Kinetic modelling of network formation in styrene–butadiene emulsion copolymers: a comparative study with the generalized form of Flory's theory of gelation

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A theoretical model is proposed for the distribution of molecular weight, branching and crosslinking in styrene–butadiene emulsion copolymers. The main objective is to compute the instantaneous distributions of primary macroradicals and primary dead chains with zero, one, two or more crosslinks as the reaction proceeds. The amount of gel is calculated on the assumption that each chain with at least two (or three) crosslinks is withdrawn from the sol fraction. The network thus formed is characterized by its crosslink density and number average length of the primary chains. This model has been compared with a mean field theory of network formation derived recently by Hamielec *et al.* Both models were used to predict the extent of gel *versus* conversion and the crosslink density of the gel polymer, differentiating between elastically active and inactive crosslinking points. The same value of the adjustable parameter (i.e. reactivity ratio of the butadiene pendent double bond) can be used in the two models to account for gel formation with fairly good accuracy.

(Keywords: emulsion polymers; styrene–butadiene; gel formation; crosslinks density; kinetic modelling)

INTRODUCTION

Polymer gels obtained by radical copolymerization of mixtures of monovinyl and divinyl monomers are gaining increasing importance in industry through the development of membranes, superabsorbent materials and macroreticular resins, and also diene rubber technology.

End-use properties of these polymer gels are, of course, closely related to their network structure. The building of polymer networks in the course of polymerization has been studied using models which are derived mainly from the original theory of Flory–Stockmayer[1,2] and from similar statistical theories[3,4]. Other authors[5] applied a typical scheme of radical copolymerization kinetics and used the method of molecular weight moments to calculate the gel point and average number of crosslinks per polymer chain; however, it could not estimate the amount of crosslinked polymer and the molecular weight distribution of the sol and gel fractions.

On the other hand, the classic gelation theory gives a full description of the system, provided the drift in crosslinking density during polymerization is small; in other words the number of crosslinks per monomer unit is assumed to be the same for all the primary chains. This assumption is quite unrealistic in high conversion polymerization carried out most often on an industrial scale. Hamielec *et al.*[6,7] recently proposed a generalized form of Flory's theory in which they introduced the concept of 'birth conversion' to better describe the crosslinking distribution of primary chains.

This paper deals with a totally different approach based on the instantaneous primary chain distributions; thus, the primary chain length distribution functions are derived for linear chains and primary chains having one, two, three or more crosslinked units. The key assumption to estimate the amount of polymer gel is that each chain with a number of crosslinking points greater than a given critical number ($\geqslant 2$) is considered as insoluble material. In Flory's mean-field theory, the gel point corresponds to the formation of an infinite network. Our model should give an accurate description of what happens before the so-called gel point, namely the formation of highly branched chains of finite sizes.

Our model is illustrated by the semi-continuous emulsion polymerization of styrene and butadiene.

Experimental data are compared with theoretical predictions from the instantaneous distribution model (ID model) and from the generalized form of Flory's theory derived by Hamielec *et al.*

EXPERIMENTAL

Styrene–butadiene copolymers were prepared by emulsion polymerization in a 25 l stainless steel pressure reactor in a semi-continuous mode, either seeded or unseeded, using sodium lauryl sulphate as emulsifier and ammonium persulphate as initiator. The reaction temperature was 75°C. The monomer feed composition ranged from styrene–butadiene 62–38 to 75–25 (wt%). Tertiary dodecyl mercaptan (TDM), supplied by Phillips Petroleum (Belgium), was used as a transfer agent. Conversion was measured gravimetrically. Particle size was centred around 150 nm and monodispersity was

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fairly good. In some cases where copolymer composition was needed, copolymer samples were analysed by ^{13}C n.m.r. and Fourier transform i.r. spectroscopy.

