Critical properties for gelation in free-radical crosslinking copolymerization

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(Received: January 16, 1995; revised manuscript of February 24, 1995)

SUMMARY:

A kinetic model was used to predict the molecular weight developments and the critical properties in free-radical crosslinking copolymerization. The predictions of the model were compared to the experimental data reported previously. Agreement of the kinetic model with experiments is satisfactory for both low and high crosslinker contents. The model parameters indicate increasing extent of shielding of pendant vinyl groups as the reaction proceeds due to the increasing number of multiple crosslinkages. The calculation results indicate that the real critical exponents can only be observed in the region $\varepsilon < 10^{-2}-10^{-3}$ where experimental studies are very difficult. Outside of this region, the apparent critical exponent γ describing the divergence of the weight-average molecular weight was found to deviate from the classical value due to the conversion dependent kinetics of free-radical crosslinking copolymerization.

Introduction

Free-radical crosslinking copolymerization (FCC) has been widely used to synthesize polymer gels having a variety of applications. Several theories have been developed in the past half century to describe gel formation in FCC. Statistical theories originate from Flory and Stockmayer and they initially assume equal reactivities of the functional groups and the absence of cyclization reactions[1–5]. However, these assumptions are unrealistic in FCC[6,7]. Although several attempts have been made to remove the above mentioned assumptions[8–10], the results are still inadequate to describe gel formation for general FCC systems. In addition, statistical theories consider the average properties over the whole reaction system, i. e., they are mean-field theories and, therefore, they cannot deal exactly with existing spatial correlations due to cyclization or excluded volume.

In FCC, the concentration of reactive species in the microenvironment of a radical center changes throughout the course of the reaction. Therefore, the formation of bonds building the infinite network can be described using differential equations with reaction time or monomer conversion as the independent variable. Compared to the statistical theories, kinetic approaches can take into account all the kinetic features of copolymerization and crosslinking reactions and so may offer a more realistic

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approach to the mechanism of the network formation process. Recently, kinetic models have been extensively used to describe the relations among the molecular weight of polymers and the conversion or reaction time during crosslinking[11-17]. In the classical kinetic theory, the rate constant is proportional to the product of the number of functional groups in each reactant. However, by modifying the classical kinetic theory, i.e., by using rate constants that also depend on the structural features of the reactants, one may get reasonable approximations for the effect of spatial correlations. Thus, although kinetic theories belong to the mean-field category, they may account for spatial correlations if the rate constants are defined properly[18].

Another type of theories called non-mean-field theories such as the percolation theory bases on simulation in n-dimensional space[19-21]. The percolation theory can take spatial correlations into account but at present the result of this theory is unrealistic due to the difficulty of introduction of realistic mobilities. The main domain of application of percolation techniques to polymer networks seems to be near the sol-gel transition called the critical region in which the system-specific parameters are not important. For this region, percolation theory predicts exponents different from those predicted by the mean-field theories[20]. To answer the question which theory agrees with reality, experimental data in the critical region are necessary. However, since the width of this region is presently unknown, this question is open and should be explored[22]. Furthermore, as was recently shown by Dotson et al.[23], conversion-dependent kinetics in free-radical crosslinking copolymerization may also cause deviations from the mean-field exponents.

To contribute to the solution of this problem, we used a kinetic model for several FCC systems to calculate the critical exponent γ describing the divergence of the weight-average molecular weight $\overline{M}_w$. According to the mean-field theories, γ is equal to 1, whereas the percolation theory gives $\gamma = 1.7$. Although the model used in the present study considers non-idealities such as cyclization and substitution effect, it belongs to the mean-field category and therefore yields the classical value $\gamma = 1$ in the critical region. However as will be seen below, the non-classical exponents observed by experiments can also be predicted by the model due to the kinetics of FCC. The model has allowed us to observe the effect of conversion-dependent kinetics on the apparent value of the critical exponent γ in FCC.

Kinetic model

FCC of vinyl/divinyl monomers involves three types of vinyl groups; those on vinyl and divinyl monomers and those on polymer chains, i.e., pendant vinyls. The pendant vinyl groups are consumed by cyclization, crosslinking, or multiple crosslinking reactions, or remain pendant. A cycle is formed when a macroradical attacks the pendant vinyl groups in the same kinetic chain, while multiple crosslinkages are formed if the radical attacks double bonds pendant on other chains already chemically connected with the growing radical (Fig. 1). Thus, the divinyl monomer can be found in the polymer as units bearing pendant vinyl groups, cycles, crosslinks or multiple crosslinks. A schematic representation of the polymerization system prior to gelation is shown in Fig. 2. The consumption of pendant vinyl groups by other macroradicals,

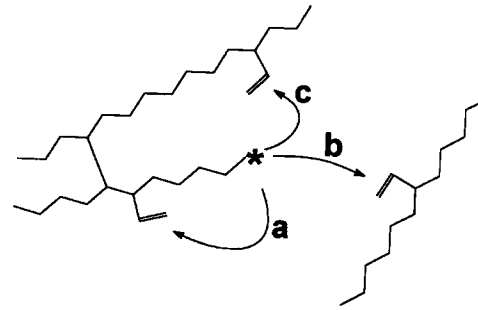

Fig. 1. Schematic picture of cyclization (a), crosslinking (b), and multiple crosslinking (c) in free-radical crosslinking copolymerization

