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# Computer Simulation of Kinetics of Gelation by Addition Polymerization in a Solvent


**Rama Bansil,* Hans J. Herrmann,[1] and Dietrich Stauffer[2]**

*Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215.*

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ABSTRACT: We have performed Monte Carlo simulations on the kinetics of free radical initiated addition copolymerization in a solution of vinyl and divinyl monomers, using the kinetic gelation model recently proposed by Herrmann et al. The simulation is done on $20 \times 20 \times 20$ and $45 \times 45 \times 45$ simple cubic lattices and allows for mobility of unreacted vinyl and divinyl monomers. The extent of reaction at the gel point, $p_c$, increases with decreasing fraction of divinyl monomer, with increasing solvent concentration, and with increasing initiator concentration. These predictions, and the observed trends for the dependence of the overall polymerization rate on the same concentrations, are in qualitative agreement with laboratory experiments. Trapping of radicals in this simulation gives an upper limit to the extent of reaction and can be used to construct a phase diagram of gel (infinite cluster) vs. no gel (only finite cluster).


## Introduction

The copolymerization of vinyl and divinyl monomers in a suitable solvent is a commonly used procedure for preparing irreversible gels. In such systems the properties of the gel such as the extent of cross-linking at the gel point and various molecular weight averages are strongly dependent on the proportion of divinyl to vinyl monomer and total monomer concentration. The earlier theoretical investigations of this type of gelation process have been based on the Flory–Stockmayer theory[3-6] and on the cascade model developed by Gordon and co-workers,[5] and more recently modified by Miller and Macosko.[6] The kinetics of such reactions have usually been analyzed in the framework of mass-action kinetics.[4]

There exists an extensive literature dealing with the measurement of the kinetics of free radical initiated vinyl polymerization.[7] Recently, Hild and Rempp[8] reported a very detailed quantitative study of the kinetics of network formation in free radical initiated copolymerization of styrene with a variety of divinyl monomers. Also there have appeared a few studies[9] investigating the critical behavior in this type of gelation and the results are mixed—some of the critical behavior is in agreement with percolation models[10] while others are in agreement with the classical approach based on the Flory–Stockmayer theory.

The recognition that the Flory–Stockmayer theory is equivalent to percolation on a Bethe lattice has led to the notion that perhaps percolation on a lattice may be appropriate to gelation,[10] and this offers one way of incorporating loops (or cycles) that were neglected in the Flory–Stockmayer theory. However, as pointed out by Manneville and de Seze[11] standard percolation models may not be appropriate for free radical initiated addition polymerization reactions; and they developed a computer model that took into account some of the features of radical-initiated polymerization. More recently, Herrmann et al.[12] performed extensive simulations of a model very similar to that of Manneville and de Seze[11] and discussed how the critical behavior very close to the gel point of this model differs from the standard percolation models.

In contrast to earlier theories in the Flory–Stockmayer spirit,[4] this computer model[12] takes into account the excluded volume effects which prohibit different macro-

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molecules or two parts of the same macromolecule from occupying the same space. Also, the model allows for arbitrary loop formation. In contrast to percolation theories,[10] this computer model does not assume that the bond formation is completely random, and it does incorporate the kinetic aspect of irreversible gelation.

However, the question whether such a computer model even qualitatively mimics the kinetics of vinyl–divinyl reactions has not been discussed in the previous work based on the model of ref 11 and 12. Clearly, the model is too simplified to make any quantitative comparison with experimental data. Nevertheless one can compare the overall trends and the directions in which the gel point and rate of polymerization change with varying experimental conditions in a zeroth-order attempt at discussing the relevancy of such a simulation. It is important to recognize that the kinetic equations for free radical initiated copolymerization can be solved only with certain approximations and are particularly difficult to study analytically once the gel point is approached and passed. On the other hand, computer simulation of reaction kinetics, even though it may be based on simplified models at present, does offer a viable approach to studying these problems close to the gel point and beyond. Also, in principle, computer models can be generalized to include complexities of particular systems, although in practice limitations of computer memory and computation time provide constraints.

Several recent articles[13-15] have shown important differences in the critical behavior predicted by computer simulations based on the above model and standard percolation. However, if this type of computer simulation is to provide a realistic description of gelation in vinyl–divinyl systems, then several of the complexities of the free radical polymerization technique should be incorporated in these simulations. As a first step toward making the model more realistic we have incorporated a mobile solvent and allowed for mobility of monomers. Pandey et al.[14] discuss other modifications of the model, such as the inclusion of different mechanisms of chain termination and unequal reactivities of the monomers.

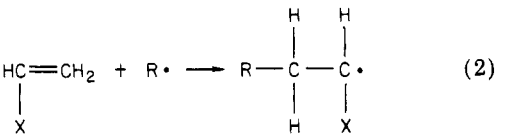
In this paper we consider the effects of incorporating solvent and mobility of monomers on the kinetics of free radical initiated copolymerization of a schematic vinyl and divinyl monomer whose reactivities are assumed to be equal. We determine the dependence of the reaction kinetics and gel point on the concentrations of initiators, divinyl monomers, and solvent.