The gel fraction of the copolymers was obtained by chloroform extraction in a Soxhlet and expressed as the ratio m_e/m_0, where m_0 is the initial weight of the polymer sample and m_e the weight of dried, unextracted material (gel). The swelling ratio was given by:

$$\mathrm{Ig} = (m_{eg} - m_e)/m_e$$

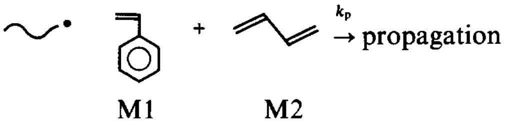
where m_{eg} is the weight of the swollen gel. The polymer volume fraction, v_2, in the swollen gel at equilibrium is computed as:

$$v_2 = \frac{1}{(\mathrm{Ig}/1.478 + 1)}$$

where 1.478 is the density of chloroform.

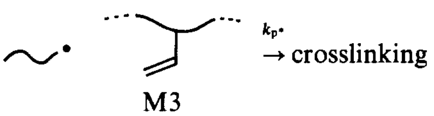
Kinetic modelling

In a vinyl–divinyl copolymerization, the main steps involved in the reaction scheme are:

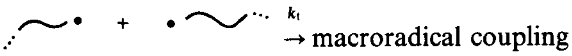


$$R_p = k_p[\mathrm{M}][\mathrm{R}^0] \tag{1}$$

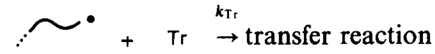
where [M] is monomer concentration and $[\mathrm{R}^0]$ is radical concentration.



$$R_p^* = k_p^*[\mathrm{M3}][\mathrm{R}^0] \tag{2}$$



$$R_{tc} = k_t[\mathrm{R}^0]^2 \tag{3}$$



$$R_t = k_{Tr}[\mathrm{Tr}][\mathrm{R}^0] \tag{4}$$

where [Tr] is the concentration of the chain transfer agent.

In equation (2) [M3] is the concentration of pendent vinyl groups resulting from 1,2 addition on butadiene. The double bonds in the main chain (1,4 addition) are assumed to be unreactive towards crosslinking reactions.

This kinetic scheme is equivalent to a terpolymerization system in which M1, M2 and M3 stand, respectively, for the monovinyl monomer, the divinyl monomer and the pendent double bond. The terms k_p, k_p^*, k_t and k_{Tr} are the apparent rate constants which make the mathematical treatment much easier since multicomponent polymerization reduces to homopolymerization (formally these apparent rate constants are equivalent to the pseudo-kinetic rate constants in the formalism of Hamielec *et al.*[8]). The pseudo-kinetic rate constants are related to the elementary kinetic rate constants by:

$$k_p = \sum_{i=1}^{n} \sum_{j=1}^{n} k_{p_{ij}} F_j R_i \tag{5}$$

$$k_t = \sum_{i=1}^{n} \sum_{j=1}^{n} k_{tij} R_i R_j \tag{6}$$

$$k_{Tr} = \sum_{i=1}^{n} \sum_{j=1}^{n} k_{Tr_{ij}} R_i S_j \tag{7}$$

where F_j is the mole fraction of monomer j, R_i is the mole fraction of polymer radical of type i and S_j is the mole fraction of chain transfer of type j. The term k_p^*/k_p characterizes the reactivity of the pendent vinyl group.

Computation of primary chain distribution

The objective is to compute the amount and distribution of primary chains with zero, one, two, three or more crosslinked units, as the reaction proceeds. Primary macroradical distributions are readily obtained using conditional probability P_i, P_{aa} and P_{ab} which represent the probability for a macroradical, respectively, to terminate, to propagate or to add onto a pendent double bond:

$$P_i = \frac{(R_t + R_{tc})}{(R_t + R_{tc} + R_p + R_p^*)} \tag{8}$$

$$P_{aa} = \frac{R_p}{(R_t + R_{tc} + R_p + R_p^*)} \tag{9}$$

$$P_{ab} = \frac{R_p^*}{(R_t + R_{tc} + R_p + R_p^*)} \tag{10}$$

The calculation, whose details have been published elsewhere[9], leads to the distribution function $N(n, m)$ of macroradicals of length n with m crosslinked units:

$$N(n, m) = \left(\frac{n^m}{m!}\right) P_{ab}^m P_{aa}^n P_i \tag{11}$$

In order to obtain the distribution of the deactivated primary chains, the termination reaction must be taken into account. As macroradical coupling occurs, primary chains crosslinked twice may result from the deactivation of a macroradical with $m = 2$ by a transfer reaction or by coupling of radicals with $m = 1$ (*Figure 1*).

