Modeling of Effective Crosslinking Density of the Gel in Free-Radical Copolymerization of Vinyl/Divinyl Monomers

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ABSTRACT: The concept of effective crosslinking density proposed by Scanlan is extended to heterogeneously crosslinking polymer. A kinetic-statistical model of effective crosslinking density of the gel is developed in free-radical heterogeneously crosslinking polymerization. The model is applied to the vinyl chloride (VC)/dially phthalate (DAP) suspension process. It is concluded that the model successfully predicts the development of effective crosslinking density of the gel. It is suggested that the degree of swelling of the gel is determined by its effective crosslinking density. However, when the crosslinking density is high, the physical entanglements would greatly influence the degree of swelling. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1691–1699, 1997

Key words: crosslinking copolymerization; free radical; effective crosslinking density; degree of swelling

INTRODUCTION

Recently, much attention has been paid to free-radical crosslinking copolymerization in the fields of theory and industry. On one hand, the cross-linked polymers made by free-radical crosslinking polymerization, i.e., the superadsorbent resin, have been widely used.[1] On the other hand, the classical Flory-Stockmayer[2] crosslinking theory has been criticized for incapability of coping with the kinetically controlled systems,[3] exemplified by the free-radical crosslinking copolymerization, and many attempts have been made to modify it.[4–6] In a series of papers[6–8] by Tobita and Hamielec, this incapability of the Flory-Stockmayer model was attributed to the nonrandom distribution of crosslinking density, and a model of the distribution of crosslinking density was proposed. Tobita and Hamielec inserted the model of the distribution of crosslinking density into the Flory model and proposed a statistical-kinetic crosslink-

ing model for the postgelation period in the free-radical crosslinking polymerization. However, the Tobita model turned out to be a self-crosslinking one,[9] where the intermolecular crosslinking reactions take place only among those chains born at the same time. Most recently, Luo, Weng, and Huang[9] proposed a new modeling idea based on the distribution of crosslinking density for the postgelation period, and a model of the gel fraction of polymer was built in the free-radical crosslinking copolymerization of vinyl/divinyl monomers.

The effective crosslinking density is one of the most important structure properties of cross-linked polymer in that physical properties are dependent on it.[2] A model of effective crosslinking density has been developed in a randomly cross-linking system.[10] In a series of papers,[9,11,12] we tried to propose a model for the free-radical crosslinking polymerization by combining the kinetic and statistical methods. In this paper, an attempt is made to model the effective crosslinking density of the gel in the free-radical heterogeneously crosslinking copolymerization of vinyl/divinyl monomers.

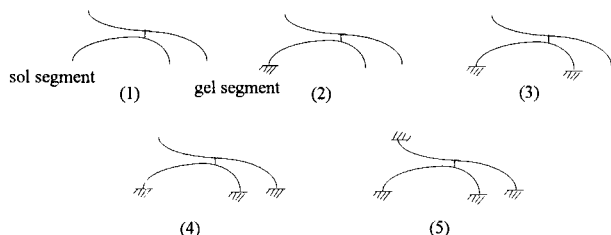*Correspondence to:* Dr. Yingwu Luo.

Figure 1 Classification of crosslinking points.

MODEL DEVELOPMENT

The Effective Crosslinks

In 1960, Scanlan[13] proposed the concept of effective crosslinks according to Figure 1, where crosslinks are classified into five kinds according to the situations of their connection in the four directions. Only the fourth and fifth kinds of crosslinks that have three and four directions that led to a gel segment, respectively, are elastically effective and are called the effective crosslinks.

Modeling of Effective Crosslinking Density

As shown in Figure 2, a crosslink C consisting of two crosslinking units $c1$ and $c2$, connects two primary chains A born at α and B born at β. The primary chain A is distinguished from B in that they are born at different times. The probabilities by which they are a part of a sol are called $W_s(\alpha)$ and $W_s(\beta)$, respectively. As an approximation, it is assumed that directions $d1$ and $d2$ (or $d3$ and $d4$) are probabilitically equivalent, for the crosslinking unit $c1$ (or $c2$) is randomly distributed on the primary chain A (or B). As a result, it is reasonable to assume:

$$W_s(1) = W_s(2) = \sqrt{W_s(\alpha)} \quad (1)$$
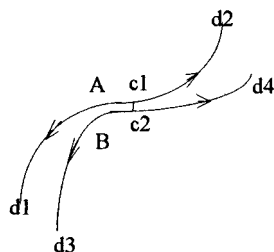
$$W_s(3) = W_s(4) = \sqrt{W_s(\beta)} \quad (2)$$

