

# A Model of the Gel Fraction of Polymer in the Vinyl Chloride/Divinyl Monomers Suspension Copolymerization

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**ABSTRACT:** Based on our previous general model of the gel/sol partition, a model of the gel fraction of polymer is developed in the VC heterogeneously crosslinking suspension polymerization, where the kinetic factors such as two-phase polymerization mechanism, distinction of the gel and sol radicals, and the effects of the gel on kinetics are taken into account. The model is applied to the VC/diallyl phthalate (DAP) suspension copolymerization. The model parameters are obtained by fitting the experimental data with the model. The model turns out to be successful to predict the development of the gel fraction with conversion. It is inferred that the intermolecular crosslinking reaction is affected by diffusion. In addition, the crosslinks prove to be nonrandomly distributed in the VC/DAP suspension copolymerization. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1681–1690, 1997

**Key words:** crosslinking copolymerization; free radical; gel fraction; vinyl chloride

## INTRODUCTION

Modeling of the gel fraction of polymer in the crosslinking copolymerization is a real challenge.<sup>1</sup> Based on the statistics theory, many models have been presented,<sup>2–8</sup> but they were criticized for the equilibrium-like nature and inability to deal with kinetically controlled systems such as the crosslinking free-radical copolymerization. Some attempts have been made to avoid that criticism.<sup>9–13</sup> A general model of the sol/gel partition in the vinyl/divinyl monomer crosslinking copolymerization was developed in our previous paper.<sup>14</sup> However, all kinetic factors have to be allowed for and inserted into before the general model can be applied to a real system. In this paper, we try to illustrate how to convert our general model into a realistic one of the VC/divinyl monomer suspension copolymerization.

## DEVELOPMENT OF A REALISTIC MODEL OF THE GEL FRACTION OF POLYMER IN THE VC/DIVINYL SUSPENSION COPOLYMERIZATION

According to the VC suspension polymerization mechanism, the following kinetic factors must be considered to build a practical model of the gel fraction of polymer.

### VC Suspension Polymerization Mechanism

VC suspension polymerization becomes heterogeneous at very low conversion because PVC is insoluble in the VC monomer.<sup>15,16</sup> The auto-acceleration effect starts at the very beginning of polymerization.<sup>17–19</sup> In order to explain it, many hypotheses<sup>15,16,20–22</sup> have been assumed, among which the two-phase mechanism<sup>15,16</sup> by Talamini is well-accepted. According to this mechanism, polymerization takes place in two phases, a monomer-rich phase and a polymer-rich phase. There are nearly no macromolecules in the monomer phase where macromolecules formed will precipi-

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tate out rapidly to the polymer phase. But in the polymer phase, the polymer is swollen by the monomer and the concentration of polymer is determined by the swelling equation.

Based on the above mechanism, it is reasonable to assume that the crosslinking reactions take place only in the polymer phase, but the primary chains are born in both phases in the VC/divinyl monomer suspension copolymerization.

### Effects of Diffusion

The high concentration of polymer (up to 70%) forces us to consider the effects of diffusion in the polymer phase.

Reactions involving two molecules might be affected by diffusion. Generally speaking, when the effects of diffusion are taken into account, the apparent rate constant of a reaction might be defined<sup>23</sup> as

$$\frac{1}{k} = \frac{1}{k_{\text{diff}}} + \frac{1}{k_{\text{chem}}} \quad (1)$$

Let

$$\omega' = \frac{k_{\text{diff}}}{k_{\text{chem}}}$$

then if  $\omega' \gg 1$ , the reaction is chemically controlled, otherwise it is diffusion-controlled.

For the VC suspension polymerization, it has been proved that the termination reaction is diffusion-controlled in the polymer phase. However, the propagation reaction is still chemically controlled, for the rate constant of propagation is lower than that of termination by four orders.<sup>24</sup>

### Effects of Diffusion on the Termination Reaction

As the termination reaction is diffusion-controlled in the polymer phase, the rate constant can be formulated with<sup>24</sup>:

$$g_t = \exp \left[ -A^* \left( \frac{1}{v_{fp}} - \frac{1}{v_{fcri}} \right) \right] \quad (2)$$

where

$$g_t = \frac{k_{t2}}{k_{t1}}$$

and  $k_{t1}$  is the rate constant of termination in the

monomer phase, which is considered to be equal to the rate constant of termination in chemistry.

### Effects of Diffusion on the Intermolecular Crosslinking Reaction

An intermolecular crosslinking reaction takes place between two macromolecules, where the diffusion rate of reactants is much lower than that of the propagation reaction, so it is probable that the crosslinking reaction is affected by diffusion.<sup>25</sup> The rate constant of intermolecular crosslinking reaction is assumed to be:

$$\frac{1}{k_p^*} = \frac{1}{\omega' k_{p0}^*} + \frac{1}{k_{p0}^*} \quad (3)$$

and

$$g_c = \frac{k_p^*}{k_{p0}^*} = \frac{\omega'}{1 + \omega'} \quad (4)$$

where the parameter  $g_c$  represents the extent of reduction of the reactivity.