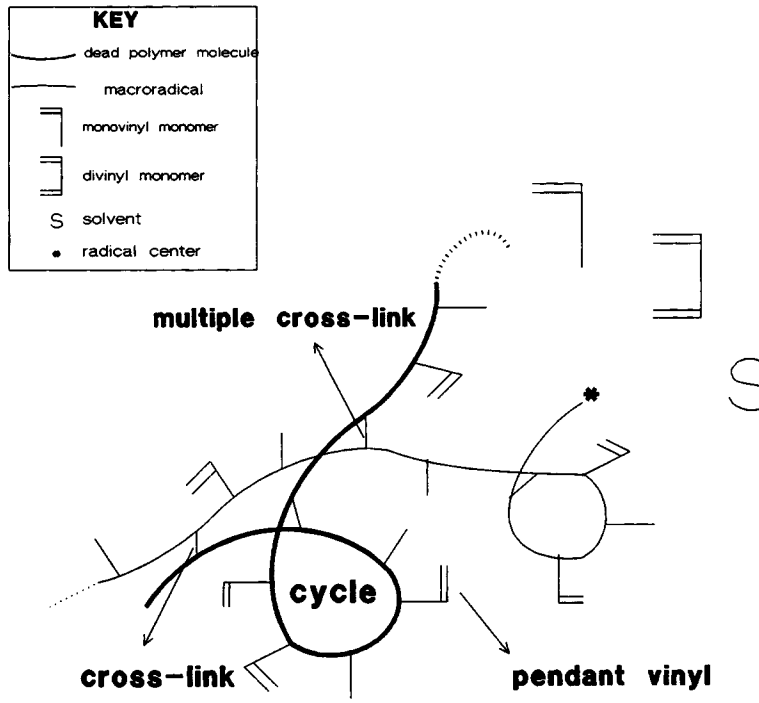

Fig. 2. Schematic representation of the pre-gelation period in free-radical crosslinking copolymerization

namely the crosslinking reactions, is only responsible for gelation while cyclization and multiple crosslinking reactions do not change the degree of polymerization of the macroradicals.

Let k_{cyc} be the fraction of pendant vinyls in cycles at zero conversion and k_{mc} be the average number of multiple crosslinkages per crosslink, then, based on the kinetic

equations given previously[11–17], the following rate equation for the weight-average molecular weight $\bar{M}_w$ can be written

$$\frac{d(x\bar{M}_w)}{dx} = \bar{M}_w^{\bullet}\left[1 + \frac{r_{21}\bar{r}_{32}(1 - x_3)\bar{F}_2}{1 + (2r_{21} - 1)f_2}\left(\frac{x}{1 - x}\right)\frac{\bar{M}_w}{\bar{M}_u}\right]^2 \qquad \begin{array}{l}\bar{M}_w(0) = M_{w,0}^{\bullet} \\ \bar{M}_w(x_c) = \infty\end{array} \tag{1}$$

where $\bar{M}_w^{\bullet}$ is the weight-average molecular weight of the primary chains, $\bar{M}_u$ is the average molecular weight of the repeating unit, r_{21} is the reactivity ratio of vinyls on divinyl to monovinyl monomers, $\bar{r}_{32}$ is the reactivity ratio of pendant vinyl to monomeric vinyl on divinyl monomer, f_2 and $\bar{F}_2$ are the accumulated mole fractions of divinyl monomer in the reaction mixture and in the copolymer, respectively, x is the monomer conversion, x_c the critical conversion at the gel point, and x_3 is the pendant vinyl conversion. The mole fraction of divinyl monomer in the reaction mixture f_2 can be calculated from its initial mole fraction using the Skeist equation[24]. The rate equation for the pendant conversion is given by

$$\frac{dx_3}{dx} = \frac{r_{21}}{1 + (2r_{21} - 1)f_2}\left[\frac{\bar{r}'_{32}(1 - x_3)}{(1 - x)} - \frac{2f_2}{\bar{F}_2}\frac{x_3 - k_{cyc}}{x}\right] \qquad x_3(0) = k_{cyc} \tag{2}$$

where $\bar{r}'_{32}$ is the apparent reactivity ratio of pendant to monomeric vinyl and is related to the actual reactivity ratio through the equation:

$$\bar{r}'_{32} = \bar{r}_{32}(1 + k_{mc}) \tag{3}$$

Note that the derivation of the equations given above makes the following assumptions: (1) steady-state approximation for the radical species; the reactivities are independent of the type of the radical end, (2) every polymer radical possesses only one radical center, (3) the mole fraction of pendant vinyl groups is independent of chain length of the polymer molecules, and (4) chain transfer reactions do not occur.

Previous kinetic models assume that the multiple crosslinking reactions occur at constant rates, i.e., k_{mc} remains constant during the reaction. However, since multiple crosslinking is a second-order reaction, one may expect that k_{mc} is zero at zero monomer conversion and it increases as the reaction proceeds because multiple crosslinking becomes the more probable the greater the molecules formed. Indeed, a percolation model proposed recently by Anseth and Bowman also indicates this trend[25]. Furthermore, increasing number of multiple crosslinkages during the reaction would lead, at high crosslinker contents, to the formation of microgel-like particles with internal "frozen" pendant vinyl groups[26]; thus, the average reactivity of pendant vinyls should decrease as the reaction proceeds due to the increasing extent of shielding of pendant vinyl groups. Accordingly, increase in k_{mc} would lead to a decrease of the pendant reactivity represented by $\bar{r}_{32}$. In order to account for decreasing pendant reactivity and increasing rate of multiple crosslinking reactions during the polymerization, $\bar{r}_{32}$ may be represented empirically by the equation

$$\bar{r}_{32} = \bar{r}_{32}^{0}\exp(-ax) \tag{4}$$

where $\bar{r}_{32}^{0}$ is the reactivity ratio of pendant to monomeric vinyl at zero monomer conversion and a is an adjustable parameter.