For any values of m, $N_p(n, m)$, the number of primary chains of length n can be written as:

$$N_p(n, m) = \left(\frac{1}{\tau + \beta/2}\right) \times \left[\tau N(n, m) + \beta/2 \sum_{s=0}^{n} \sum_{r=1}^{m} N(n - s, m - r) N(s, r)\right] \tag{12}$$

where τ and β have the same meaning as in reference 8 (i.e. $\tau = R_t/R_p$, $\beta = R_{tc}/R_p$).

An example of the calculation is shown for $N_p(n, 2)$:

$$N_p(n, 2) = \left(\frac{1}{\tau + \beta/2}\right)\Bigg\{\tau N(n, 2) + \beta/2\Bigg[\sum_{s=0}^{n} N(n - s, 2) N(s, 0) + N(n - s, 1) N(s, 1) + N(n - s, 0) N(s, 2)\Bigg]\Bigg\} \tag{13}$$

$$N_p(n, 2) = \left(\frac{P_i P_{ab}^2}{\tau + \beta/2}\right)\left(\tau n^2 + \frac{\beta}{2} P_i \frac{n^3}{6}\right) \tag{14}$$

Extending the calculation to any value of m, we found an analytical expression for the primary chain distribu-

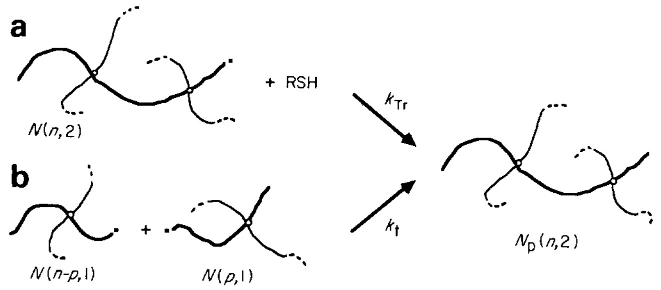


Figure 1 Primary chain of length n crosslinked twice ($m = 2$) terminated by (a) transfer reaction or (b) macroradical coupling

tion function $N_p(n, m)$, given by:

$$N_p(n,m)=\left(\frac{P_iP_{ab}^m}{\tau+\beta/2}\right)\times\left[\tau P_{aa}^n\frac{n^m}{m!}+\frac{\beta}{2}P_iP_{aa}^n\frac{n^{m+1}}{(m+1)!}\right] \quad (15)$$

$W_p(n, m)$, the weight distribution function, is simply related to $N(n, m)$ by:

$$W_p(n,m)=N_p(n,m)n(\tau+\beta/2) \quad (16)$$

Such distribution functions are quite useful for computing gel characteristics, as will be seen later; their evolution in the course of the polymerization is also helpful in the interpretation of network formation. *Figures 2a* and *b* show the weight distribution functions $W_p(n, m)$ calculated from kinetic data obtained in semi-continuous styrene–butadiene polymerization.

At low conversion (*Figure 2a*), the chains are mostly linear; on the other hand, primary chains formed at high conversion beyond the gel point, are highly branched. Nevertheless it is interesting to note that linear chains are still produced.

Gel content

The gel fraction is a useful macroscopic characteristic of a crosslinked polymer which can be measured by a number of methods. However, the definition of a gel polymer is still controversial whether or not it is considered as microgels built-up from crosslinked chains of finite sizes. In our definition we assume that *any chains with a number of crosslinks greater than a critical number* N_{crit} *belong to the gel fraction.* In this paper we assess two values of N_{crit}, respectively, 2 and 3 to test how sensitive the gel computation is to N_{crit}.