## Model

In this section we outline briefly the simulated model; for greater details the reader is referred to Herrmann et al.[12] The first step involves distribution of vinyl (or bifunctional) monomers, abbreviated by subscript B, divinyl (or tetrafunctional) monomers (T), and solvent (or inert) molecules (S), with concentrations $C_B$, $C_T$, and $C_S$, respectively, on a simple cubic lattice with $L^3$ sites, with the conservation condition

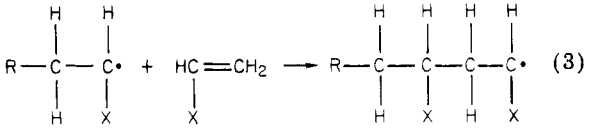
$$C_B + C_T + C_S = 1 \tag{1}$$

The next step is to initiate the growth process. This is done by randomly placing a free radical on a fraction $C_I$ of the bi- and tetrafunctional monomers (thereby reducing the functionality of this bi- or tetrafunctional monomer by one) and drawing a bond along the lattice between the monomer and the radical to represent one of the reacted functionalities of the bi- or tetrafunctional monomer. In other words, this process represents the reaction of radical transfer



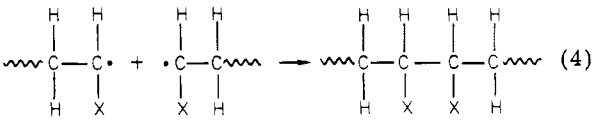

(2)

Here X denotes the side chain of the vinyl monomer and R· the free radical obtained by the dissociation of the initiator. The polymer growth process, i.e., the reaction




(3)

is simulated by transferring a randomly chosen radical from its present position to a nearest-neighbor site along one of the six bonds emanating from each lattice site and occupying this bond, provided the neighbor chosen is not occupied by a solvent molecule and has at least one free functionality left. If these conditions are not met, the radical stays, for the present time, on the initial site. If the nearest-neighbor site also has a radical on it, then the two radicals combine, thereby simulating the reaction of chain termination by combination:




(4)

In the present version of this model, other mechanisms of chain termination such as transfer to solvent or disproportionation are not taken into account. Nor are other mechanisms of polymer growth allowed here. Another drawback of the present model is that the number of radicals decreases in time; the creation of new radicals is not included. However, the model can be generalized to allow for conservation of radicals, chain transfer to solvent, poisoning of radicals, and some spontaneous growth, and the effects of these modifications are discussed in Pandey et al.[14] The growth process is continued by randomly choosing a radical at each step, and hence by drawing bonds along the path of radical movement polymer molecules (both linear and branched) are generated.

The picture described so far has a serious drawback, namely that all molecules (polymer and monomer) remain at fixed position; i.e., molecules have no mobility. To remedy this situation of zero mobility, we have included as a first step the diffusion of monomers only. We allow each solvent molecule to exchange position with a nearest-neighbor molecule, provided the nearest-neighbor site is occupied by an unreacted bi- or tetrafunctional monomer or by another solvent molecule. The mobility can be varied by changing the ratio of the number of exchange attempts for solvent molecules to the number of bonds grown between exchange attempts. This ratio is referred to as the diffusivity $D$.

The growth process is continued until a specified number of bonds has been produced. However, in many situations the growth process terminates due to the trapping of radicals.[12] This trapping process occurs since a radical attempting to transfer may find all its neighbor sites occupied either by solvent molecules or by fully reacted monomers. If all radicals in the system are trapped, then no further growth is possible, and the reaction is terminated. (For details of how exactly we implement this situation on the computer see ref 12.) The entire process is simulated $N$ times by starting with a new initial distribution of monomers on the lattice. In the work de-

scribed here, always $N = 50$.

The program keeps track of chemical reactions, diffusion, and growth of clusters in a number of variables $z$, which are printed after every $n$ C–C bonds have been formed; typically, $n = 50$ was taken. These variables are as follows:

$t$ is the number of radical transfer attempts made in reaching the specific step and $p(t)$ is the number of C–C bonds produced up to that step divided by $L^3(C_B + 2C_T)$.

$C_T''(t)$ is the fraction of tetrafunctional monomers with both carbon double bonds reacted and $C_I(t)$ is the number of radicals that are still active divided by $L^3(1 - C_S)$.

$v(t) = \sum_{s=2} N_s(t)s/(L^3(1 - C_S))$, where $N_s(t)$ is the number of polymer molecules of $s$ monomers each generated up to that step (including the largest cluster) and $G(t)$ is the number of sites belonging to the largest macromolecule divided by $v(t)L^3(1 - C_S)$.

$DP_w(t) = \sum'_{s=2} N_s(t)s^2/\sum'_{s=2} sN_s(t)$, where the sum $\sum'$ excludes the largest cluster, and $D = L^3/$(number of bonds grown between the two exchange steps) is the diffusivity.

