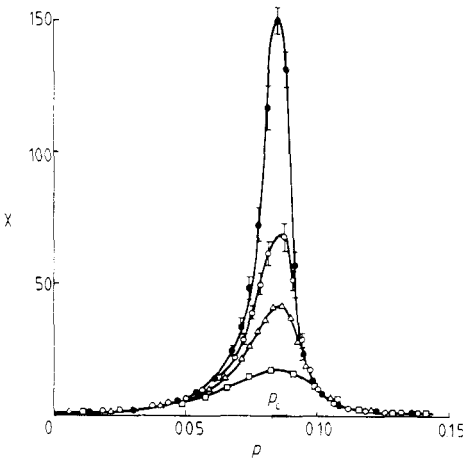

Figure 9. Average molecular weight χ against p for $c_I = 0.003$, $c_t = 0.4$, $c_s = 0$ and different lattice sizes: $\square$, 20^3; $\triangle$, 30^3; $\bigcirc$, 40^3; $\bullet$, 60^3. The statistical error bars are shown whenever they are larger than the symbols.

verified in the log–log plot of figure 10. The two curves have a linear region given by (4) which breaks down near p_c because of the finite lattice size, as can be seen by the guides to the eye (broken curves) that are plotted through the points below p_c. As we expect the exponent γ to be equal above and below p_c, the gel point can now be localised much more accurately by using the criterion that the two straight lines
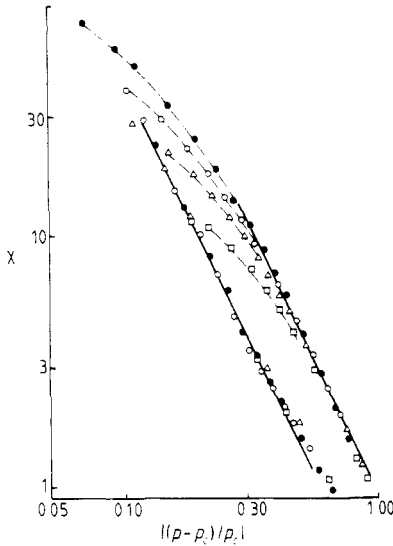
Figure 10. Average molecular weight χ plotted double logarithmically against $|p - p_c|/p_c$ for $p_c = 0.0835$. The parameters are $c_I = 0.003$, $c_t = 0.4$ and $c_s = 0$. The finite size effects are indicated by broken curves. Lattice size: $\square$, 20^3; $\triangle$, 30^3; $\bigcirc$, 40^3; $\bullet$, 60^3.

in figure 10 should be parallel. This gives us the value $p_c = 0.0835 \pm 0.0005$ which is also the value for p_c used in figures 7 and 10. The ratio R given by the distance of parallel lines in figure 10 is roughly estimated to be 2.8 ± 1.0 and the slope is $\gamma = 1.98 \pm 0.10$.

The extrapolation to the straight line of the infinite lattice in figure 10 is of course not a very reliable method as it is done by eye; therefore we made a careful finite size analysis (Fisher 1971, Landau 1976). Using the analogy of χ to the magnetic susceptibility at Curie points finite size scaling asserts

$$\chi(L, p) = L^{\gamma/\nu}\mathcal{F}[(p - p_c)L^{1/\nu}] \tag{6}$$

where $\mathcal{F}$ is a scaling function. The asymptotic limit $L \to \infty$ and $p \to p_c$ should give equation (4). So we plotted in figure 11 $\chi L^{-\gamma/\nu}$ against $L^{1/\nu}|p - p_c|/p_c$ for γ, ν and p_c adjusted in that way that both curves have straight lines in an intermediate region of slope $-\gamma$. The latter property must hold because in order to retain (4) from (6) $\mathcal{F}(x) \propto |x|^{-\gamma}$ for $|x| \to \infty$. For the fitting we used a computer program that gave us $p_c = 0.0835 \pm 0.0004$, $\gamma = 2.0 \pm 0.1$ and $\nu = 1.0 \pm 0.2$. The errors arise from the statistical errors in χ and it is seen that the fitting is not very sensitive to the exponents γ and ν. The fact that in figure 11 the points for the different lattice sizes all lie on a single curve indicates that equation (6) is correct. The ratio R is determined from the finite size plot to be $R = 2.5 \pm 0.8$ and so we see that our first analysis without the finite size scaling already gave the correct result; the effect of the finite size does not substantially distort our results.