In order to evaluate the weight-average molecular weight of the pre-gel polymers as a function of monomer conversion, the simultaneous differential equations (1) and (2) were solved numerically using the Runge-Kutta method. The calculations were carried out for several vinyl/divinyl monomer systems as well as for polymerization systems involving the divinyl monomer only. To apply the model to actual systems, six parameters (r_{21}, k_{mc}, k_{cyc}, $\bar{M}_w^{\bullet}(x)$, $\bar{r}_{32}^{0}$ and a) must be known, or the model parameters can be extracted from the experimental data as follows: First, using the experimental pendant vinyl group conversion (x_3) versus monomer conversion (x) data, Eq. (2) may be solved for the parameters k_{cyc} and $\bar{r}_{32}'$. Second, simultaneous solution of the model equations to fit the experimental weight-average molecular weight $\bar{M}_w$ data and for the condition $\bar{M}_w(x_c) = \infty$ yields the parameters $\bar{r}_{32}^{0}$ and a. The drift in the primary chain length is included into the calculations by fitting the experimental time-conversion data[27]. The weight-average molecular weights at zero monomer conversion may be obtained from the $x = 0$ intercept in the experimental $\bar{M}_w$ versus x plots. The parameter r_{21} necessary for the calculations can be found in the literature for various comonomer systems.

Results and discussion

Systems with low crosslinker content

Figs. 3 and 4 show the variation of the weight-average molecular weight of polymers $\bar{M}_w$ with the monomer conversion x in crosslinking copolymerization of styrene with

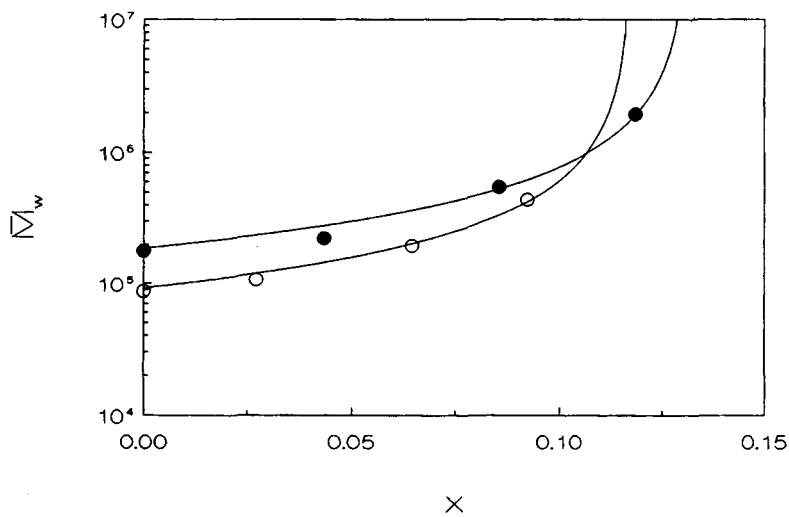

Fig. 3. $\bar{M}_w$ versus x plots in the free-radical crosslinking copolymerization (FCC) of styrene with ethylene dimethacrylate. Experimental data points are from Vijayakumar and Fink[29]. $f_{20} = 0.005$ (●) and 0.010 (○). The curves were calculated using the kinetic model with the parameters listed in Tab. 1

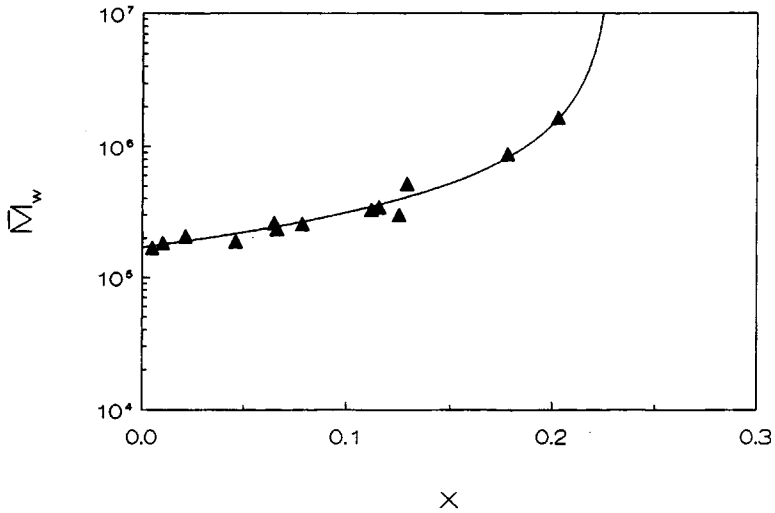

Fig. 4. $\overline{M}_w$ versus x plots in FCC of styrene with 1,3-divinylbenzene (1,3-DVB). Experimental data points are from Fink[28]. $f_{20} = 0.006$. The curve was calculated using the kinetic model with the parameters listed in Tab. 1