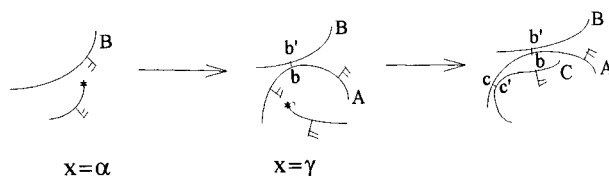**Figure 2** Schematic drawing of a crosslinking point.

Figure 3 Schematic drawing of crosslinking reactions.

The Crosslinking Density of the Fourth Kind of Crosslinks

For the fourth kind of crosslinks, one of the four leading directions of a crosslink is led to a sol segment, and the others are led to a gel segment, so the probability by which the crosslinking unit $c1$ on the primary chain A is one of two units of the fourth kind of crosslinks is:

$$P_3(\beta, \alpha) = 2\{[1 - W_s(1)]W_s(2)[1 - W_s(3)] \\ \times [1 - W_s(4)] + [1 - W_s(1)] \\ \times [1 - W_s(2)][1 - W_s(3)]W_s(4)\} \quad (3)$$

Substituting eqs. (1) and (2) into eq. (3) gives:

$$P_3(\beta, \alpha) = 2[(1 - \sqrt{W_s(\beta)})^2(1 - \sqrt{W_s(\alpha)})\sqrt{W_s(\alpha)} \\ + (1 - \sqrt{W_s(\alpha)})^2(1 - \sqrt{W_s(\beta)})\sqrt{W_s(\beta)}] \quad (4)$$

On the primary chain A, two types of the crosslinking units from the kinetic viewpoint must be distinguished. As shown in Figure 3, at conversion α, the free radical R, which is the predecessor of the primary chain A, attacks the pendent double bonds on the primary chain B, which was born at conversion β to produce the crosslink units b and b'. Afterward, the free-radical R' reacts with a pendent double bond on A to form the crosslink units c and c' at conversion γ. The crosslink unit b differs kinetically from c on A because their born times are different. Thus, making material balance of the fourth kind of crosslinking units on A gives:

$$\rho_3(\alpha)W_g(\alpha) = \int_0^\alpha \frac{\partial \rho_{At}(\beta, \alpha)}{\partial \beta} P_3(\beta, \alpha)\, d\beta \\ + \int_\alpha^\gamma \frac{\partial \rho_{At}(\alpha, \gamma)}{\partial \gamma} P_3(\alpha, \gamma)\, d\gamma \quad (5)$$

where $\beta < \alpha < \gamma$ and $\rho_3(\alpha)$ is defined with respect to the gel.

Substituting eq. (4) into eq. (5) gives:

$$\rho_3(\alpha) = \frac{2}{W_g(\alpha)} \left\{ \int_0^\alpha \frac{\partial \rho_{At}(\beta, \alpha)}{\partial \beta} [(1 - \sqrt{W_s(\beta)})^2 \right.$$

$$\times (1 - \sqrt{W_s(\alpha)})\sqrt{W_s(\alpha)} + (1 - \sqrt{W_s(\alpha)})^2$$

$$\times (1 - \sqrt{W_s(\beta)})\sqrt{W_s(\beta)}] \, d\beta$$

$$+ \int_\alpha^\psi \frac{\partial \rho_{At}(\alpha, \gamma)}{\partial \gamma} [(1 - \sqrt{W_s(\gamma)})^2$$

$$\times (1 - \sqrt{W_s(\alpha)})\sqrt{W_s(\alpha)} + (1 - \sqrt{W_s(\alpha)})^2$$

$$\left. \times (1 - \sqrt{W_s(\gamma)})\sqrt{W_s(\gamma)}] \, d\gamma \right\} \quad (6)$$

At the end of polymerization, the system is composed of the primary chains born between conversion $0 \sim \psi$, thus the average crosslinking density of the fourth kind of crosslinks:

$$\bar{\rho}_3 = \frac{\int_0^\psi \rho_3(\alpha) W_g(\alpha) \, d\alpha}{\int_0^\psi W_g(\alpha) \, d\alpha} \quad (7)$$