The values γ and ν we obtain cannot be distinguished reliably from the random percolation exponents $\gamma = 1.8$ and $\nu = 0.9$, but the ratio R, which because of ε expansion studies (Aharony 1980) is also expected to be universal, is clearly smaller than the percolation value of about 10. (In two dimensions, complicated percolation
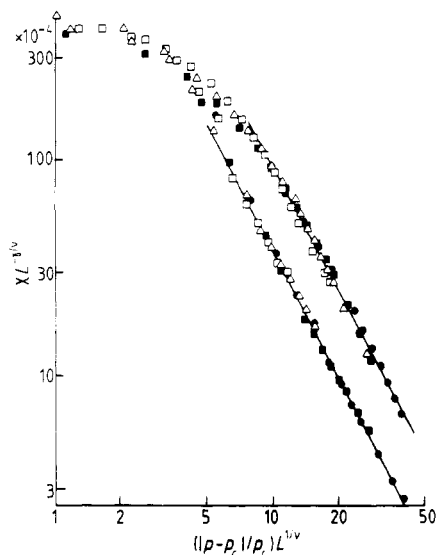
Figure 11. Finite size scaling of χ for $c_I = 0.003$, $c_t = 0.4$, $c_s = 0$ with $p_c = 0.0835$, $\gamma = 2$ and $\nu = 1$. Lattice size: $\square$, 20^3; $\triangle$, 30^3; $\blacksquare$, 40^3; $\bullet$, 60^3. The straight lines have a slope of -2; $R = 2.6 \pm 0.8$.

models sometimes show an R different from random lattice percolation; it is not entirely clear if these differences are real or an artifact of insufficient data (Gawlinski and Stanley 1981, Nakanishi, private communication).) For the sake of comparison the random percolation values have been evaluated in the same way as just described and presented by Herrmann *et al* (1982). We can summarise at this stage that for $c_I = 0.003$, $c_t = 0.4$ and $c_s = 0$ we found exponents roughly in agreement with random percolation and in disagreement with the classical Flory–Stockmayer theory and a ratio R which clearly differs from both the percolation value of ten and the Flory–Stockmayer value of unity. This means that our model is in neither one of the two universality classes.

The above rationale was already presented in a compact version by Herrmann *et al* (1982) for the values $c_I = 0.003$, $c_s = 0$ and $c_t = 0.1$ and $c_t = 1$. Taking together the values for $c_t = 1$, 0.4 and 0.1 we can see that variation of c_t does not change the universality class but that the gel point is shifted to larger p_c if we decrease c_t. In figure 12 we show the phase diagram for $c_s = 0$. For small concentration of tetrafunctional units long chains will be grown with sparse crosslinking and for $c_t \to 0$ we expect to have a crossover to self-avoiding walks. Our simulations at small c_t are limited by entrapment which for $c_t = 0.05$ already occurs near the gel point. Therefore we cannot reliably extrapolate the gelation point to $c_t \to 0$, but we assume that it will go to $p_c = \frac{1}{3}$ which is the maximum number of bonds that can be occupied if all units are bifunctional. It is nevertheless worthwhile to study more carefully the region of small c_t as this is an interesting case from the experimental point of view.