As discussed in ref 12, $t/C_I(t)$ can be taken as a measure of time. $p(t)$ is proportional to the fraction of reacted C=C bonds, i.e., the extent of reaction. Another measure of the progress of the reaction is $v(t)$, which gives the total number of monomers with at least one functionality reacted (excluding those monomers that have only reacted with the initiator and have not yet grown). The quantities $v(t)$ and $p(t)$ differ because a divinyl monomer can be incorporated in the polymer with a pendant double bond, and thus the difference $p(t) - v(t)$ is a measure of the number of pendant double bonds. Similarly the quantity $C_T''$ is a measure of the fraction of divinyls with both vinyl groups reacted and thus related to the total number of cross-links in the infinite or "gel" molecule and the finite or "sol" molecules. $G(t)$ is a measure of the weight fraction in the "gel", and $DP_w(t)$, the weight-average degree of polymerization, is proportional to the weight-average molecular weight measured by light scattering.[16] At the gel point $t = t_c$, $DP_w(t)$ should diverge[10,16] in an ideal infinite system. However, because of the finite size of the system, $DP_w(t)$ only reaches a maximum; we consider the value of $t$ at which $DP_w(t)$ is maximal as an operational definition[12] of the gel point $t_c$ and denote by $p_c$ the critical extent of reaction, $p_c = p(t = t_c)$.

## Results and Discussion

**Effects of Varying Sample Composition.** In this section we discuss the reaction kinetics for simulations done with different sample compositions. We shall specify the sample composition by $C_S$, the concentration of solvent, $f_T = C_T/(C_T + C_B)$, the fraction of tetrafunctional monomers, and $C_I$, the initial concentration of radicals. Figure 1 shows the time course of the reaction [$p(t)$ vs. $t$] for different values of initial radical concentration, solvent, and fraction of tetrafunctional monomers. As seen in Figure 1a–c the reaction kinetics predicted by the simulation is approximately first order as observed in experiments.[7,8] We see that the overall rate of polymerization increases with increasing concentration of initiator, increasing total monomer concentration (i.e., decreasing solvent concentration), and decreasing fraction of tetrafunctional as opposed to bifunctional monomers. The result that overall rate of polymerization decreases with increasing fraction of tetrafunctional monomers may be indicative of some shielding of the second vinyl group in the tetrafunctional monomer.[17] This can also be seen from Figure 1d, which shows the variation of $C_T''$ (the fraction of divinyl monomers with both vinyl groups reacted) and $v$ the fraction of reacted monomers vs. $p(t)$, the extent of