The Crosslinking Density of the Fifth Kind of Crosslinks

In the same way as eqs. (6) and (7) were developed, the crosslinking density of the fifth kind of the crosslinks is represented as:

$$\rho_4(\alpha) = \frac{[1 - \sqrt{W_s(\alpha)}]^2}{W_g(\alpha)}$$

$$\times \left\{ \int_0^\alpha \frac{\partial \rho_{At}(\beta, \alpha)}{\partial \beta} (1 - \sqrt{W_s(\beta)})^2 \, d\beta \right.$$

$$\left. + \int_\alpha^\psi \frac{\partial \rho_{At}(\alpha, \gamma)}{\partial \gamma} (1 - \sqrt{W_s(\gamma)})^2 \, d\gamma \right\} \quad (8)$$

$$\bar{\rho}_4 = \frac{\int_0^\psi \rho_4(\alpha) W_g(\alpha) \, d\alpha}{\int_0^\psi W_g(\alpha) \, d\alpha} \quad (9)$$

The Effective Crosslinking Density

The fourth kind of the crosslinks contributes less than the fifth kind to the effective crosslinking density. It was suggested that[14]:

$$\bar{\rho}_{eff} = \bar{\rho}_4 + 0.75\bar{\rho}_3 \quad (10)$$

From eqs. (6)–(10), one can calculate the effective crosslinking density of the gel on the condition that $W_s(\alpha)$, $\partial \rho_{At}(\beta, \alpha)/\partial \beta$, and $\partial \rho_{At}(\alpha, \gamma)/\partial \gamma$ be given. $W_s(\alpha)$ can be calculated by the models proposed by Luo, Weng, and Huang.[9,12] $\partial \rho_{At}(\beta, \alpha)/\partial \beta$ and $\partial \rho_{At}(\alpha, \gamma)/\partial \gamma$ will be modeled below.

Modeling of $\partial \rho_{At}(\beta, \alpha)/\partial \beta$ and $\partial \rho_{At}(\alpha, \gamma)/\partial \gamma$

In the free-radical crosslinking copolymerization, it was found that the pendent double bonds can take part in the intermolecular, the primary intramolecular, and the second intramolecular crosslinking reactions.[15] Besides the intermolecular crosslinking reaction, the second intramolecular crosslinking reaction contributes to the effective crosslinks. However, the primary intramolecular crosslinking reaction does not contribute to the effective crosslinks.[8] Thus, for the primary chain A, we get:

$$\rho_{At}(\beta, \alpha) = \rho_A(\beta, \alpha) + \rho_{Acs}(\beta, \alpha) \quad (11)$$

$$\rho_{Bt}(\beta, \alpha) = \rho_B(\beta, \alpha) + \rho_{Bcs}(\beta, \alpha) \quad (12)$$

Differentiating eqs. (11) and (12) with respect to β and α, respectively, gives:

$$\frac{\partial \rho_{At}(\beta, \alpha)}{\partial \beta} = \frac{\partial \rho_A(\beta, \alpha)}{\partial \beta} + \frac{\partial \rho_{Acs}(\beta, \alpha)}{\partial \beta} \quad (13)$$

$$\frac{\partial \rho_{Bt}(\beta, \alpha)}{\partial \alpha} = \frac{\partial \rho_B(\beta, \alpha)}{\partial \alpha} + \frac{\partial \rho_{Bcs}(\beta, \alpha)}{\partial \alpha} \quad (14)$$

According to Tobita and Hamielec[8]:

$$\frac{\partial \rho_{Acs}(\beta, \alpha)}{\partial \beta} = k_{cs}\overline{DP}_{np}(\beta)F_3(\beta, \alpha)\frac{\partial \rho_A(\beta, \alpha)}{\partial \beta} \quad (15)$$

$$\frac{\partial \rho_{Bcs}(\beta, \alpha)}{\partial \alpha} = k_{cs}\overline{DP}_{np}(\beta)F_3(\beta, \alpha)\frac{\partial \rho_B(\beta, \alpha)}{\partial \alpha} \quad (16)$$

According to Luo, Weng, and Huang[9]:

$$\frac{\partial \rho_A(\beta, \alpha)}{\partial \beta} = \frac{k_{p13}F_3(\beta, \alpha)}{k_p(1 - \alpha)} \quad (17)$$

$$\frac{\partial \rho_B(\beta, \alpha)}{\partial \alpha} = \frac{k_{p13}F_3(\beta, \alpha)}{k_p(1 - \alpha)} \quad (18)$$