At conversion $X = X_c$ and for a given conversion increment dX, the differential gel weight fraction dW^{gel} is readily obtained by solving a set of balance equations formulated as follows:

For $N_{crit} = 2$:

$$dw^{sol}(n,0)=n[\mathcal{N}_p(p,0)-W_c(n,0)dM3] \quad (17)$$

$$dw^{sol}(n,1)=n\left[\sum_{p=1}^{n}\mathcal{N}_p(p,1)W_c(n-p,0)-W_c(n,1)dM3\right] \quad (18)$$

where $\mathcal{N}_p(n, m)$ is the number of primary chains of length n with m crosslinked units, formed during the increment dX. $\mathcal{N}_p(n, m)$ is related to $N_p(n, m)$ by:

$$\mathcal{N}_p(n,m)=dXM_0(\tau+\beta/2)N_p(n,m)$$

where M_0 is the molar quantity of the monomer mixture.

The terms $dw^{sol}(n, m)$ and $W_c(n, m)$ are the differential and cumulative weight fractions of soluble chains of length n with m crosslinked units.

To establish equation (17) growing linear macroradicals of length n produced for conversion increment dX, and dead chains of length n which disappear at the same time by crosslinking reactions are taken into consideration. In a first approximation the number of these crosslinked chains is simply computed as $W_c(n, 0)dM3$, where $dM3$ is the number of pendent double bonds consumed during dX and $W_c(n, 0)$ is the cumulative weight fraction of linear chains of length n in the polymer particle.

The same procedure is applied to soluble chains crosslinked once (see equation (18)).

It is to be noted that we are dealing now with real chains: this means that n is the sum of the lengths of the primary chains linked together in a branched macromolecule. Finally,

$$dW^{gel}(X_c)=\frac{1}{dP}\sum_{n=1}^{\infty}[dP-dw^{sol}(n,0)-dw^{sol}(n,1)] \quad (19)$$

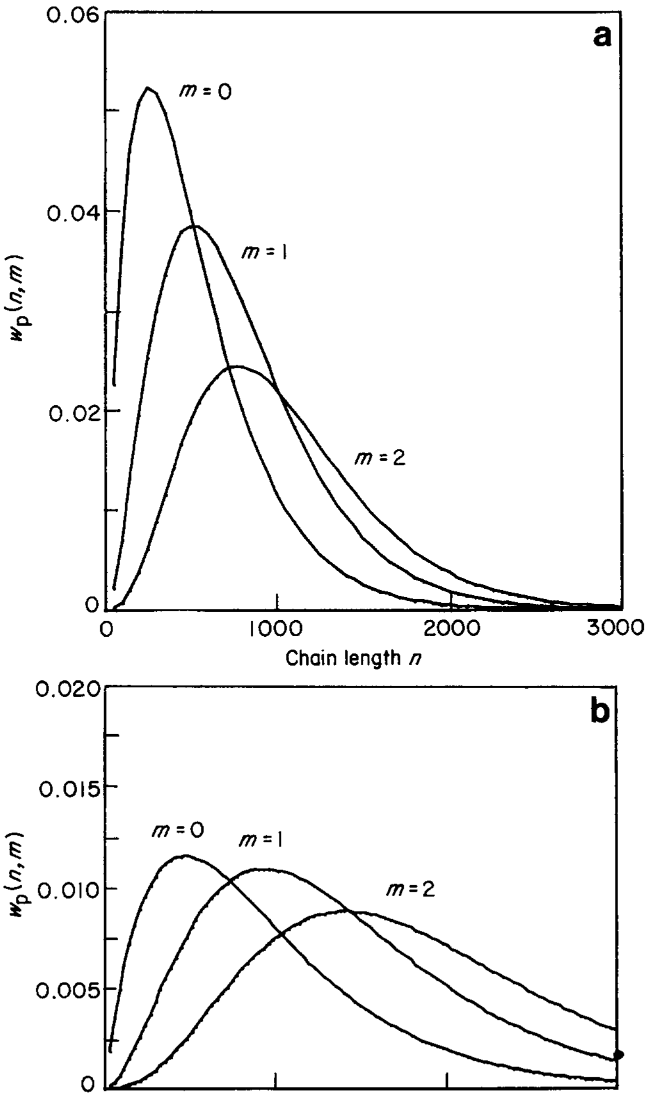


Figure 2 Instantaneous weight distribution functions $w_p(n, m)$ of primary chains in semi-continuous emulsion polymerization of styrene–butadiene (62–38 wt%). TDM (%): 0.5. Monomer feed rate (%h^{-1}): 14.3. (a) Calculated at $X_c = 0.2$; (b) calculated at $X_c = 0.85$