### Effects of Gel on the Diffusion-Controlled Reactions

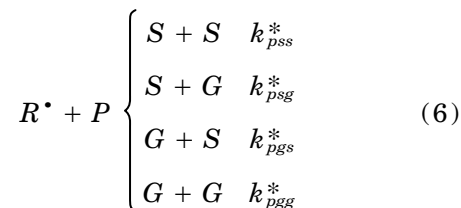
For the translational diffusion, the diffusion rate constant is dependent on the size of reactants<sup>23</sup>

$$k_{\text{diff}} \propto D(l_1) + D(l_2) \quad (5)$$

where  $D(l)$  is the diffusion rate constant of the polymer chains with length  $l$ , which is inversely proportional to their chain length<sup>22</sup>:

$$D(l) \propto l^{-\alpha'} \quad \alpha' > 1$$

It is clear that the larger a macromolecule is, the lower the diffusion rate constant is. A gel is an infinite macromolecule, so its diffusion rate constant can be assumed to be zero. The gel macromolecules have to differ from the sol macromolecules in terms of the above assumption, so the intercrosslinking reaction has to be divided into the following four kinds of reactions:



where  $S$  and  $G$  stand for the sol and gel macromolecules, respectively. Clearly,

$$k_{pgg}^* = 0$$

$$k_{psg}^*, k_{pgs}^* < k_{pss}^*$$

### Effects of the Gel on Intercrosslinking Reaction

According to eq. (6), the number of the crosslinkages born between  $t \sim t + dt$  (time  $t$  corresponding to the conversion  $\alpha$ ) can be represented as follows:

$$dN_{cr}(\beta, \alpha) = k_{pss}^* F_3(\beta, \alpha) N_{\beta s} [R]_{2s}$$

$$+ k_{psg}^* F_3(\beta, \alpha) N_{\beta g} [R]_{2s}$$

$$+ k_{pgs}^* F_3(\beta, \alpha) N_{\beta s} [R]_{2g} \quad (7)$$

where

$$N_{\beta s} = (1 - W_g(\beta, \alpha)) N_{\beta}$$

$$N_{\beta g} = W_g(\beta, \alpha) N_{\beta}$$

and  $[R]_{2g}$  and  $[R]_{2s}$  are the concentration of the gel radicals and sol radicals in the polymer phase, respectively. It has been proven that the gel radicals are difficult to terminate and the hypothesis of pseudo-steady-state is not valid any longer in the MMA crosslinking copolymerization.<sup>25</sup> However, for VC polymerization, if the crosslinking density is not very high, the gel radicals can be converted into the sol radicals, which can terminate by the chain transfer to monomers because the VC monomer chain transfer constant is very high, up to  $\sim 10^{-3}$ .<sup>24</sup> In fact, our experimental results showed that the polymerization rate of VC was not increased, but reduced when the crosslinking agent (DAP) was introduced, which was ascribed to the well-known degradative chain transfer for allylic monomer.<sup>26</sup> It seems to be reasonable to assume that the hypothesis of pseudo-steady-state should be still valid in the VC crosslinking copolymerization. The hypothesis of pseudo-steady-state with respect to the gel radicals gives:

$$k_{fm} [R]_{2g} [M]_2 = k_{psg}^* [R]_{2s} \bar{F}_3^{\text{gel}} M_0 \alpha W_g^{\psi=\alpha} / V_2 \quad (8)$$

$$[R]_{2g} + [R]_{2s} = [R]_2 \quad (9)$$

where  $M_0 \alpha / V_2$  is the concentration of polymer in

the polymer phase. From eqs. (8) and (9), one obtains:

$$[R]_{2g} = \frac{[R]_2}{1 + \frac{k_{fm} [M]_2 V_2}{k_{psg}^* \bar{F}_3^{\text{gel}} M_0 \alpha W_g^{\psi=\alpha}}} \quad (10)$$

According to the two-phase mechanism<sup>15,16</sup>:

$$[M]_2 V_2 = M_2 (1 - x_p) \quad (11)$$

$$M_0 \alpha = M_2 x_p \quad (12)$$

Substituting eqs. (11) and (12) into eq. (10) gives:

$$[R]_{2g} = \frac{[R]_2}{1 + A} \quad (13)$$

where:

$$A = \frac{k_{fm} (1 - x_p)}{k_{psg}^* \bar{F}_3^{\text{gel}} x_p W_g^{\psi=\alpha}} \quad (14)$$