Substituting eqs. (15) and (17) into eq. (13) and

eqs. (16) and (18), into eq. (14), respectively, gives:

$$\frac{\partial \rho_{At}(\beta, \alpha)}{\partial \beta}$$

$$= \frac{k_{p\,13}F_3(\beta, \alpha)(1 + k_{cs}\overline{DP}_{np}(\beta)F_3(\beta, \alpha))}{k_p(1 - \alpha)} \quad (19)$$

$$\frac{\partial \rho_{Bt}(\beta, \alpha)}{\partial \alpha}$$

$$= \frac{k_{p\,13}F_3(\beta, \alpha)(1 + k_{cs}\overline{DP}_{np}(\beta)F_3(\beta, \alpha))}{k_p(1 - \alpha)} \quad (20)$$

Equation (20) is equal to:

$$\frac{\partial \rho_{At}(\alpha, \gamma)}{\partial \gamma}$$

$$= \frac{k_{p\,13}F_3(\alpha, \gamma)(1 + k_{cs}\overline{DP}_{np}(\alpha)F_3(\alpha, \gamma))}{k_p(1 - \gamma)} \quad (21)$$

where $\overline{DP}_{np}$ can be modeled in the same way as in the vinyl homopolymerization and $F_3(\beta, \alpha)$ can be calculated by[9]

$$\frac{\partial F_3(\beta, \alpha)}{\partial \alpha}$$

$$= -\frac{k_{p\,13}F_3(\beta, \alpha)(1 + k_{cs}\overline{DP}_{np}(\beta)F_3(\beta, \alpha))}{k_p(1 - \alpha)} \quad (22)$$

with initial conditions:

$$F_3(\beta, \beta) = F_2(\beta) - \rho_{cp}(\beta) \quad (23)$$

$$\rho_{cp}(\beta) = k_{cp}F_2(\beta) \quad (24)$$

In most cases, f_{20} is far less than unity, and then

$$F_2(\beta) = \frac{2}{r_1}(1 - \beta)^{2/r_1 - 1}f_{20} \quad (25)$$

So far, we have developed a theoretical model consisting of eqs. (6–10), (19), and (21–25) to calculate the effective crosslinking density of the gel in the free-radical heterogeneously crosslinking copolymerization of vinyl/divinyl monomers.

A Practical Model in the VC/DAP Suspension Crosslinking Copolymerization

To predict the effective crosslinking density, the theoretical model must be modified according to the specific mechanism of a polymerization system. The way to modify VC/DAP crosslinking polymerization was proposed in the previous paper.[12] In the same way, we can obtain:

$$\frac{\partial \rho_{At}(\beta, \alpha)}{\partial \beta}$$

$$= \frac{c_1 Pg_c(1 - c_2 W_g(\beta, \alpha))F_3(\beta, \alpha) \times (1 + k_{cs}\overline{DP}_{np}(\beta)F_3(\beta, \alpha))}{r_1(1 + q\alpha)} \quad (26)$$

$$\frac{\partial \rho_{At}(\alpha, \gamma)}{\partial \gamma}$$

$$= \frac{c_1 Pg_c(1 - c_2 W_g(\beta, \alpha))F_3(\alpha, \gamma) \times (1 + k_{cs}\overline{DP}_{np}(\alpha)F_3(\alpha, \gamma))}{r_1(1 + q\gamma)} \quad (27)$$

$$\frac{\partial F_3(\beta, \alpha)}{\partial \alpha}$$

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

That eqs. (26–28) take the place of eqs. (19), (21), and (22) modifies the theoretical model into a practical one where $W_g(\beta, \alpha)$, $\overline{DP}_{np}(\alpha)$ and all the model parameters were obtained from the previous paper.[12]

MEASUREMENT OF THE EFFECTIVE CROSSLINKING DENSITY

The fundamental equation correlating the degree of swelling with the effective crosslinking density is the Flory-Rehner equation as follows[16]:

$$v_e = \frac{d_p}{\overline{M}_c} = -\frac{\ln(1 - v_r) + v_r + \chi v_r^2}{\phi_{p0}^{-2/3}v_r^{1/3} - 0.5v_r}\frac{1}{v_1} \quad (29)$$
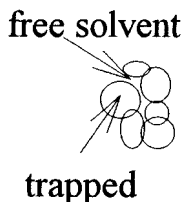
where

$$v_r = \frac{1}{Q_v} \quad (30)$$

Figure 4 Schematic drawing of a swollen sample.

$$\bar{\rho}_{eff} = \frac{m_0}{\bar{M}_c} \qquad (31)$$

According to eqs. (29–31), one can calculate the effective crosslinking density from the degree of swelling that is measured experimentally.