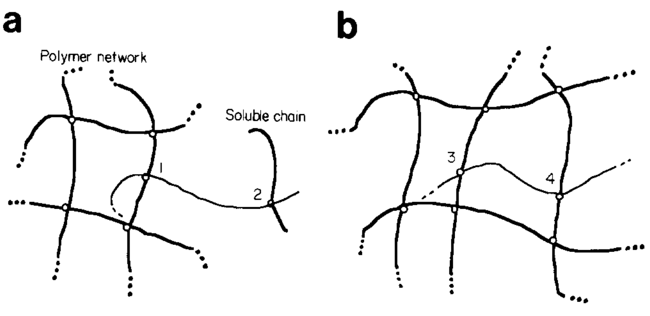


Figure 3 (a) Ineffective crosslinks (1 and 2) and (b) effective crosslinks (3 and 4)

where dP is the amount of polymer formed during the conversion increment dX.

For $N_{\mathrm{crit}} = 3$:

$$\begin{aligned} \mathrm{d}w^{\mathrm{sol}}(n,2) &= n\Bigg[\sum_{p=1}^{n}\sum_{r}^{n-p} \mathcal{N}_{\mathrm{p}}(p,2)W_{\mathrm{c}}(r,0)W_{\mathrm{c}}(n-p-r,0) \\ &\quad + \sum_{p=1}^{n} \mathcal{N}_{\mathrm{p}}(p,1)W_{\mathrm{c}}(n-p,1) - W_{\mathrm{c}}(n,2)\mathrm{d}M3\Bigg] \end{aligned} \tag{20}$$

$$\begin{aligned} \mathrm{d}W^{\mathrm{gel}}(X_{\mathrm{c}}) &= \frac{1}{d\mathrm{P}}\sum_{n=1}^{\infty}\Big[\mathrm{dP} - \mathrm{d}w^{\mathrm{sol}}(n,0) \\ &\quad - \mathrm{d}w^{\mathrm{sol}}(n,1) - \mathrm{d}w^{\mathrm{sol}}(n,2)\Big] \end{aligned} \tag{21}$$

Finally the weight gel fraction is obtained by integrating d$W^{\mathrm{gel}}(X)$ over the total conversion:

$$W^{\mathrm{gel}}(X_{\mathrm{c}}) = \frac{1}{X_{\mathrm{c}}}\int_{0}^{X_{\mathrm{c}}} \mathrm{d}W^{\mathrm{gel}}(X)\,\mathrm{d}X \tag{22}$$

If the transfer reaction to the polymer backbone occurs (through allylic proton abstraction in the case of styrene–butadiene copolymers) one has to consider the recombination reaction between pendent macroradicals which gives rise to the gel; this can be included quite easily in the model but is not shown here for the sake of clarity.

Crosslink density

Crosslink density ρ_{t} can be simply expressed as the number of crosslinked units per monomer unit as stated in the classical theory of gelation. It is given by:

$$\rho_{\mathrm{t}} = \frac{1}{X_{\mathrm{c}}}\int_{0}^{X_{\mathrm{c}}} \frac{R_{\mathrm{p}}^{*}}{R_{\mathrm{p}}}\,\mathrm{d}X \tag{23}$$

In fact we are more interested in the effective crosslink density which contributes to the elastic properties of the material. In the lifetime of a primary chain, the macroradical propagates and attacks pendent vinyl groups located either on soluble chains or on the polymer network; let us consider a growing macroradical which first binds to the polymer network (*Figure 3a*), then propagates and reacts with a soluble chain and eventually terminates (in this instance, termination takes place by transfer reaction, but radical coupling can be envisaged in the same way). It is obvious from *Figure 3a* that the two tetrafunctional crosslinking points (1 and 2) thus established are not elastically active since at most two of the branches are connected to the gel. If the same primary macroradical reacts twice successively with the gel, the two resulting crosslinks (3 and 4) will be considered as effective because each binds together at least three elastically active network chains (*Figure 3b*).