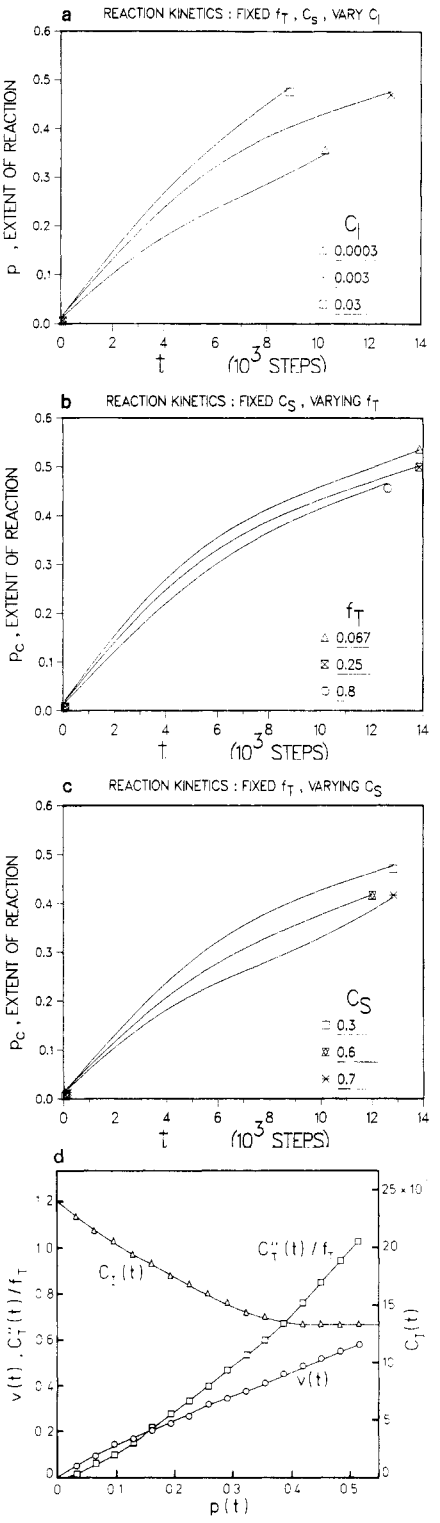



**Figure 1.** (a) Dependence of the kinetics of vinyl–divinyl copolymerization on the concentration of initiator, $C_I$, for fixed values of $C_S = 0.3$ and $f_T = 0.5$. The other parameters are $L = 20$, $N = 50$, and $D = 160$. Note that the $x$ axis is in units of Monte Carlo steps, $t$ which is related to real time as given in the text. (b) Kinetics of copolymerization as a function of the fraction of tetrafunctional monomers, $f_T$, for fixed initiator and solvent concentrations $C_I = 0.003$ and $C_S = 0.4$. The other parameters are the same as in part a. (c) The kinetics of copolymerization for fixed $f_T = 0.5$ and $C_I = 0.003$ as function of solvent concentration $C_S$. Since $C_S = 1 - C_T - C_B$, this graph also shows the dependence on total vinyl and divinyl monomer concentration. The other parameters are the same as in part a. (d) Dependence of $C_I(t)$, $v(t)$, and $C''_T(t)$ on the extent of reaction $p(t)$. The results are for the case $C_S = 0.4$, $f_T = 0.3$, $C_I = 0.003$, $L = 20, N = 50$, and $D = 160$.

reaction measured as the total number of reacted vinyl groups. From this figure it is clear that in the early stages of the reaction many of the divinyl monomers have a pendant double bond, which reacts later as the polymerization progresses. Figure 1d also shows how the number of radicals decreases with time due to radical combination. This feature of the computer simulation shows up one of the drawbacks of the present model, since in most such reactions a steady state for initiator concentration is established very early in the reaction. Pandey et al.[14] have modified the computer simulations to include the steady state behavior of $C_I(t)$.

Although the overall trends found in our model are in agreement with experimental results on the gelation of vinyl–divinyl polymerization,[8] the model is too simplified to make any *quantitative* comparison with the dependence of overall rate of polymerization on the parameters $C_I$, $C_B$, $C_T$, and $C_S$. (In comparing these calculated kinetic curves with experimental data, one should recognize that since the simulations are done on a lattice $C_B$, $C_T$, and $C_S$ correspond to volume fractions of the relevant monomers. Also, for the sake of simplicity, we have taken the molar volumes of both vinyl and divinyl monomers to be the same and the two monomers are assumed to be equally reactive.)

From Figure 1 it is clear also that the gel point $t_c$ is affected by changing $C_I$, $C_T$, and $C_S$. This result is illustrated in Figure 2, which shows the variation of $t_c$, the time at which the gel is formed (Figure 2a), and of $p_c$, the extent of reacted vinyl bonds at the gel point (Figure 2b), as a function of $f_T$, the fraction of tetrafunctional monomers, for different solvent concentrations. The reasons for showing the variation in $t_c$ as well as $p_c$ are that in most of the commonly used techniques for measuring the gel point (such as timing the movement of a bubble or ball), the quantity directly measured is time, $t_c$, at which gelation occurs, and not the extent of reaction $p_c$. We note from Figure 2a that for a fixed total monomer concentration $C_B + C_T$, the gel point is significantly decreased as the fraction of tetrafunctional monomers is increased. This delay of gel points with increasing fraction of bifunctional monomer has been observed in several experiments on vinyl–divinyl gelation.[3,5,18] The Flory–Stockmayer theory also predicts a decrease in $p_c$ with increasing concentrations of tetrafunctional monomers. According to these theories,[4] $p_c \propto 1/(f_T DP_w)$, where $DP_w$ is the weight-average degree of polymerization; the computer simulation, on the other hand, predicts a much steeper dependence of $p_c$ on $f_T$, $p_c \propto f_T^{-0.5}$. This variation of $p_c$ with $f_T$ was also reported by Herrmann et al.[12] for simulation in the absence of solvent. The slope in the linear relationship between log $p_c$ and log $f_T$ that we observe in the simulation agrees surprisingly well with the experimental data of Walling[3] and Gordon[5] on gelation of methyl methacrylate and ethylene dimethacrylate, as shown in the inset to Figure 2b. However, the range of $f_T$ at which the sharp drop in gel points is observed is off by an order of magnitude. This discrepancy is not surprising in view of the simplicity of the computer model and is discussed again in the last section. The inclusion of solvent does not change the overall dependence of $p_c$ on $f_T$; increasing solvent concentration shifts the sol–gel transition to higher extent of reaction (see Figure 2b). The data of Walling[3] also show the increase in gel point with increasing dilution.