EXPERIMENT

Samples

Some of extracted insoluble residues from the previously researched work.[12]

Measurement of Degree of Swelling

A dry sample weighing m_g in a clean funnel of sand core weighing m_1 was immersed to swell in tetrahydrofuran (THF) under constant temperature (25°C) for 72 h. After that, the funnel and the swollen gel were centrifuged and weighed (m_s). The degree of swelling was calculated by using the following equation:

$$G = \frac{m_s - m_1}{m_g} \qquad (32)$$

$$Q_v = 1 + (G - 1)\frac{d_p}{d_s} \qquad (33)$$

Determination of Centrifuge Speed

A swollen body is made of many swollen particles, for samples were made by suspension polymerization. As shown in Figure 4, the swelling agent molecules that fill the free space among the swollen particles do not contribute to swelling, and are nominated as "free solvent." To remove the free solvent, a suitable centrifuge speed must be determined, because if the speed were too low, the free solvent would not be removed completely in short

time, and if the speed were too high, the trapped solvent would be centrifuged away.

The variation of the apparent degree of swelling with centrifuge speed is shown in Figure 5. It is seen that when the centrifuge speed is <500 rpm, the apparent degree of swelling reduces dramatically with the increase of the speed, but no change is observed in the speed range of 500–3000 rpm. It shows the existence of the free solvent in the swollen body, which can be removed by centrifugation. For the present research, the centrifuge speed of 1000 rpm is considered enough to remove the free solvent in the swollen body without losing the trapped solvent.

PARAMETERS

Physical Constants Used for Calculating the Effective Crosslinking Density from the Degree of Swelling

Polymer[17]:
$$d_p = [\exp(0.4926 - 3.274 \times 10^{-4}T)] \times 10^3$$
$$(g/L) \quad (34)$$

Monomer: $m_0 = 62.5$
Swelling Agent[18]: $d_s = 889.2$ (g/L)
$$v_1 = 81.0 \quad (mL/mol)$$
Huggins Parameter for PVC-THF at 25°C:
  Averaging the values listed in Table I gives:
  $\chi = 0.24$ (25°C)
The Volume Fraction of Polymer During the Crosslinking Reaction
  The volume fraction of polymer during the crosslinking reaction can be calculated with
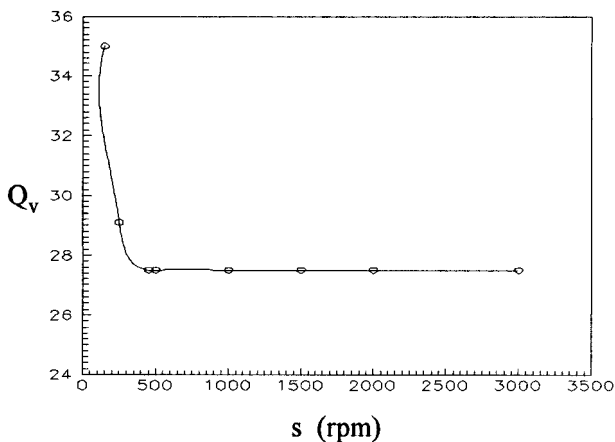

Figure 5 Ratio of swelling versus centrifuge speed.