Substituting eq. (13) into eq. (9) gives:

$$[R]_{2s} = \frac{A [R]_2}{1 + A} \quad (15)$$

It is concluded from eqs. (13) and (15) that the larger  $A$  is, the lower the concentration of the gel radicals is. Let  $k_{pgs}^* = b_1 k_{pss}^*$ ,  $k_{psg}^* = b_2 k_{pss}^*$ , and it is clear that  $b_1$  and  $b_2$  are not bigger than unity. Substituting eqs. (13) and (15) into eq. (7), and making an arrangement, give:

$$dN_{cr}(\beta, \alpha) = c_1 k_{pss}^* F_3(\beta, \alpha) (1 - c_2 W_g(\beta, \alpha)) N_{\beta} [R]_2 \quad (16)$$

where

$$c_1 = \frac{A + b_1}{1 + A} \quad (17)$$

$$c_2 = 1 - \frac{b_2 A}{b_1 + A} \quad (18)$$

### The Effects of the Gel on the Termination Reaction

For VC suspension polymerization, the termination reaction takes place mainly between the small radicals, especially between the primary radicals in the polymer phase.<sup>24</sup> Thus, the rate constant of termination in the literature repre-

sents the average rate constant of termination between the small radicals. So, it can be assumed that the termination reaction should not be affected by the gel.

On the other hand, the gel might affect the diffusion reactions in the aspect of the phase composition of the polymer phase. If this effect is taken into account, the volume fraction of polymer in the polymer phase would be calculated by the following equation<sup>27</sup>:

$$\ln(1 - \phi_p) + \phi_p + \chi_1 \phi_p^2 + v_1 v_e (\phi_p^{2/3} \phi_p^{1/3} - 0.5 \phi_p) = 0 \quad (19)$$

However, our results showed that this effect could be ignored in the present scope of study.<sup>28</sup>

### Modeling the Gel Fraction of Polymer in the VC Crosslinking Copolymerization

According to the two-phase mechanism of VC suspension polymerization, the number of the monomer units on polymers born between  $t \sim t + dt$  is:

$$dM = k_{p1}[M]_1[R]_1V_1 + k_{p2}[M]_2[R]_2V_2 \quad (20)$$

where

$$[M]_1V_1 = \frac{M_0(x_p - \alpha)}{x_p} \quad (21)$$

$$[M]_2V_2 = \frac{M_0\alpha(1 - x_p)}{x_p} \quad (22)$$

Substituting eqs. (21) and (22) into eq. (20) gives:

$$dM = (1 + q\alpha)k_{p1}[R]_1 \quad (23)$$

where

$$q = \frac{P(1 - x_p) - 1}{x_p}$$

where  $P$  is defined as

$$P = \frac{k_{p2}\sqrt{k_{d2}/k_{t2}}}{k_{p1}\sqrt{k_{d1}/k_{t1}}} \quad (24)$$

Let  $g_p = k_{p2}/k_{p1}$ ,  $g_d = k_{d2}/k_{d1}$ , then

$$P = g_p\sqrt{g_d/g_t} \quad (25)$$

Dividing eq. (16) by eq. (23) gives

$$\frac{\partial \rho_A(\beta, \alpha)}{\partial \beta} = \frac{c_1 P g_c (1 - c_2 W_g(\beta, \alpha)) F_3(\beta, \alpha)}{r_1 (1 + q\alpha)} \quad (26)$$

where  $g_c = k_{pss}^*/k_{p12}$ .

In the same way, eqs. (11) and (14) in reference [14] are converted into:

$$\frac{\partial \rho_A(\alpha, \gamma)}{\partial \gamma} = \frac{c_1 P g_c (1 - c_2 W_g(\alpha, \gamma)) F_3(\alpha, \gamma)}{r_1 (1 + q\gamma)} \quad (27)$$

$$\begin{aligned} \frac{\partial F_3(\beta, \alpha)}{\partial \alpha} \\ = - \frac{c_1 P g_c (1 - c_2 W_g(\beta, \alpha)) F_3(\beta, \alpha)}{r_1 (1 + q\alpha)} \\ \times (1 + k_{cs} \overline{DP}_{np} F_3(\beta, \alpha)) \end{aligned} \quad (28)$$

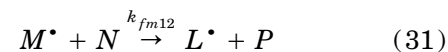
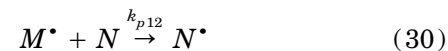
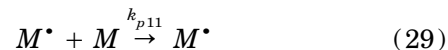
After eqs. (9), (11), and (14) in reference [14] were replaced by eqs. (26)–(28), the general model would be converted into a realistic model in the VC/divinyl monomer suspension polymerization.

### VC/DAP Copolymerization

DAP has a very high chain transfer constant,<sup>26</sup> which results in the reduction of the level of the pendent double bonds and the primary chain length.