The gel point also depends on the initiator concentration $C_I$, increasing to higher values if $C_I$ increases. (This result was reported in ref 12 for the case of no solvent and no mobility.) In Figure 2c we show the dependence of $p_c$ on

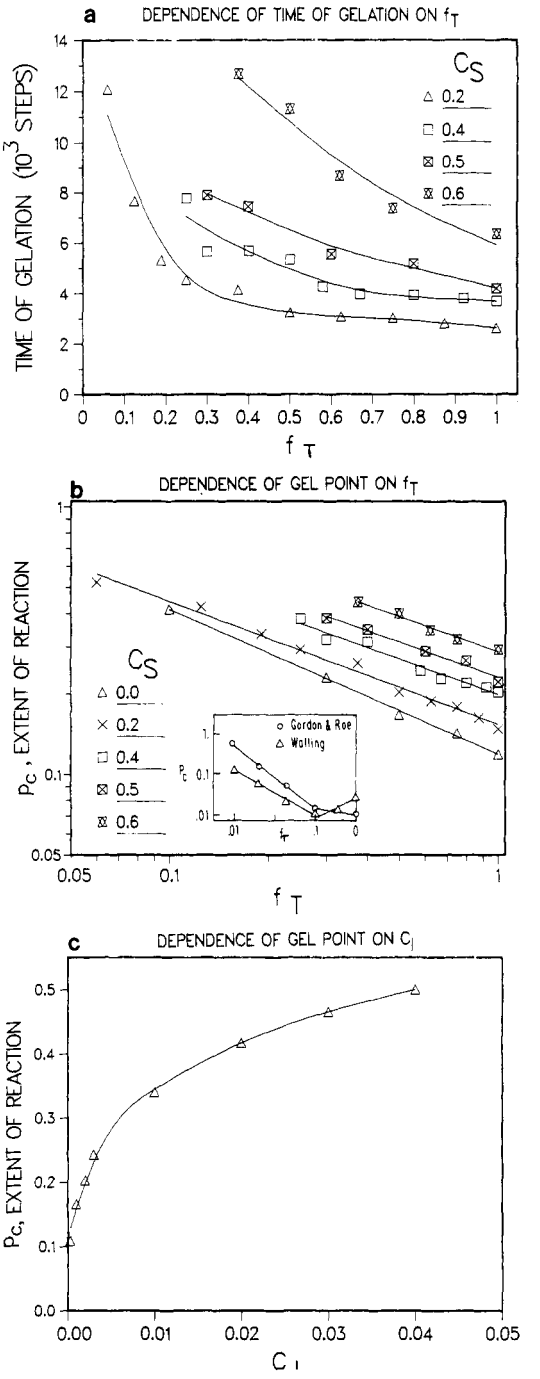



**Figure 2.** (a) Dependence of $t_c$, time to reach gel point (in dimensionless units), on fraction of tetrafunctional monomers, $f_T$, for fixed $C_I = 0.003$ and various concentrations $C_S$ of solvent as indicated. The other parameters are the same as in Figure 1a. (b) log–log plot showing the dependence of $p_c$, the extent of reaction at the gel point, on $f_T$ for the same simulations as in (a). The inset shows data of Walling[3] and Gordon[5] on gelation of methyl methacrylate and ethylene dimethacrylate. (c) Dependence of $p_c$ on initiator concentration $C_I$ for $C_S = 0.3$, $f_T = 0.5$, and $D = 160$.

$C_I$ for the case of $C_S = 0.3$, $f_T = 0.5$, and $D = 160$. Experiments to simultaneously determine the extent of reaction (by Raman spectroscopy) and the gel time (by measurement of the intensity of scattered light) as a function of $C_I$, $C_S$, and $f_t$ are currently under way in our laboratory. Finally, it should be noted that the calculated gel point of course depends on the lattice size.[12] For example, $p_c$ changes from 0.223 to 0.235 when the lattice length $L$ is changed from 20 to 45 in the case $C_I = 0.003$, $f_T = 0.6$, $C_S = 0.3$, and $D = 160$. One may assume[12] here $p_c(L) - p_c(\infty) \propto (1/L)^\nu$, with $\nu = 1 \pm 0.15$; thus $p_c = 0.24$

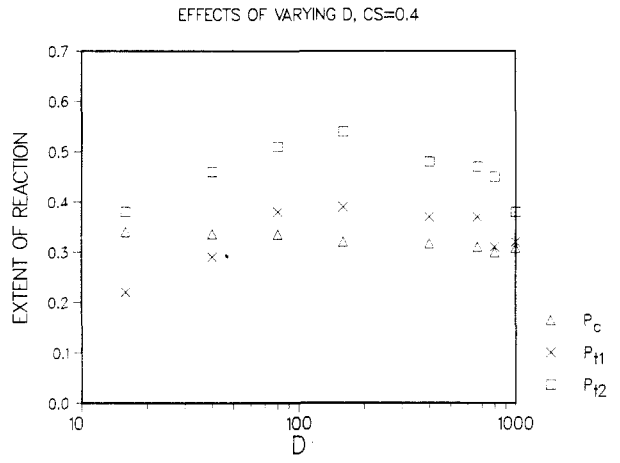



**Figure 3.** Effects of varying the mobility $D$ on gel point and trapping. The triangles represent $p_c$, the extent of reaction at gel point; the crosses represent the extent of reaction $p_{t1}$ by which at least one of the $N = 50$ realizations was trapped and the squares represent $p_{t2}$ by which all 50 realizations were trapped. The simulation was for $C_I = 0.003$, $C_S = 0.4$, $f_T = 0.3$, and $L = 20$.