ethylene glycol dimethacrylate (EGDM; system. name: ethylene dimethacrylate) and 1,3-divinylbenzene (1,3-DVB) as crosslinker, respectively. The experimental data were taken from Fink et al.[28,29] and they are shown as symbols. The curves were calculated using the kinetic model and with the parameters listed in Tab. 1. The agreement between the model calculations and the experimental data is good. The model predicts every trend observed by experiments. Tha parameters given in Tab. 1 indicate that both cyclization and multiple crosslinking reactions are not significant for these systems, probably due to the low concentration of the divinyl monomers used. Moreover, 2- to 7-fold decrease in the reactivity of pendant vinyls compared to the monomeric vinyls is seen from the r_{32} values listed in Tab. 1. In Fig. 5, the weight-average molecular weight of pre-gel polymers $\overline{M}_w$ is plotted as a function of the dimensionless distance to the gel point ε, defined as $\varepsilon = 1 - x/x_c$. The curves were calculated using the kinetic model. The results are described by the law

$$\overline{M}_w \sim \varepsilon^{-\gamma} \tag{5}$$

where not too far from the gel point i.e. in the critical region, γ is called a critical exponent. The apparent value of the exponent $\gamma = 1.1$ found by experiments for the region $\varepsilon = 1$ to 0.1 is rather close to that predicted by both the kinetic model and the statistical theory, $\gamma = 1$. Thus, we can conclude that the polymerization systems studied by Fink et al. can be described by mean-field models at least up to the region $\varepsilon = 0.1$.

Tab. 1. Initial conditions and kinetic parameters for the free-radical crosslinking copolymerization of styrene with various crosslinkers[a)]

$c/(g \cdot dL^{-1})$	Crosslinker	f_{20}	$10^{-6} \times \bar{M}_w^{\bullet}$	x_c	r_{21}	$\bar{r}_{32}^{0}$	a	k_{cyc}	$\bar{r}'_{32}$
bulk	1,3-DVB	6×10^{-3}	0.18[28)] [b)]	0.23[c)]	1.28[28)]	0.15	0	0[28)]	1.2[28)]
bulk	EGDM	5×10^{-3}	0.19[29)] [b)]	0.13[c)]	1.11[30)]	0.35	0	0[29)]	0.35[30)]
bulk	EGDM	10×10^{-3}	0.09[29)]	0.12[c)]	1.11[30)]	0.40	0	0[29)]	0.4[30)]
5	1,4-DVB	1.00	0.11[27)] [d)]	0.43[27)]	—	0.01	2	0.30[27)]	0.9[27)]
2	1,4-DVB	1.00	0.03[27)]	0.56[27)]	—	0.07	5.4	0.28[27)]	1.6[27)]
0.5	1,4-DVB	1.00	0.02[27)]	0.79[27)]	—	0.07	4.5	0.63[27)]	0.5[27)]

a) c = Initial monomer concentration; f_{20} = initial mole fraction of the vinyl groups contributed by the crosslinker; $\bar{M}_w^{\bullet}(x)$ = weight-average molecular weight of the primary chains; x_c = critical monomer conversion at the gel point. The reactivity ratios r_{21}, $\bar{r}_{32}^{0}$ and $\bar{r}'_{32}$, and the parameters k_{cyc} and a are explained in the text. Reference numbers are given. Please note that the 1,4-DVB homopolymers prepared at c = 5 and 0.5 g/dL correspond to the polymers given in series II of Tab. II in ref.[27)] The homopolymer with c = 2 g/dL was reported in ref.[27)] as a series III polymer with an initiator concentration of 2.6×10^{-3} mol/L.

b) $\bar{M}_w^{\bullet}$ was assumed to be constant in the pre-gel regime.

c) x_c was estimated from the experimental molecular weight data of Fink et al.[28, 29)]

d) Variation of $\bar{M}_w^{\bullet}$ with conversion is taken into account as given in ref.[27)] The values shown in the table are the weight-average molecular weights at zero monomer conversion. In ref.[27)], these values were evaluated from the $\varepsilon = 1$ intercept in the linear $\log \bar{M}_w$ vs. ε regression lines. However, in the present study, since we take into account conversion-dependent reactivity of pendant vinyls, $\log \bar{M}_w$ vs. ε plots become nonlinear. Therefore, initial molecular weights were evaluated here by extrapolating $\bar{M}_w$ versus x plots to zero monomer conversion.

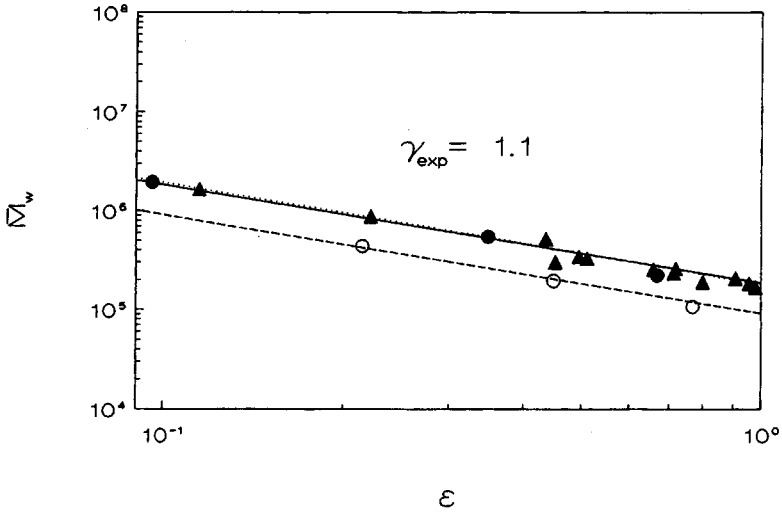

Fig. 5. Weight-average molecular weight of the pre-gel polymers $\overline{M}_w$ shown as a function of the dimensionless distance to the gel point ε in FCC of styrene with ethylene dimethacrylate and 1,3-DVB as crosslinker. Curves were calculated using the kinetic model (γ = 1.0). Crosslinker: 1) ethylene dimethacrylate; f_{20} = 0.005 (●) and 0.010 (○); 2) 1,3-DVB; f_{20} = 0.006 (▲)