Another parameter that can be varied is c_I, the concentration of initiators. c_I determines the number of clusters and therefore essentially the size of the clusters at a fixed p. For $c_t = 1$ and $c_s = 0$, we show in figure 13 the log–log plot of χ against $|p - p_c|/p_c$ for $c_I = 0.0003$ and $c_I = 0.03$. The smaller c_I, the more pronounced are finite size effects. The exponent γ increases only slightly for small c_I, still being within
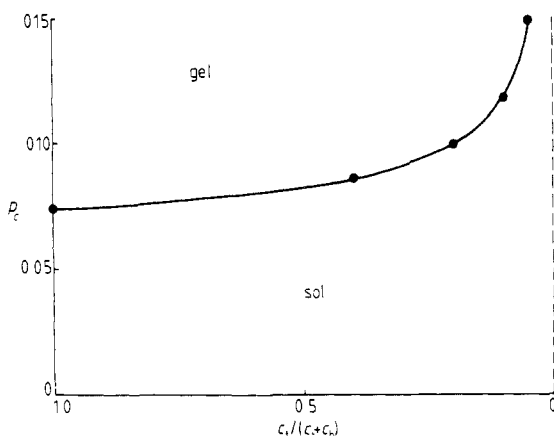
Figure 12. Phase diagram for varying ratio of number of tetrafunctional units to total number of polymerisable units for the case of no solvent and $c_I = 0.003$.
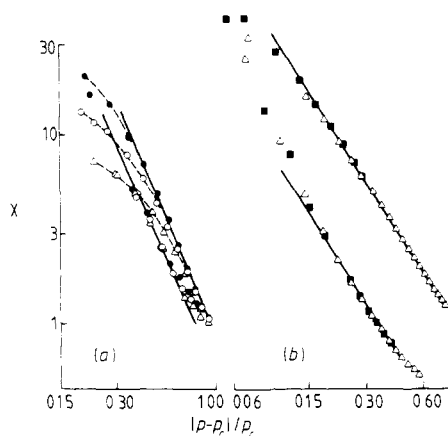

Figure 13. Susceptibility against $|p - p_c|/p_c$ for $c_t = 1$ and $c_s = 0$: (a) $c_I = 0.0003$ and $p_c = 0.032$; (b) $c_I = 0.03$ and $p_c = 0.166$. The broken curves are guides to the eye. Lattice sizes: $\triangle$, 30^3; $\bigcirc$, 42^3; $\blacksquare$, 40^3; $\bullet$ 60^3.

the error bars of percolation ($\gamma = 2.3 \pm 0.4$ for $c_I = 0.0003$). On the other hand, the ratio R clearly shows a systematic change to smaller values for decreasing c_I.

Although the error bars of R are so big that the value for $c_I = 0.03$ ($R = 4.2 \pm 1.2$) and for $c_I = 0.0003$ ($R = 1.7 \pm 0.6$) each overlap with the R for $c_I = 0.003$, it does not seem likely that R has the same value for all c_I. For c_I larger than 0.1 we find a ratio compatible with random percolation; however, as mentioned in the previous section, the model is only realistic for $c_I \ll 0.33$. It is possible that in the limit $c_I \to 0$ the ratio goes to unity, thus agreeing with measurements of Schmidt and Burchard (1981). We point out that this does *not* mean that the case $c_I \to 0$ is in the universality class of the classical Flory–Stockmayer theory as the exponent γ clearly does not go to unity. On the contrary, although γ tends to increase slightly, it still agrees, within the error bars,

with the random percolation value for $c_I \to 0$. It is more plausible that $c_I \to 0$ represents a new universality class that might be similar to backbone animals (Coniglio, private communication) and that the continuous change in R from 8 at $c_I = 0.1$ to 1.7 at $c_I = 0.0003$ is a crossover between this universality class and percolation. For lattice sizes, which we can study, it is possible that the asymptotic critical behaviour is observed in the region dominated by finite size rounding; however, the finite size scaling plots should in the case of crossover show two different exponents or at least different amplitudes. Although it is possible that this occurs in our finite size plot quite close to p_c, we do not have sufficient accuracy in the data to identify systematic differences clearly. Since it is possible that 10 to 100 times more data are needed to settle this question, we defer this problem to a later study. At this point we should remember that the concept of universality has not yet been worked out for kinetic processes, and it might also well be that the kinetics makes R a non-universal quantity. Further investigation is necessary in order to clarify this interesting question.