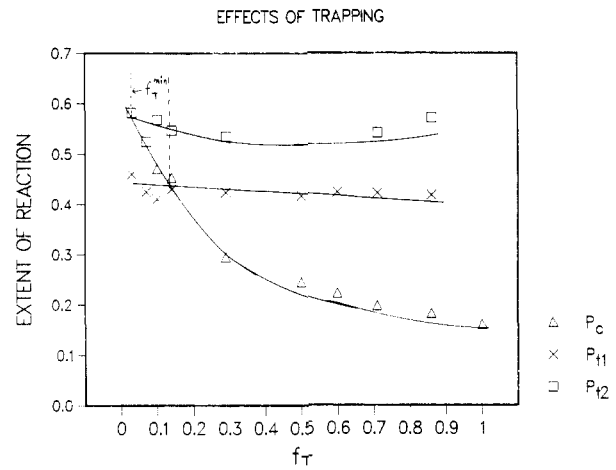



**Figure 4.** Variation of trapping with varying $f_T$ for $C_I = 0.003$, $C_S = 0.3$, $L = 20$, $N = 50$, and $D = 160$. The symbols have the same meaning as in Figure 3. See text for discussion of the meaning of $f_T^{min}$.

is the value extrapolated for infinite systems, only slightly different from the one determined for the $20^3$ system. The overall rate of polymerization and the gel point are also affected by a change in the diffusivity, $D$. These effects are discussed in the next section.

**Effects of Trapping and Mobility.** As mentioned earlier in the description of the model, one of the problems with this simulation is that at some step in the growth process all the radicals get trapped and further growth becomes impossible. Let us denote by $t_1$ the earliest time at which *at least one* of the $N = 50$ realizations is trapped and by $t_2$ the time at which *all* $N = 50$ realizations are trapped. Let $p_{t1}$ and $p_{t2}$ denote the corresponding extent of reaction at these two times. We find that for fixed initiator and solvent concentrations $p_{t1}$ and $p_{t2}$ decrease slightly as the fraction $f_T$ of tetrafunctional monomers increases. Similarly, for fixed $C_I$ and $f_T$, trapping occurs at smaller extent of reaction as the solvent concentrations $C_S$ increases. And finally, for fixed $C_T$ and $C_S$, trapping occurs earlier as initiator concentration $C_I$ decreases. The use of a larger lattice delays the onset of trapping (for example $p_{t1}$ increases from 0.39 to 0.46 if $L$ changes from 20 to 45 at $C_I = 0.003$, $C_S = 0.4$, and $f_T = 0.3$). However, the extent of reaction by which all realizations had trapped, $p_{t2}$, decreased from 0.53 to 0.49 as $L$ increased from 20 to 45, implying that as system size increases the radicals tend to trap within a time interval of decreasing width. Thus one can obtain a unique definition of the extent of reaction at trapping $p_t$ for $L \to \infty$.

The two reasons for the occurrence of trapping are that a radical is surrounded by solvent molecules or that a radical is surrounded by polymer molecules. If trapping is largely caused by the former, then increasing the diffusivity, $D$, may delay the onset of trapping. We find that this is true provided $D$ is less than $D_{max}$, where $D_{max}$ depends on the value of $C_S$. This is shown in Figure 3, which plots the extent of reaction at the two trapping times $p_{t1}$ and $p_{t2}$ as a function of $D$ for the case $C_S = 0.4$. However, if we increased $D$ beyond 160, we found that trapping occurred earlier with increasing diffusivity. This may imply that a significant cause of trapping is due to the presence of polymer chains surrounding an initiator and thereby preventing further growth. It should also be pointed out that increased mobility allows for the onset of gelation at slightly lesser extent of reaction (see Figure 3). However, we note that varying diffusivity has only a small effect on $p_c$. Nevertheless, the inclusion of diffusion can have pronounced effects on the critical properties.[19] A more detailed study of the effects of varying $D$ for different sample compositions is under way.

From a computational point of view, the occurrence of trapping reduces the statistical accuracy of the calculated quantities since the average values are based on fewer realizations once trapping has occurred in at least one sample. If one is interested in the pregel properties or the behavior at the gel point only, then trapping is not such a serious problem if gelation occurs prior to trapping. This was the case in the simulation of Herrmann et al.[12] for zero solvent concentration. But at solvent concentrations comparable to those used in conventional methods of gel preparation, trapping is a serious problem since it may occur before the gel point is reached. This effect is illustrated in Figure 4, where the extent of reaction at the gel point $p_c$ and the trapping points $p_{t1}$ and $p_{t2}$ are plotted vs. the fraction of tetrafunctional monomers, $f_T$, for the case $C_I = 0.003$ and $C_S = 0.3$. As seen from this figure, samples with $f_T < 0.05$ never gel and samples with $0.05 < f_T < 0.12$ gel only rarely (i.e., at least one out of 50 realizations was trapped in this case).