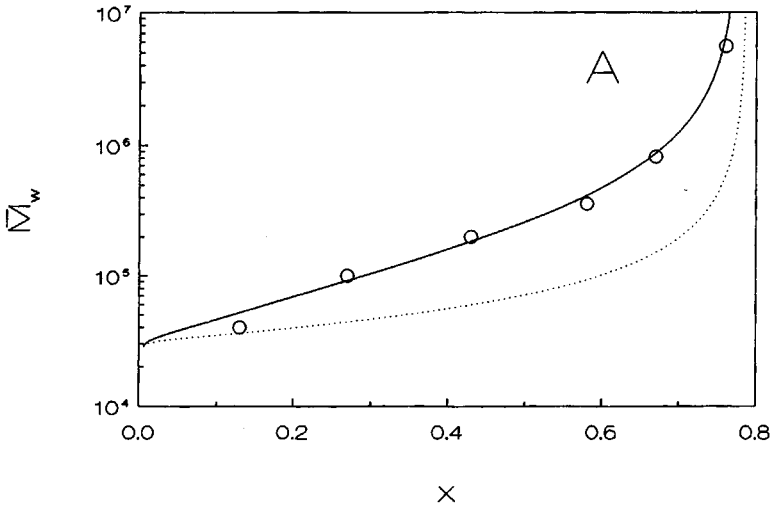

Fig. 6. A.

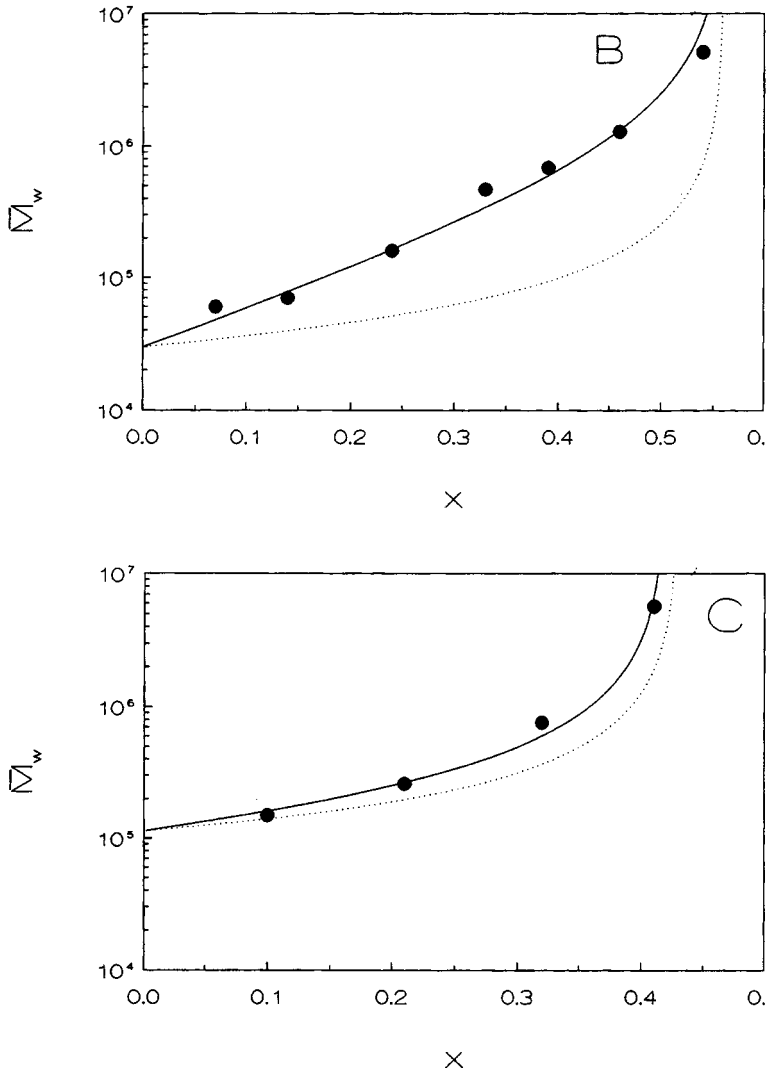

Fig. 6. Variation of $\overline{M}_w$ with the monomer conversion x in FCC of 1,4-DVB at an initial monomer concentration of 0.5 (A), 2 (B), and 5 g/dL (C). Experimental data points are from Okay et al.[27] The curves were calculated using the kinetic model for $a = 0$ (dotted curves) and $a \neq 0$ (solid curves)

Systems with higher crosslinker content

In this section the model predictions are compared to the experimental data obtained in an extremely non-ideal system, namely in the polymerization of pure 1,4-DVB in highly dilute solutions. The experimental data were taken from Okay et al.[27] Under

these reaction conditions, one may expect extensive cyclization and multiple crosslinking reactions which may lead to the formation of microgels as intermediates of macrogelation. Indeed, the values of the parameters k_{cyc} and $\bar{r}'_{32}$ calculated using the pendant conversion data[27] and also shown in Tab. 1 indicate this trend.