### Copolymer Composition

If the chain transfer to DAP is allowed for, the copolymer composition is determined by the following elementary reactions:



After a DAP molecule is transferred to, the molecule will not take part in a crosslinking reaction any longer, though it might be copolymerized, so

$$- \frac{d[M]}{dt} = k_{p11}[M^\bullet][M] \quad (32)$$

$$-\frac{d[N]}{dt} = 2k_{p12}[M^*][N] + k_{fm12}[M^*][N] \quad (33)$$

$$\frac{d[N']}{dt} = 2k_{p12}[M^*][N] \quad (34)$$

eq. (34) represents the forming rate of the units of DAP being able to participate in a crosslinking reaction in the macromolecules. From eqs. (32)–(34), one obtains:

$$F_2(\beta) = \frac{2}{r_1} (1-x)^{2/r_1+C_{m2}-1} f_{20} \quad (35)$$

### The Size Distribution of the Primary Chains

In the VC/DAP copolymerization, both the monomers have a big chain transfer constant and the rate pseudo-constant of the monomer transfer is defined as:

$$k_{fm} = \sum_{i,j=1}^2 k_{fmij} \Phi_i^* f_j \quad (36)$$

Generally speaking, the feeding concentration of DAP is very low ( $\sim 0.1\%$ ),  $\Phi_1^* \approx 1.0$  and  $\Phi_2^* \approx 0.0$ , so

$$k_{fm} = k_{fm11} + (k_{fm12} - k_{fm11})f_2 \quad (37)$$

Thus, the pseudo-constant of the monomer chain transfer is:

$$C_m = C_{m1} + (C_{m2} - C_{m1})f_2 \quad (38)$$

The pseudo-constant of the monomer chain transfer is not constant any longer, but varies with  $f_2$  during the polymerization. From eqs. (33) and (34), one obtains:

$$f_2 = (1-x)^{2/r_1+C_{m2}-1} f_{20} \quad (39)$$

The size of the primary chains is determined by the monomer chain transfer, and the instantaneous size distribution is<sup>29</sup>:

$$W_r = C_m^2 r \exp(-C_m r) \quad (40)$$

### The “Back-biting” Reaction of the DAP Radicals

For a DAP radical, it is easy to “back-bite” the pendent double bond on the same DAP unit in the homo-polymerization. However, for VC/DAP copolymerization, the “back-biting” reaction

would be suppressed very much because of  $r_2 \ll 1$  and high concentration of VC monomer. As a result, the “back-biting” reaction of the DAP radicals can be ignored.<sup>28</sup>

### A Model of the Gel Fraction of Polymer in the VC/DAP Suspension Copolymerization

After the above modifications, the previous general model<sup>14</sup> is converted into:

$$W_g(\alpha, \psi) = 1 - \sum_{r=2}^{\infty} W_r(\alpha) \times \left( 1 - \int_0^{\alpha} \frac{\partial \rho_A(\beta, \alpha)}{\partial \beta} W_g(\beta, \psi) d\beta - \int_{\alpha}^{\psi} \frac{\partial \rho_A(\alpha, \gamma)}{\partial \gamma} W_g(\gamma, \psi) d\gamma \right)^r \quad (41)$$

$$W_g = \frac{1}{\psi} \int_0^{\psi} W_g(\alpha, \psi) d\alpha \quad (42)$$

$$\frac{\partial \rho_A(\beta, \alpha)}{\partial \beta} = \frac{c_1 P g_c (1 - c_2 W_g(\beta, \alpha)) F_3(\beta, \alpha)}{r_1 (1 + q\alpha)} \quad (43)$$

$$\frac{\partial \rho_A(\alpha, \gamma)}{\partial \gamma} = \frac{c_1 P g_c (1 - c_2 W_g(\alpha, \gamma)) F_3(\alpha, \gamma)}{r_1 (1 + q\gamma)} \quad (44)$$

$$W_r(\alpha) = [C_m(\alpha)]^2 r \exp(-C_m(\alpha)r) \quad (45)$$

$$\frac{\partial F_3(\beta, \alpha)}{\partial \alpha} = - \frac{c_1 P g_c (1 - c_2 W_g(\beta, \alpha)) F_3(\beta, \alpha)}{r_1 (1 + q\alpha)} \quad (46)$$

$$F_3(\beta, \beta) = F_2(\beta) - \rho_{cp}(\beta) \quad (47)$$

$$\rho_{cp}(\beta) = k_{cp} F_2(\beta) \quad (48)$$

$$F_2(\beta) = \frac{2}{r_1} (1-\alpha)^{2/r_1+C_{m2}-1} f_{20} \quad (49)$$

$$C_m = C_{m1} + (C_{m2} - C_{m1})f_2 \quad (50)$$

$$f_2 = (1-\alpha)^{2/r_1+C_{m2}-1} f_{20} \quad (51)$$

Equations (41)–(51) constitute the present model of the gel fraction of polymer in VC/DAP suspension copolymerization.

## EXPERIMENTAL

### Main Reagents

VC polymerization grade; DAP  $n^{25^\circ\text{C}} = 1.5180$ , Initiator: dicyclohexyl peroxy dicarbonate purified twice by recrystallization.