Does trapping have any significance for real polymers as opposed to our computer model? The observation that properties of a gel vary slowly with curing time would suggest that there is some trapping of radicals in the late stages of gelation, due to the fact that monomer diffusion is significantly reduced beyond the gel point and radicals are trapped at the ends of growing chains and branched molecules. Occurrence of trapping is also suggested by the observation that not all the vinyl groups of the tetrafunctional monomer react, the so-called shielding of the pendant double bond.[17] Entanglements would also contribute to trapping of radicals in small localized regions. It is, of course, true that the extent of trapping is considerably lower in the actual gelation process than in this model. In particular, if the steady-state condition on the conservation of number of radicals is included in the model, then trapping is considerably delayed.[14] On the other hand, in this model to some extent trapping compensates for the various other mechanisms of chain termination that have been neglected in the simulation. As stated above the only mechanism for termination included is that of chain combination (annihilation of two radicals). However, in the process of free radical initiated vinyl polymerization in a solvent, the transfer of radicals to solvent molecules is a significant factor in chain termination.

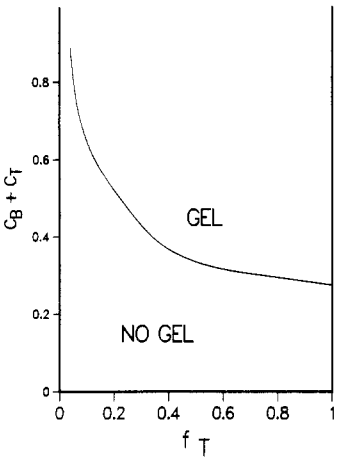



**Figure 5.** Plot of $f_T^{min}$ vs. total monomer concentration $C_B + C_T$. As discussed in the text $f_T^{min}$ is the minimum fraction of tetrafunctional monomers necessary to achieve gelation and was determined by taking the intersection of the line of trapping points with the gelation curve $p_c$, as shown in Figure 4. The results are based on simulations with $C_I = 0.003$, $L = 20$, $N = 50$, and $D = 160$. The region marked "no gel" indicates the range of values for $C_B$ and $C_T$ where trapping prevents the gel point to be reached.

Moreover, poisoning of radicals also contributes to chain termination in real polymers. Some of these effects have been incorporated by Pandey et al.[14] Because of these various termination processes, gelation in such systems cannot occur for all possible values of $f_T$ and $C_B + C_T$. For example, in the case of acrylamide–bisacrylamide copolymerization in $H_2O$, Bansil and Gupta[20] measured the dependence of $f_T^{min}$ on $C_S$, where $f_T^{min}$ is the minimum value of the fraction of tetrafunctional monomers at which a gel would form. Samples with a lower percentage of tetrafunctional monomers did not gel in months and for all practical purposes will never gel. If we make the ansatz that trapping represents the termination of growth, then simulations where trapping occurred before the gel point is reached could be regarded as equivalent to those samples which for all practical purposes "never" gel.

It should be reiterated that the mechanisms of termination of reaction in real experiments are much more complex than the simple combination and trapping that occur in computer simulation. Keeping this difference in mind we use as an operational definition of $f_T^{min}$ the value of $f_T$ where the line of trapping points $p_{t2}$ crosses the gelation curve $p_c$ in Figure 4. For fixed $C_I$, $L$, and $D$ we determined $f_T^{min}$ by this procedure for a number of different values of total monomer concentration $C_B + C_T$ (=1 − $C_S$). Figure 5 shows $f_T^{min}$ vs. $C_B + C_T$. All points to the right of this curve correspond to samples where trapping occurred after the gel point is reached (i.e., an infinite cluster is formed) and thus the sample becomes gel, whereas all points to the left of this curve represent samples where trapping prevented the gel point from being reached (i.e., only finite clusters are formed).

Figure 5 can be compared with the gel–no gel phase diagram found in laboratory experiments on aqueous copolymerization of acrylamide and bisacrylamide.[20] The computer-simulated curve has essentially the same shape as the experimental curve reported in ref 20, although the values for $f_T^{min}$ and $C_B + C_T$ on the gel–no gel boundary curve differ significantly. In view of the simplifying assumptions made in the calculation of Figure 5 it is not surprising that the agreement is only qualitative. Pandey et al.[14] have shown that allowing for chain transfer to solvent and conserving the number of initiators (steady-state condition) delays the onset of trapping and thus shifts the calculated curve in the direction of the experimental curve. Since increasing the lattice size delays the onset of trapping, the calculated curve would be somewhat closer to the measured curve had larger lattices been employed.

## Conclusions

We find that the simplified kinetic gelation model of ref 12 is at least qualitatively in agreement with laboratory measurement of gelation kinetics. It correctly predicts the direction of the shift in the gel point as concentrations of radicals, tetrafunctional monomers, and solvent are changed. This model incorporates several realistic features such as formation of loops, excluded volume effects of molecules, the kinetic aspects of irreversible gelation, and presence of mobile monomers and solvent.