Fig. 6A–C show the variation of $\bar{M}_w$ with the monomer conversion x at different reaction conditions. The dotted curves were calculated using the kinetic model and for $a = 0$. Thus, it was assumed that, as in the previous section and in ref.[27], $\bar{r}_{32}$ and k_{mc} remain constant during the reaction. In contrast to the low-crosslinked systems, there is a large discrepancy between the experiment and the kinetic model for $a = 0$. The weight-average molecular weight of the polymers increases much more rapidly than predicted by the model. Similar deviations between the predicted behavior for $a = 0$ (dotted curves) and experiment indicate that these deviations are real and can be attributed to the inconsistency of the model assumptions in such highly crosslinked systems. The solid curves in Fig. 6A–C were calculated for $a \neq 0$, i.e., by taking into account the increase in the number of multiple crosslinkages and the resulting decrease of the pendant vinyl group reactivity during the reaction. The parameters used in the calculations are collected in Tab. 1. One can see that the calculation results provide good agreement with the experimental data. The results indicate that both dilution and high crosslinker content significantly increase the long-range correlations within the molecules which is reflected in the values of k_{cyc} shown in Tab. 1. According to the k_{cyc} values, 30 to 60% of the pendant vinyl groups are consumed by cyclization reactions. Fig. 7 shows the variation of r_{32} and k_{mc} with the monomer conversion for the reaction

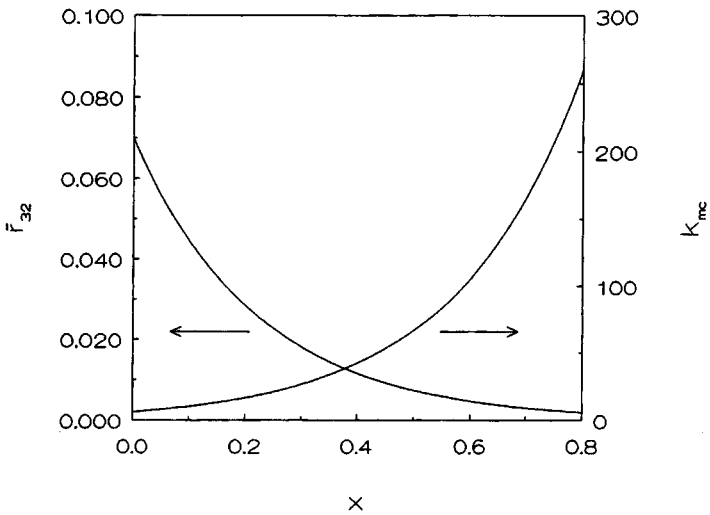

Fig. 7. Pendant reactivity $\bar{r}_{32}$ and the average number of multiple crosslinkages per crosslink k_{mc} shown as a function of the monomer conversion x in FCC of 1,4-DVB at a monomer concentration of 0.5 g/dL