Table I Huggins Parameter for PVC-THF (at 25°C) in the Literature

χ	Measurement Method	Reference
0.265	light scattering	19
0.21	swollen	20
0.26	osmotic pressure	20
0.22	osmotic pressure + intrinsic viscosity	21

the swelling equilibrium equation for PVC-VC:

$$\ln(1.0 - \phi_{p0}) + \phi_{p0} + \chi_1(\phi_{p0})^2 = 0 \quad (35)$$

where χ_1 is Huggin's parameter for PVC-VC, which is correlated with temperature with the following equation[17]:

$$\chi_1 = 1286.4/T - 3.02 \quad (36)$$

Model Parameters (at 50°C)[12]

$r_1 = 1.475 \qquad k_{cp} = 0.0126 \qquad k_{cs} = 0.144$

$c_2 = 0.236 \qquad g_c c_1 = 70.32 f_{20} + 0.3379 \qquad P, q$ calculated in the previous paper[12]

RESULTS AND DISCUSSION

After having measured the degree of swelling of a gel sample, one can calculate the effective crosslinking density from eqs. (29–31). On the other hand, one can predict the effective crosslinking density by combining the present model of the effective crosslinking density of the gel with the model of the gel fraction of polymer proposed in the previous paper.[12] The results are shown in Figures 6 and 7.

From the figures, it is concluded that the model prediction is in good agreement with the experimental results, i.e., the effective crosslinking density increases during the polymerization. The model prediction fits well with the experimental results with the exception at the high conversion. In the late stage of polymerization, the effective crosslinking density increases dramatically, but the model predicts it to be more constant. That
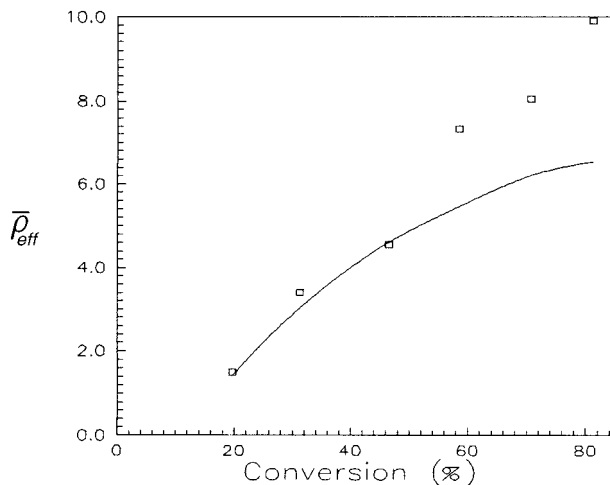

Figure 6 Development of crosslinking density with conversion $f_{20} = 8.02 \times 10^{-4}$, 50°C; □, experimental data; —, model prediction.

may be attributed to the two-phase mechanism of VC suspension polymerization.[22] In this late stage, the amount of VC monomer in the monomer phase is reduced sufficiently to make the agglomerates fuse together, as illustrated in Figure 8. Subsequently, the crosslinking reaction might be enhanced via the fusion, which was not taken into account in the present model.

According to the two-phase mechanism of VC suspension polymerization,[17] the crosslinking reaction takes place in the polymer phase where the concentration of polymer is high (up to $\sim 70\%$). It is inferred that the concentration of physical entanglements in the crosslinked product should
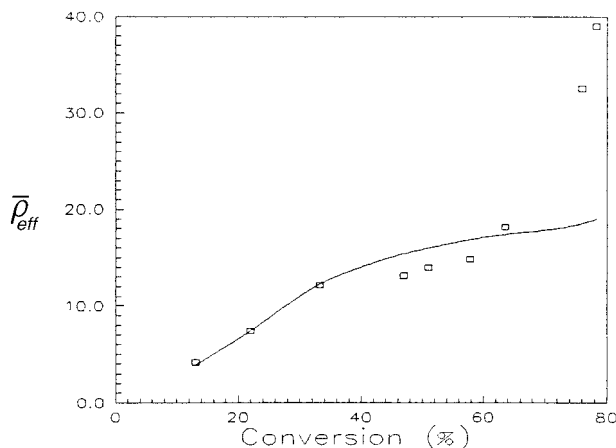

Figure 7 Development of crosslinking density with conversion $f_{20} = 1.09 \times 10^{-3}$, 50°C; □, experimental data; —, model prediction.

Figure 8 Schematic representation of the mechanism of VCM polymerization.