We find that inclusion of solvent and mobility does not change the overall trends predicted by the simulation. However the gel point and rate of polymerization are affected, and the changes are in agreement with experimental observations. In this paper we have not discussed the critical behavior very close to the gel point. This aspect is discussed in ref 15, where we show that inclusion of solvent does not change the critical exponents or amplitudes near the gel point.

In the present version of the model several features could be improved. For example in a realistic situation, polymer molecules have a finite mobility whereas we only allowed unattached monomers to move; agreement with experiment would improve if mobility could be treated more realistically ("reptation of branched molecules").[21] Greater mobility would also reduce the trapping of radicals. Another feature that can be incorporated into the model is the inclusion of mechanisms of chain termination other than that of radical combination and growth mechanisms other than that of radical transfer. Some of these effects have been incorporated in the recent work of Pandey et al.,[14] who also discuss the case where radical concentration is conserved as appropriate to steady-state conditions. They have also considered the possibility that the reaction tends to grow chains rather than loops. Allowing the diffusive exchange and/or the radical transfer to occur between more than just nearest neighbors may reduce trapping (see Manneville and de Seze[11]). These improvements may make it feasible to meaingfully simulate irreversible gelation in dilute solutions where the monomer weight fraction is of the order of 10% as in most practically used gels and to discuss questions such as the relative importance of loops, radical trapping, and shielding of the second vinyl group of the divinyl monomer.

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## References and Notes

(1) Present address: Service de Physique Theorique, CEN Saclay, 91191 Gif-sur-Yvette, Cedex, France.
(2) Present address: Institut für Theoretische Physik, Universität Zu Köln, 5000 Köln 41, West Germany.
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# Thermotropic Polypeptides. 1. Investigation of Cholesteric Mesophase Properties of Poly(γ-methyl D-glutamate-*co*-γ-hexyl D-glutamate)s

**J. Watanabe,* Y. Fukuda, R. Gehani, and I. Uematsu**

*Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152 Japan.* *Received April 15, 1983*

ABSTRACT: A series of poly(γ-methyl D-glutamate-*co*-γ-hexyl D-glutamate)s were prepared with varying hexyl content by an ester exchange method from poly(γ-methyl D-glutamate). Copolymers with intermediate hexyl contents from 30% to 70% indicated different structure and mechanical properties compared to those of the constituent homopolymers by X-ray and viscoelastic measurements. The most predominant property, induced newly in copolymers, is the formation of thermotropic liquid crystals reflecting visible light in the high-temperature range above around 150 °C. The cholesteric pitches were measured by circular dichroism as a function of temperature and hexyl content. The results confirmed the same cholesteric nature as that observed in the lyotropic cholesteric mesophases of polypeptides. The present liquid crystals were easily solidified on cooling, offering films with various colors.

## Introduction

Polymers, whose degree of molecular order either in solution or in melt is intermediate between the perfect long-range order found in crystals and the statistical disorder in liquids, are called lyotropic or thermotropic liquid crystalline polymers. Since these polymers are able to form partially ordered solutions or melts, they are expected to produce fibers with high degrees of molecular orientation and order,[1,2] giving superior mechanical strength, and films with properties useful for photoelectrics.[3] In addition to the development of materials based on this concept, biological implications of liquid crystallinity of many biopolymers and membranes are also attracting a great deal of interest.[4]

Extensive studies have been conducted on lyotropic systems of natural[5,6] and synthetic polypeptides,[7-9] synthetic polymers such as polyamides[10,11] and polyisocyanates,[12,13] and cellulose derivatives.[14-16] More recently, thermotropic liquid crystalline polymers have been synthesized. The synthesis of these polymers can be achieved by using suitable mesogenic monomers, which are able to build up a liquid crystalline phase. There are two possible ways of obtaining the thermotropic polymers with liquid crystalline properties: (1) side-chain liquid crystalline polymers with mesogenic groups attached to a polymer backbone;[17-19] (2) main-chain liquid crystalline polymers with mesogenic groups incorporated into a polymer backbone.[20-28] In principle, thermotropic liquid crystals in these polymers could be achieved by decoupling the motions of the mesogenic units from the motions of polymer segments by introducing flexible spacers. Up to the present time, many types of liquid crystalline phases (smectic, nematic, and cholesteric phases) have been obtained, mainly depending on the nature of mesogenic unit.

The study of thermotropic liquid crystals has been directed to synthetic polypeptides. In their lyotropic liquid crystalline state,[7] the rigid α-helix forces a parallel orientation of the chains, the chirality of main chain imports a twist to the parallel arrangement, and the solvent allows the mesogenic main chains to migrate and form the equilibrium cholesteric arrangement. By analogy with the above mentioned liquid crystalline polymers, the role of solvent would be replaced by the flexible long side chains. Thus, it is possible that thermotropic liquid crystals may be induced in the polypeptides with long flexible side chains. This approach, however, failed for homopolymers of hexyl glutamate and octyl glutamate.

Recently, it was found that the poly(γ-benzyl L-glutamate-*co*-γ-methyl L-glutamate)s with intermediate benzyl contents showed different structures and properties

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