In the light of the above, it is not surprising that p_c changes with c_I drastically if $c_I \to 0$. From figure 14 we see that presumably $p_c \to 0$ for $c_I \to 0$. The lowering of c_I also produces an earlier trapping because of the smaller number of active centres available, but this is well compensated by the earlier onset of gelation so that the limit of small c_I is easily accessible for our simulations.
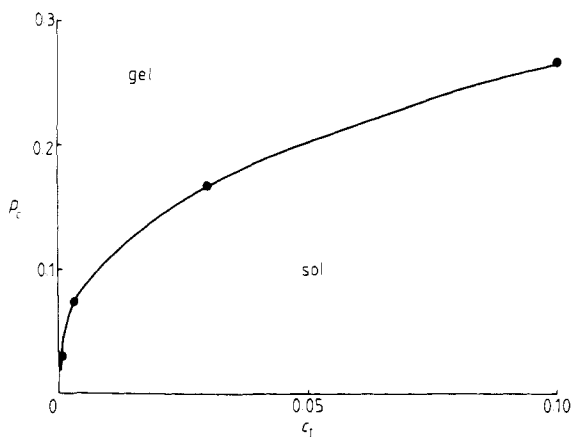

Figure 14. Phase diagram for varying concentration of initiator c_I for $c_t = 1$ and $c_s = 0$.

Up to this point we had set the concentration of solvent c_s to be zero. Since the solvent essentially decreases the number of polymerisable units to which an active centre could grow, the trapping is very much enhanced by an increase of c_s. Thus, for $c_s = 0.6$ trapping occurs already at $p = 0.033$ for $c_I = 0.003$ and $c_t = 0.4$, that is, much earlier than gelation. We must therefore restrict ourselves to small c_s and will restrict ourselves now only to $c_s = 0.1$. More extensive work for higher concentrations is also under way. For $c_t = 0.9$ and $c_I = 0.003$ we see within our error bars no difference in the gel point, the exponents or the ratio R to the case without solvent. For $c_t = 0.1$ and $c_I = 0.003$ the gel point is 30% higher than in the dense case, $c_s = 0$, and unfortunately the critical quantities cannot be determined because of the early trap-

ping. A detailed investigation of the effect of a solvent without mobility is pursued by D Matthews-Morgan, D P Landau and H J Herrmann (1983 in preparation).

Of course the experimentally interesting case has larger solvent concentrations (0.5 and more) and therefore the model must be modified so that the early trapping is avoided. This can be done by the inclusion of mobility. In a very rough approximation we include mobility by going once through all the solvent units in the lattice every 280 growth steps and interchanging the solvent unit with an adjacent (nearest neighbour) polymerisable unit with less than two occupied bonds if any such unit exists. With this mobility the trapping time becomes roughly twice as large, making it possible to see the gel point beyond $c_s = 0.6$ for $c_t = 0.4$. Unfortunately the mobility just described needs about 10 times more computer time than the simulation without mobility, making it impossible to study critical phenomena accurately with reliable precision. Nonetheless the simulations of small lattice sizes already show that the mobility reduces the gel point (about 5% for $c_s = 0.1$, $c_t = 0.9$, $c_I = 0.003$). The concept of the mobility is developed in more detail by Bansil *et al* (1982), where extensive data are also presented.

5. Discussion

Our results have shown that quantities of experimental interest can be calculated with this Monte Carlo simulation of irreversible gelation, both near the gel point and far away from it. The gel point and its critical exponents can be determined with reasonable accuracy.