Figure 10 Development of crosslinking density with conversion $f_{20} = 1.98 \times 10^{-3}$, 50°C; $\square$, experimental data; —, model prediction.
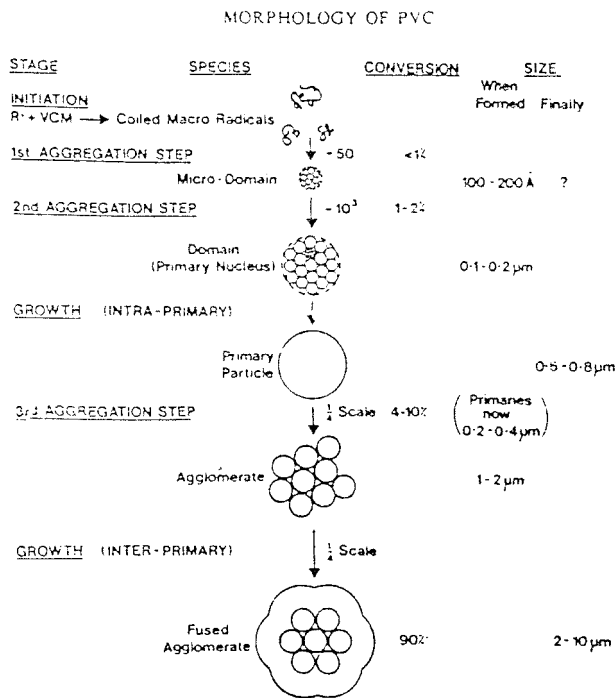
quently, the effects of physical entanglements can be ignored.

As shown in Figure 10, some interesting results are obtained when we increase the DAP concentration to reduce the length of network chains. The experimental effective crosslinking density was much larger than that of the model prediction, and the difference becomes greater during the process of polymerization. It is evident that the physical entanglements come into effect.

It is practice to correlate the degree of swelling of the gel with its total crosslinking density with the Flory-Rehner equation, where a factor was introduced by Flory to correct network imperfections resulting from chain ends. In fact, Tobita applied the method to MMA/EGMA copolymerization, and obtained a good agreement between the model prediction and experimental results.[8] However, the method did not work in the present research.[23] Instead, we extended the concept of the effective crosslinking density by Scanlan to the heterogeneously crosslinking copolymerization. The experimental points are seen to be in good agreement with the model prediction. It is worth notice that no adjustable parameters were introduced in the present model prediction, as used in Tobita's work. We infer that the concept of effective crosslinking density proposed by Scanlan is experimentally substantiated.

be very high. However, it seems to be concluded from Figures 6 and 7 that the effect of the physical entanglements on the degree of swelling could be ignored. As a matter of fact, only those so-called trapped entanglements,[10] as shown in Figure 9, are effective to the equilibrium degree of swelling. The concentration of network chains from entanglements is given by[10]:

$$v_{et} = \zeta W_g^4 \qquad (37)$$

where ζ is the effective concentration of entanglements. The higher the chemical crosslinking density, the larger ζ is. Owing to the very low chemical crosslinking density, ζ and W_g are low. Conse-
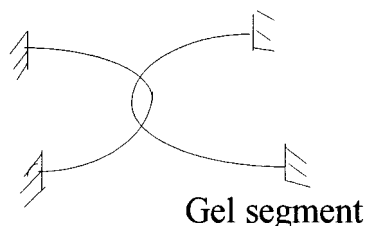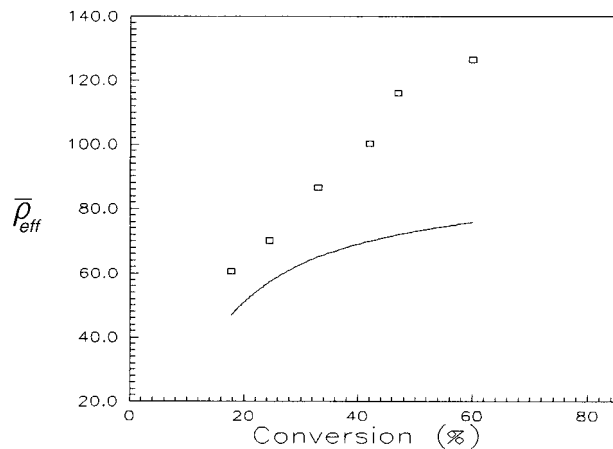

Gel segment

Figure 9 Schematic drawing of a trapped entanglement.

CONCLUSION

A model of effective crosslinking density of the gel was developed in the heterogeneously crosslink-

ing copolymerization. It is concluded that the present model of effective crosslinking density of the gel successfully predicts the development of the effective crosslinking density in the free-radical suspension crosslinking copolymerization of VC/DAP.