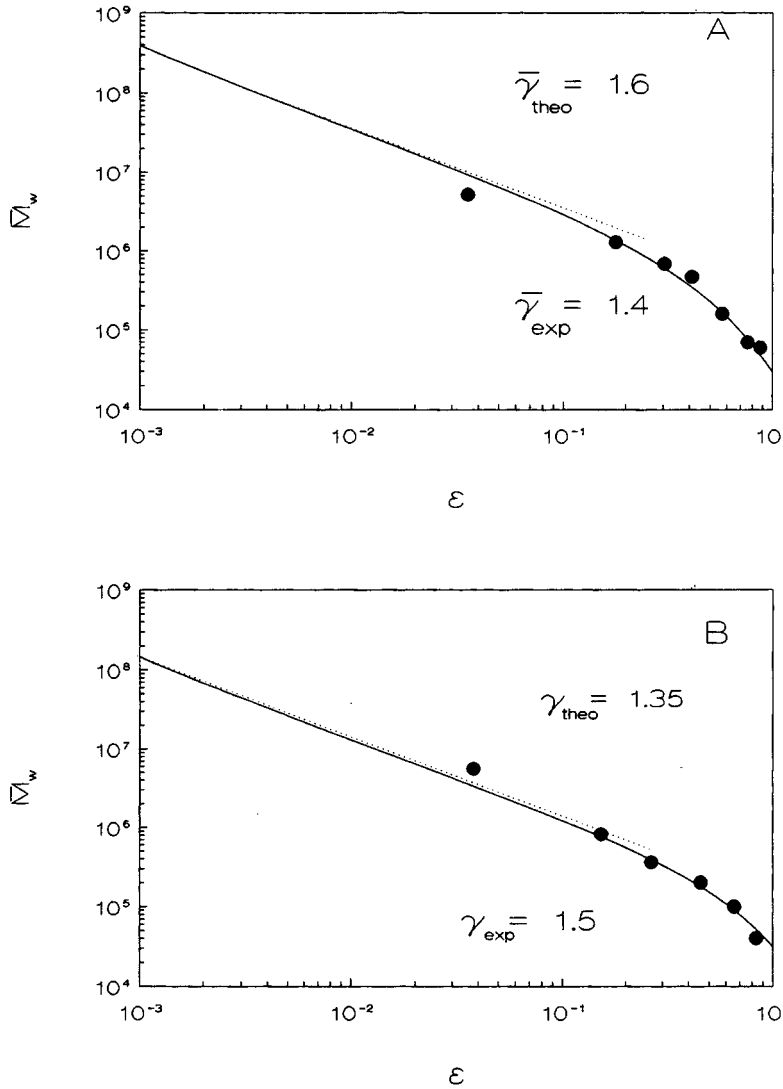

Fig. 8. $\bar{M}_w$ versus ε plots in crosslinking polymerization of 1,4-DVB. Initial monomer concentration = 2 (A) and 0.5 g/dL (B). Experimental data points are from Okay et al.[27] The solid curves were calculated using the model. The dotted lines represent the real mean-field behaviour. The critical exponent $\bar{\gamma}_{theo}$ was calculated in the range $\varepsilon = 1 - 1 \times 10^{-3}$

system in Fig. 6A. It seems that, in such highly crosslinked systems, both the pendant reactivity and the number of multiple crosslinks are functions of the monomer conversion. Thus, the polymers formed in the pre-gel regime should exhibit highly intramolecular crosslinked structures; vinyl groups in such molecules are less reactive

than those on monomers and their reactivity decreases further as the polymerization proceeds due to the increasing extent of shielding of the pendant vinyls.

The variations of $\bar{M}_w$ with the distance to the gel point ε are shown in Fig. 8A and B. The experimental data are shown as symbols. The solid curves were calculated using the kinetic model. The values of the apparent exponent $\bar{\gamma}$ (slope of the linear regression line $\bar{M}_w$ versus x) observed and calculated are also shown in the figures. It can be seen that the divergence of the molecular weight can be described well using the model. Note that in ref.[27] we neglected the conversion dependence of the pendant reactivity (i.e., $a = 0$) and the critical exponent γ calculated using the kinetic model were between 0.8 – 1.0 depending on the reaction conditions. Thus, this discrepancy is now removed after taking into account the increasing extent of shielding of pendant vinyls due to the increasing number of multiple crosslinkages as the reaction proceeds. Another important point shown in the figures is that the variation of $\bar{M}_w$ with ε is not linear; $\bar{M}_w$ increases first rapidly due to the relatively high reactivity of pendant vinyls but later on, it increases less rapidly due to the decreased pendant reactivity with increasing conversion. The experimental critical exponents of $\bar{M}_w$ lie between the predictions of the mean-field and percolation theories. At first sight, this result may indicate deviation from the gelation theories. However, the kinetic model, which is a mean-field theory, also predicts an apparent critical exponent between 1.4 and 1.6. According to the model, the real mean-field exponent can only be found for these FCC systems in the region $\varepsilon < 10^{-2}$, where experimental studies are very difficult. Thus, an apparent critical exponent γ close to 1.7 does not necessarily mean that the mean-field theory is wrong. Conversion-dependent kinetics may also be responsible for the observed deviation from the mean-field value. Fig. 9 shows two examples for such deviations.

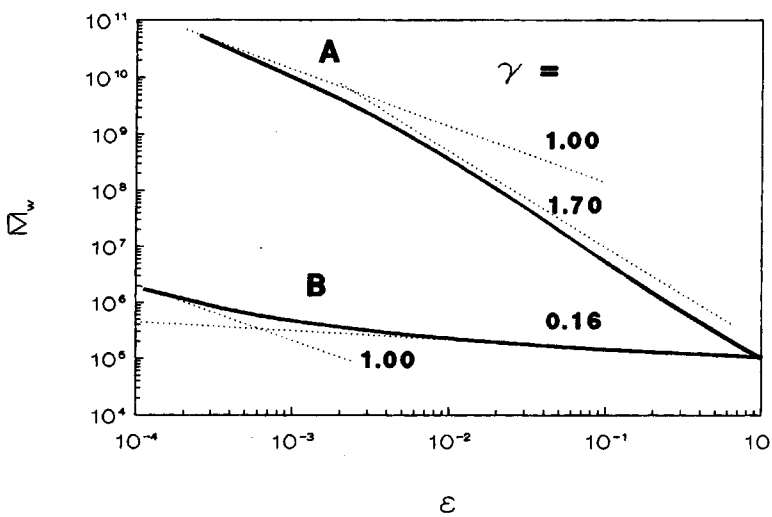

Fig. 9. $\bar{M}_w$ versus ε plots for two polymerization mixtures with $x_c = 1$ and $\bar{M}^{\bullet}_{w,0} = 100000$ g/mol. Curve A: Equal vinyl group reactivity and no cyclization, $f_{20} = 0.001$. Curve B: $f_{20} = 0.020$; $\bar{r}_{32} = 1/55$ and constant