Modifications and generalisations of the model are possible to obtain the same information for other situations of experimental interest. A detailed comparison with experiment is not undertaken for the present results since they neglect solvent effects; we refer instead to the discussion by Bansil *et al* (1982) where a mobile solvent is included in the model.

For the particular problem of critical phenomena, the main result of this work is the discovery that the critical amplitude ratio for the 'susceptibilities' (i.e. the ratio of the weight-average degree of polymerisation slightly below and above the gel point, at equal distance from it) differs strongly from random percolation theories. Moreover it seems to vary with the concentration of initiators. We leave it to future research to investigate the limit of initiator concentration going to zero where new effects seem to happen. For the present work, the critical exponent of the average molecular weight can be regarded as constant and as roughly equal to the random percolation value, within the errors of our simulation.

What does this difference in the amplitude ratio mean? Renormalisation group (Aharony 1980) theory clearly says that both the critical exponent and the amplitude ratio should be universal for random percolation. Thus our data indicate that our model does not fall into the universality class of random percolation. No renormalisation group theory has yet been developed for the kinetic percolation model discussed here, and thus we do not know if our results violate some as yet undeveloped kinetic universality principle.

How do we explain this deviation from the universality class of random percolation? One might first think that the mixture of bifunctional and tetrafunctional units is responsible. However, field-theoretical results (Lubensky and Isaacson 1978) as well as Monte Carlo simulations (Kertész *et al* 1982) indicate that for random percolation

such restrictions in the allowed valences are not important for the universality class. More likely, the kinetic aspect of our model changes the universality class. In the coagulation model it is already known that changes in the size dependence of the coagulation coefficients give changes in the critical exponents (Leyvraz and Tschudi 1981, 1982, Ziff 1980, Ziff *et al* 1982, 1983). For models of cluster growth different radius exponents were also observed in different kinetic models (Stauffer 1978, Witten and Sander 1981, Rikvold 1982). While these models do not seem relevant for gelation with many initiators and finite mobility, their main result may as well be applicable to our model: details in the kinetic assumptions change the critical behaviour.

    To what extent is our model different from other kinetic percolation models? The growth methods of Leath, Alexandrowicz, Pike and Stanley, and Grassberger seem to give the same end result as static percolation, in contrast to our results. A crucial difference here is that in these other growth models, a site which was once investigated and rejected in the Monte Carlo simulation, that is, not incorporated into the cluster, remains outside the cluster forever. (This memory effect was described as 'immunity' by Grassberger.) In contrast, in our model each polymerisable unit and each bond emanating from it may have many chances during the simulation to become part of a macromolecule. Also, none of these models employs the active centres which make bonds possible in our model; the growth tips of Alexandrowicz are created automatically as part of the cluster growth process and increase with time whereas our active centres are put into the system separately and can only annihilate later. Finally, we look in the present work at the simultaneous growth of many clusters (since the number of radicals is larger than unity) whereas these other models look at one cluster only. Thus it is not surprising that our results are different and give a different universality class.

    Our motion of active centres has some similarity with the 'ant in the labyrinth' problem (see Mitescu and Roussenq 1983 for a review) where a point moves randomly from one occupied site to a neighbouring occupied site in random percolation. This diffusion process has also given different critical exponents if seemingly minor changes were made in the kinetic assumption, further bolstering our assertion that the kinetic aspect is responsible for deviations in the universality class. A crucial difference to our model, however, is that we do not allow an occupied bond to be broken again; thus, an active centre can visit a tetrafunctional unit at most twice since then it has formed four permanent bonds. The ant, on the other hand, can visit the same place as often as it likes. In this sense, our memory effects are in between those of Leath's cluster growth method and its variants on the one side (sites once defined as empty remain always empty) and the ant problem on the other side (no memory at all): we do not allow a bond once occupied to become unbound again, but it may try again and again to become occupied.

    The model we have investigated here can also be studied in two dimensions. Work in this direction is carried out by A Rushton (Rushton *et al* 1983).

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