## Polymerization

The monomers were polymerized in a 200 ml rotating stainless steel tube. A special reverse feeding process was used: a given amount of the initiator and DAP was fed first, then the tube was sealed and oxygen was exhausted; then, a given amount of VC was pumped into the tube and pre-mixed. At last, a certain amount of dispersant and deionized water was pumped into. After all above finished, polymerization was started.

## Separation of the Sol and Gel

An amount of the dry resin was backwashed in a Soxhlet extractor for 48 h with tetrahydrofuran (THF) at 80°C under nitrogen. Then the extracted residue was dried under vacuum to constant weight. The gel fraction of polymer is the ratio of the amount of the dry residue to that of the original resin.

Backwashing time was followed from Figure 1. As shown in the figure the gel fraction is almost constant after backwashing for 24 h.

## PARAMETERS AND PARAMETER ESTIMATION

The model parameters can be divided into two groups: one is those parameters from VC homo-polymerization such as  $C_{m1}$  and  $P$ , which can be obtained from the literature; the other is those introduced in the present model, which will be determined experimentally.

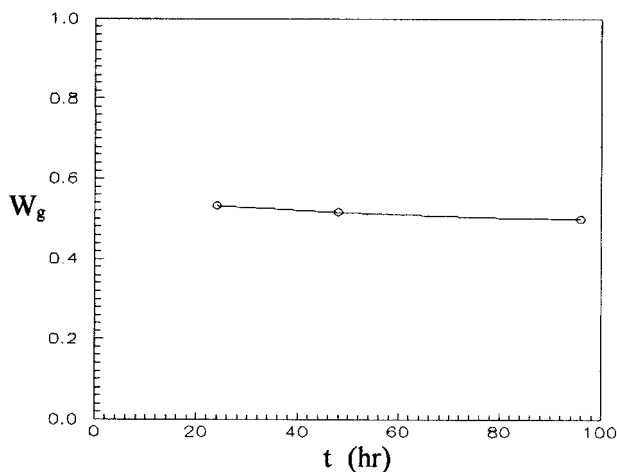


Figure 1 Gel fraction versus extracting time.

Table I  $C_{m1}$  Values Reported in the Literature for Bulk Polymerization

$T$ (°C)	$C_{m1} \times 10^3$	Reference
6	0.171	[29]
20	0.32	[30]
25	0.385	[29]
30	0.63, 0.625, 0.51	[30] ~ [32]
40	0.710, 0.71	[29], [30]
50	1.10, 0.85, 1.35, 1.05, 1.035	[30] ~ [34]
60	1.23, 1.48	[33], [30]

## The Parameters from VC Homo-polymerization

Xie<sup>24</sup> has deeply studied VC homo-polymerization. Some of his results are cited as follows:

$$k_{t2} = k_{t1} \exp \left[ -A^* \left( \frac{1}{v_{fp}} - \frac{1}{v_{fcri}} \right) \right] \quad (51)$$

$$k_{p2} = k_{p1} \exp \left[ -B^* \left( \frac{1}{v_{fp}} - \frac{1}{v_{fxf}} \right) \right] \quad (52)$$

$$k_{d2} = k_{d1} \exp \left[ -C^* \left( \frac{1}{v_{fp}} - \frac{1}{v_{fxf}} \right) \right] \quad (53)$$

where

$$A^* = 6.64 \times 10^6 \exp(-4968/T)$$

$$B^* = 1.85 \times 10^3 \exp(-2595/T)$$

$$C^* = 477.0 \exp(-2291/T)$$

$$v_{fp} = (4.748 \times 10^{-3}T - 0.00292)\phi_p + (0.09486 + 9.98 \times 10^{-4}T)(1 - \phi_p) \quad (54)$$

$$v_{fcri} = 0.0759 + 7.984 \times 10^{-4}T \quad (55)$$

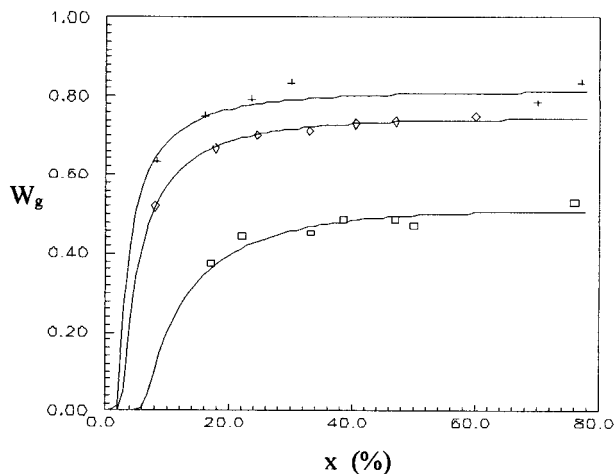
In the two-phase stage (1%–75%),  $v_{fp} = v_{fxf}$ , so

$$k_{p2} = k_{p1}$$

$$k_{d2} = k_{d1}$$

There are many reports about the chain transfer constant to the VC monomer. Some results in the bulk polymerization are listed in Table I. The average values of  $C_{m1}$  can be fitted well with the reciprocal of polymerization temperature by the equation:

$$C_{m1} = 79.312 \exp(-3639.38/T) \quad (56)$$



**Figure 2** Development of gel fraction with conversion, fitting experimental data with model.  $\square$ ,  $f_{20} = 1.09 \times 10^{-3}$ ;  $\diamond$ ,  $f_{20} = 1.98 \times 10^{-3}$ ;  $+$ ,  $f_{20} = 2.56 \times 10^{-3}$ ; —, fitting curves.