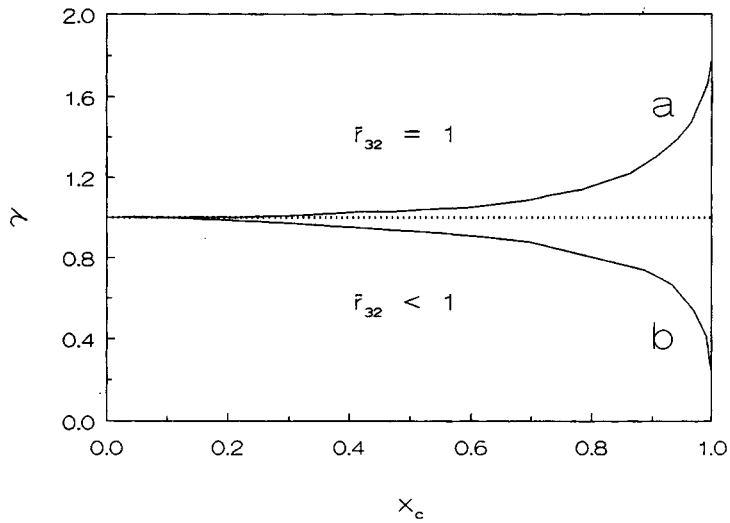

Fig. 10. Variation of γ with x_c for polymerization systems without (a) and with (b) substitution effect. γ was calculated in the range $\varepsilon = 1 - 1 \times 10^{-3}$. The drift in the primary chain length due to the monomer depletion was taken into account. Curve a: $r_{21} = \bar{r}_{32} = \bar{r}'_{32} = 1$, x_c was changed by varying the parameters $\bar{M}^{\bullet}_{w,0}$, k_{cyc} or f_{20} (the curve only depends on the value of x_c). Curve b: $f_{20} = 0.020$, $\bar{M}^{\bullet}_{w,0} = 100000$ g/mol, $r_{21} = 1$, $k_{cyc} = 0$, $a = 0$, $k_{mc} = 0$, x_c was changed by changing the parameter $\bar{r}_{32}$

Here, $\bar{M}_w$ versus ε plots are shown for two polymerization systems gelling at complete conversion ($x_c = 1.0$). Curve A was calculated for a hypothetical system with equal vinyl group reactivity and no cyclization. Thus, the assumptions of the classical theory hold except the primary chain length changes due to the monomer depletion. Curve B was calculated for a system with reduced but conversion-independent pendant reactivity. It seems that the mean-field value for γ can only be observed in the region $\varepsilon < 10^{-2} - 10^{-3}$. In the conversion region where most of the experiments were performed up to now, large deviations can be seen from mean-field value. Drift in the primary chain length shifts the apparent exponent γ towards higher values. This effect was also pointed out previously by Dotson et al.[23] and curve A is essentially the same as the curve in Fig. 1 of ref.[23] On the other hand, the reduced reactivity of pendant vinyls causes the formation of almost linear polymer chains in the pre-gel period, which is reflected from the very low value of the apparent exponent (curve B). Fig. 10 shows the variation of γ with the critical conversion x_c; positive or negative deviations are seen for late gelling systems depending on the extent of the substitution effect. In Fig. 11, $\bar{M}_w$ versus ε is plotted for a system with parameters found usually in FCC. The average slope 1.64 calculated in the range $\varepsilon = 1 - 1.17 \times 10^{-3}$ is the mean-field value for this system.

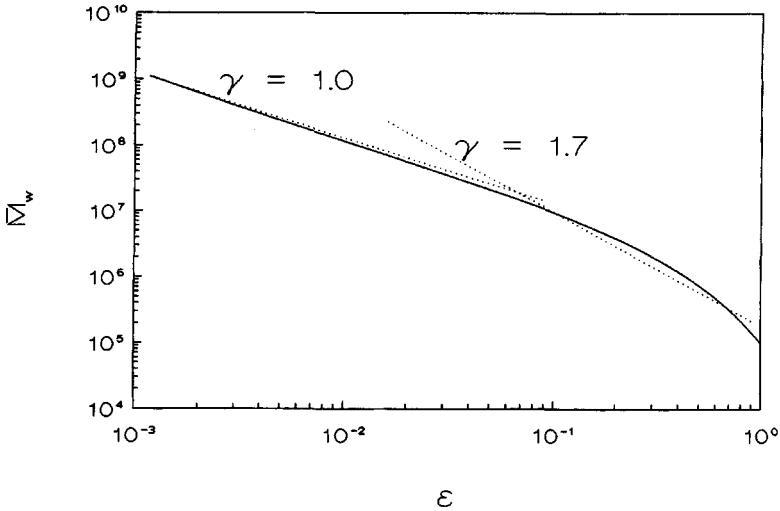

Fig. 11. $\overline{M}_w$ versus ε plot for a system gelling at $x_c = 0.43$. Parameters used in the calculations are: $r_{21} = \bar{r}^0_{32} = \bar{r}'_{32} = 1$; $k_{cyc} = 0.25$; $a = 5.4$; $f_{20} = 0.0061$; $\overline{M}^*_{w,0} = 100000$ g/mol. Molecular weight of the vinyl and divinyl monomers = 100 and 200 g/mol, respectively

Conclusions

In this paper we reexamined the molecular weight developments in free-radical crosslinking copolymerization. A kinetic model that considers all the non-idealities of free-radical crosslinking copolymerizations was used for this purpose. The predictions of the model were compared to the experimental data reported previously. The inappropriateness of the classical exponent γ especially at higher crosslinker concentrations is pointed out. This is due to the conversion-dependent kinetics and not due to the mean-field nature of the classical theory. Agreement of the kinetic theory with experiments is satisfactory both for low and high crosslinker contents. Deviations are within experimental uncertainties. The results are indicative of an increasing extent of shielding of pendant vinyls due to the increasing number of multiple crosslinkages as the reaction proceeds. Although the overall trends found in our model are in agreement with experimental results on gelation of vinyl/divinyl monomer copolymerization, the model cannot take into account spatial correlations and therefore is approximate in the region below $\varepsilon = 10^{-2}$.

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