The degree of swelling of the gel seems to be determined by its effective crosslinking density, which was defined by Scanlan, instead of its total crosslinking density modified with a factor to correct the network imperfection from chain ends. However, when the crosslinking density is high, the physical entanglements greatly influence the degree of swelling.

NOMENCLATURE

A, B — those primary chains born at conversion α and β, respectively

$d1, d2, d3, d4$ — directions

$c1, c2$ — crosslinking units

c_1, c_2 — model parameters

d_p — density of crosslinking polymer

d_s — density of swollen agent

$\overline{DP}_{np}$ — number-average degree of polymerization of the primary chains

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 β

$F_3(\beta, \alpha)$ — molar fraction of pendent double bonds in the primary chain born at conversion β at conversion α, $\beta \leq \alpha$

$\overline{F}_3^{\text{gel}}$ — average molar fraction of pendent double bonds in the gel

g_c — model parameter

k_{cp} — rate constant of the primary intra-molecular crosslinking reactions

k_{cs} — rate constant of the second intra-molecular crosslinking reactions

k_{fm} — pseudo-constant of monomer transfer rate

k_p — pseudo-constant of propagation reaction rate

k_{p13} — rate constant of the inter-molecular crosslinking reactions

m_0 — molecular weight of the structure unit of crosslinking chains

$\overline{M}_c$ — molecular weight of the network chains

P — model parameter

$P_3(\beta, \alpha)$ — the probability by which a crosslinking unit on A that connects A and B is one of two units of the fourth kind of the crosslinking points

q — model parameter

Q_v — volume degree of swelling

r_1 — reactivity ratio

T — polymerization temperature

v_1 — molar volume of swollen agent

W_g — gel fraction

$W_g(\beta)$ — probability by which the primary chains born at β is part of the gel

$W_g(\beta, \alpha)$ — probability by which the primary chains born at β is part of the gel at α

$W_g^{\psi=\alpha}$ — gel fraction at α

$W_s(\alpha)$ — probability by which the primary chains born at α is part of the sol

$W_s(1)$ — probability by which a crosslinking point leads to a sol segment in the direction $d1$

$W_s(2)$ — probability by which a crosslinking point leads to a sol segment in the direction $d2$

$W_s(3)$ — probability by which a crosslinking point leads to a sol segment in the direction $d3$

$W_s(4)$ — probability by which a crosslinking point leads to a sol segment in the direction $d4$

x — conversion

α, β, γ — conversion, $\beta < \alpha < \gamma$

$\rho_3(\alpha)$ — the crosslinking density of the fourth crosslinking points with respect to the gel on the primary born at α

$\rho_4(\alpha)$ — the crosslinking density of the fifth crosslinking points with respect to the gel on the primary born at α

$\overline{\rho}_3$ — the average crosslinking density of the fourth crosslinking points

$\bar{\rho}_4$ — the average crosslinking density of the fifth crosslinking points

$\bar{\rho}_{eff}$ — the average effective crosslinking density

$\rho_A(\beta, \alpha)$ — the crosslinking density of the inter-molecular crosslinking points connected A and B on the primary chains A, $\beta < \alpha$

$\rho_B(\beta, \alpha)$ — the crosslinking density of the inter-molecular crosslinking points connected A and B on the primary chains B, $\beta < \alpha$

$\rho_{At}(\beta, \alpha)$ — the crosslinking density of the crosslinking points connected A and B on the primary chains A, including the inter-molecular crosslinking points and intra-molecular crosslinking points, $\beta < \alpha$

$\rho_{Bt}(\beta, \alpha)$ — the crosslinking density of the crosslinking points connected A and B on the primary chains B, including the inter-molecular crosslinking points and the second intra-molecular crosslinking points, $\beta < \alpha$

$\rho_{cp}(\beta)$ — the crosslinking density of the primary intra-molecular crosslinking points on the primary chains born at β

$\rho_{Acs}(\beta, \alpha)$ — the crosslinking density of the second intra-molecular crosslinking points connected A and B on the primary chains A, $\beta < \alpha$

$\rho_{Bcs}(\beta, \alpha)$ — the crosslinking density of the second intra-molecular crosslinking points connected A and B on the primary chains B, $\beta < \alpha$

χ — Huggins parameter for crosslinking polymer/swollen agent

χ_1 — Huggins parameter for PVC/VC

ϕ_{p0} — volume fraction of polymer when the crosslinking reactions occurred

ψ — ultimate conversion

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