**The Parameters from Copolymerization and Crosslinking Reaction**

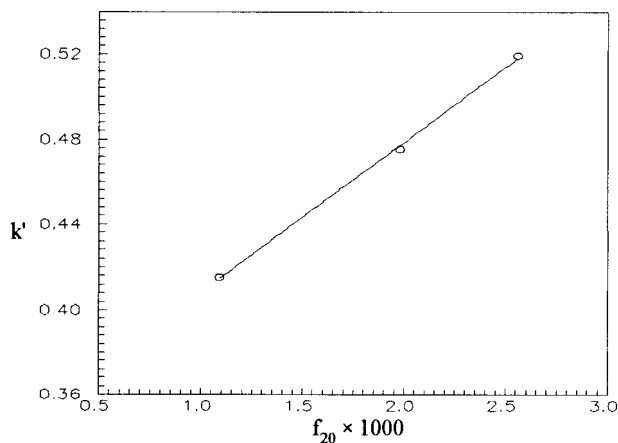
The parameters from copolymerization and crosslinking reaction in the present model include:  $C_{m2}$ ,  $r_1$ ,  $k_{cp}$ ,  $k_{cs}$ ,  $g_c$ ,  $c_1$  and  $c_2$ .  $r_1$ ,  $k_{cp}$  and  $C_{m2}$  were measured independently and the results were<sup>28</sup>:

$$\begin{aligned} r_1 &= 24.61 \exp(-909.5/T) \\ k_{cp} &= 0.0126 \text{ (50}^\circ\text{C)} \\ C_{m2} &= 0.185 \text{ (50}^\circ\text{C)} \end{aligned} \tag{57}$$

However, the parameters  $k_{cs}$ ,  $g_c$ ,  $c_1$ , and  $c_2$  can not be measured independently and are considered to be the fitting parameters in the present model. Although according to the definition,  $c_1$ ,  $c_2$  might vary during the polymerization, it is assumed that they should not vary with conversion, which will be proven below. In order to estimate these fitting parameters, the development of the gel fraction of polymer with conversion was monitored and the objective function  $\text{FUNC} = \sum (W_{gi}^{\text{exp.}} - W_{gi}^{\text{mod.}})^2$  was optimized. However, the multiple product of  $c_1$  and  $g_c$  is taken as a new fitting parameter  $k'$  because  $g_c$  and  $c_1$  are equivalent in the model. As a result, there are three fitting parameters in the model.

**RESULTS AND DISCUSSION**

The development of the gel fraction of polymer with conversion was monitored at the various feeding amounts of DAP at 50°C. Dependence of the gel fraction of polymer on conversion is shown in Figure 2. From the optimization of the objective



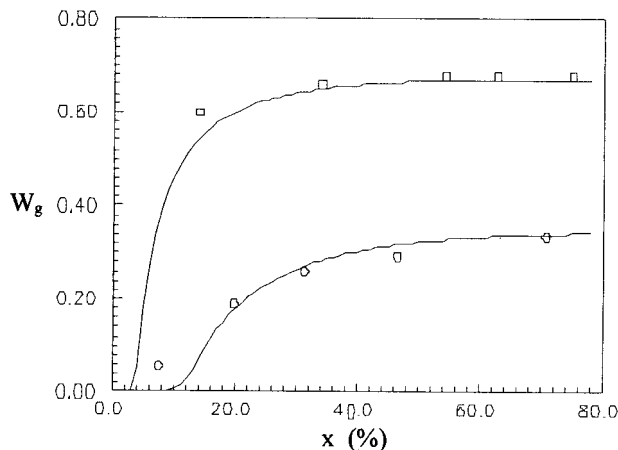
**Figure 3** Parameter  $k'$  versus feeding composition of DAP.

function, it is concluded that  $k_{cs} = 0.144$  and  $c_2 = 0.236$ , which are independent of the feeding amount of DAP. But as shown in Figure 3,  $k'$  is a linear function of the amount of DAP:

$$k' = 70.32 f_{20} + 0.3379 \tag{58}$$

After all the parameters obtained, the present model could be used to predict the development of the gel fraction of polymer. As illustrated in Figure 4, the model successfully predicts the development of the gel fraction of polymer, which substantiates the present model.

It is concluded that  $c_2$  does not vary with the feeding level of DAP in the experimental scope. According to eq. (18), in order to maintain  $c_2$ , A



**Figure 4** Development of gel fraction with conversion, comparison experimental data with model prediction  $\circ$ ,  $f_{20} = 8.20 \times 10^{-4}$ ;  $\square$ ,  $f_{20} = 1.60 \times 10^{-3}$ ; —, model prediction.

has to be far larger than  $b_1$ , namely,  $c_2 \approx 1 - b_2$ , so  $b_2 \approx 0.864$ .  $b_2 < 1$  suggests that the reactivity of the pendent double bonds in the gel is lower than that in the sol, from which it is inferred that the inter-molecular crosslinking reaction is affected by the diffusion. Thus, for the whole system, the reactivity of the pendent double bonds is heterogeneous and size-dependent; i.e., the larger a macromolecule is, the lower the reactivity of the pendent double bonds on it is. At the same time, the size of macromolecules in the sol decreases with DAP concentration, so the diffusion rate of the sol macromolecules increases with DAP concentration. As a result,  $k_{ps}^*$  increases with DAP concentration and  $k'$  consequently increases.

When  $A \gg b_1$ , one obtains from eq. (17)  $c_1 = A/1 + A$ . As shown in Figure 5, the changing rate of  $c_1$  rapidly decreases with the increase of  $A$ . Only if  $A$  is big enough,  $c_1$  and  $c_2$  might be considered to be constant. From eq. (15), it is concluded that this condition is easily met in the present experimental scope. Therefore, the assumption that  $c_1$  and  $c_2$  do not change with conversion and DAP concentration is reasonable. On the other hand, the good agreement of the model prediction with the experimental also substantiates the assumption.

While calculating the gel fraction of polymer, we can also obtain the distribution of crosslinking density of polymer with respect to the birth time of the primary chains. Development of the distribution of the crosslinking density of polymer with conversion is illustrated in Figure 6. It is clear that the distribution of crosslinking density is rather heterogeneous. The crosslinking density of the primary chains increases at first and then decreases with the birth time of the primary chains.

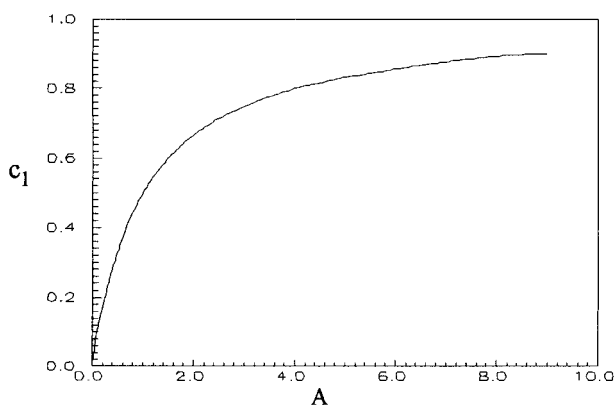


Figure 5 Influence of  $A$  on  $c_1$ .

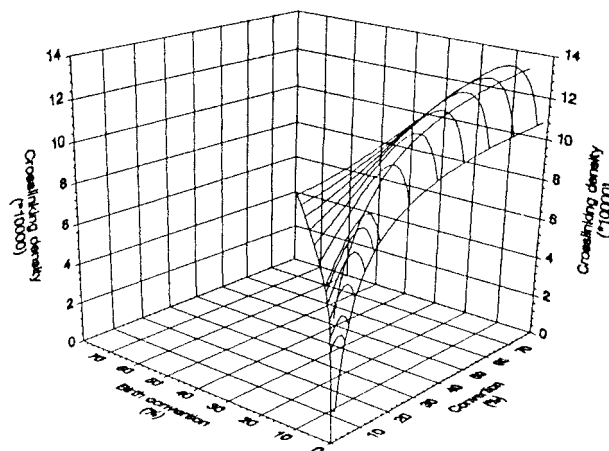


Figure 6 Development of the distribution of the crosslinking density with conversion  $f_{20} = 1.09 \times 10^{-3}$ .

## CONCLUSION

In order to build a realistic model of the gel fraction of polymer, the two-phase mechanism, distinction of the gel and sol, the effects of the gel on kinetics, and the degradative chain transfer to DAP were taken into account in the VC/DAP crosslinking suspension copolymerization. It is concluded that the present model predicts well about the development of the gel fraction of polymer with conversion, and the intermolecular crosslinking reaction is affected by diffusion. It is inferred that distribution of crosslinking density is rather heterogeneous in the VC/DAP crosslinking suspension copolymerization.

## NOMENCLATURE

$C_m$	pseudo-constant of monomer transfer
$C_{m1}$	constant of monomer transfer to VC
$C_{m2}$	constant of monomer transfer to DAP
$D(l)$	diffusion rate constant of macromolecules with length $l$
$\overline{DP}_{np}$	number-average degree of polymerization of the primary chains
$f_j, j = 1, 2$	molar fraction of $j$ monomer
$f_{20}$	initial molar fraction of DAP
$F_2(\beta)$	instantaneous composition of DAP being able to be crosslinked in the primary chain born at conversion $\beta$
$F_3(\beta, \alpha)$	molar fraction of PDB in the pri-



	primary chain born at conversion $\beta$	$k_{t2}$	rate constant of termination in the polymer phase
$\bar{F}_3^{\text{gel}}$	at conversion $\alpha$	$l_1$	polymer chain length
	average molar fraction of PDB in the gel	$l_2$	polymer chain length
$k$	apparent rate constant	$L$	allyl radicals
$k_{\text{diff}}$	diffusion constant	$M$	VC monomer or amount of VC monomer
$k_{cp}$	rate constant of the primary intramolecular crosslinking reaction	$[M]$	VC monomer concentration
$k_{cs}$	rate constant of the second intramolecular crosslinking reaction	$M_0$	initial amount of VC
$k_{\text{chem}}$	rate constant determined by chemistry of reactants	$M_2$	amount of the polymer phase
$k_{fm}$	pseudo-constant of monomer transfer rate	$[M]_1$	VC concentration in the monomer phase
$k_{fm11}$	rate constant of VC radicals transfer to VC monomer	$[M]_2$	VC concentration in the polymer phase
$k_{fm12}$	rate constant of VC radicals transfer to DAP monomer	$N$	DAP monomer
$k_{p11}$	rate constant of propagation of VC radicals and VC monomer	$[N]$	DAP monomer concentration
$k_{p12}$	rate constant of propagation of VC radicals and DAP monomer	$[N']$	concentration of DAP being able to be crosslinked in the polymer
$k_p^*$	apparent rate constant of intermolecular crosslinking reaction	$N_{cr}$	the number of crosslinkages produced by the intermolecular crosslinking
$k_{p0}^*$	rate constant of intermolecular crosslinking reaction determined by chemistry	$N_\beta$	the number of the primary chains born at conversion $\beta$
$k_{pgg}^*$	rate constant of intermolecular crosslinking reaction between a gel radical and a gel macromolecule	$N_{\beta s}$	the number of the primary chains born at conversion $\beta$ and being part of the sol
$k_{pgs}^*$	rate constant of intermolecular crosslinking reaction between a gel radical and a sol macromolecule	$N_{\beta g}$	the number of the primary chains born at conversion $\beta$ and being part of the gel
$k_{psg}^*$	rate constant of intermolecular crosslinking reaction between a sol radical and a gel macromolecule	$r$	chain length
$k_{pss}^*$	rate constant of intermolecular crosslinking reaction between a sol radical and a sol macromolecule	$r_1$	reactivity ratio
$k_{d1}$	rate constant of decomposition of initiator in the monomer phase	$r_2$	reactivity ratio
$k_{d2}$	rate constant of decomposition of initiator in the polymer phase	$[R]_1$	radical concentration in the monomer phase
$k_{p1}$	rate constant of propagation termination in the monomer phase	$[R]_2$	radical concentration in the polymer phase
$k_{p2}$	rate constant of propagation termination in the polymer phase	$[R]_{2g}$	concentration of the gel radicals in the polymer phase
$k_{t1}$	rate constant of termination in the monomer phase	$[R]_{2s}$	concentration of the sol radicals in the polymer phase
		$t$	polymerization time
		$T$	polymerization temperature
		$W_g$	gel fraction
		$W_g(\beta)$	probability by which the primary chains born at $\beta$ is part of the gel
		$W_g(\beta, \alpha)$	probability by which the primary chains born at $\beta$ is part of the gel at $\alpha$
		$W_g^{\psi=\alpha}$	gel fraction at $\alpha$
		$W_r$	weight distribution of the primary chains with respect to chain length
		$V_1$	volume of the monomer phase
		$V_2$	volume of the polymer phase

$v_{fp}$	free-volume fraction in the polymer phase
$v_{fcri}$	critical free-volume fraction
$v_{fxf}$	free-volume fraction when the monomer is disappeared
$x$	conversion
$x_p$	molar fraction of monomer in the polymer in the polymer phase
$\alpha, \beta, \gamma$	conversion
$\rho_A(\beta, \alpha)$	the crosslinking density of the intermolecular crosslinking points connected A and B on the primary chains A, $\beta < \alpha$
$\rho_B(\beta, \alpha)$	the crosslinking density of the intermolecular crosslinking points connected A and B on the primary chains B, $\beta < \alpha$
$\phi_p$	volume fraction of polymer in the polymer phase
$\Phi_1^{\bullet}$	molar fraction of VC radicals
$\Phi_2^{\bullet}$	molar fraction of DAP radicals
$\psi$	ultimate conversion

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