For a given conversion increment dX, the instantaneous effective crosslink density $\rho(2)$ due to primary chains with $m = 2$ is expressed simply as:

$$\rho(2) = \frac{2}{\mathrm{dP}}\mathcal{N}_{\mathrm{p}}(2)2(W^{\mathrm{gel}})^{2} \tag{24}$$

where $\mathcal{N}_{\mathrm{p}}(2)$ is the mole number of the primary chain with $m = 2$:

$$\begin{aligned} \mathcal{N}_{\mathrm{p}}(2) &= \sum_{n=1}^{\infty}\mathcal{N}_{\mathrm{p}}(n,2) \\ &= \mathrm{d}XM_{0}(\tau + \beta/2)\sum_{n=1}^{\infty}N_{\mathrm{p}}(n,2) \end{aligned} \tag{25}$$

For any value of m, $\rho(m)$ is given by:

$$\rho(m) = \frac{2}{\mathrm{dP}}\mathcal{N}_{\mathrm{p}}(m)\sum_{p=2}^{m} p\left[\frac{m!}{(m-p)!p!}\right]W^{\mathrm{gel}p} \tag{26}$$

Finally the accumulated effective crosslink density is obtained by summing over the m values and integrating all over conversion X:

$$\rho = \frac{2}{\mathrm{dP}}\sum_{m=2}^{\infty}\sum_{p=2}^{m}\mathcal{N}_{\mathrm{p}}(m)p\left[\frac{m!}{(m-p)!p!}\right]W^{\mathrm{gel}p} \tag{27}$$

$$\rho_{\mathrm{t}} = \frac{1}{X_{\mathrm{c}}W^{\mathrm{gel}}}\int_{0}^{X_{\mathrm{c}}}\rho\,\mathrm{d}X \tag{28}$$

When summing $\mathcal{N}_{\mathrm{p}}(n,m)$ over n (equation (25)) analytical expressions were found for finite values of m (see Appendix). Equation (27) was solved numerically and shown to converge at $m = 6$ for the kinetic conditions which prevailed.

Crosslink density from polymer swelling measurements

We applied the Flory–Huggins–Rehner equation to estimate the crosslink density of the gel fraction. In its simplest form, polymer volume fraction at swelling equilibrium, v_2, is related to the effective crosslink density ρ_{c}, according to:

$$\ln(1 - v_2) + v_2 + v_2^2\chi_{12} = \rho_{\mathrm{c}}\frac{\overline{V_1}}{\mathrm{d}\bar{M}}(v_2^{1/3} - v_2/2) \tag{29}$$

where d is the polymer density (for styrene–butadiene copolymers d is approximated to 1), $\overline{V_1}$ is the molar volume of solvent (for chloroform, $\overline{V_1} = 80.5$ cm^3 mol^{-1}), $\bar{M}$ is the molar mass of the average monomer unit and χ_{12} is the interaction parameter (for styrene–butadiene copolymers in chloroform, $\chi_{12} = 0.33$)[10].

If, instead of ρ_{c}, we use ρ_{t}, the total crosslink density, including those located on 'dangling chains' (i.e. the molar fraction of crosslinked units in the polymer gel), then the following equation is used[11]:

$$\begin{aligned} &\ln(1 - v_2) + v_2 + v_2^2\chi_{12} \\ &\quad = \rho_{\mathrm{t}}\left(1 - \frac{2}{\rho_{\mathrm{t}}DP_{\mathrm{np}}^{\mathrm{gel}}}\right)\frac{\overline{V_1}}{dM}(v_2^{1/3} - v_2/2) \end{aligned} \tag{30}$$

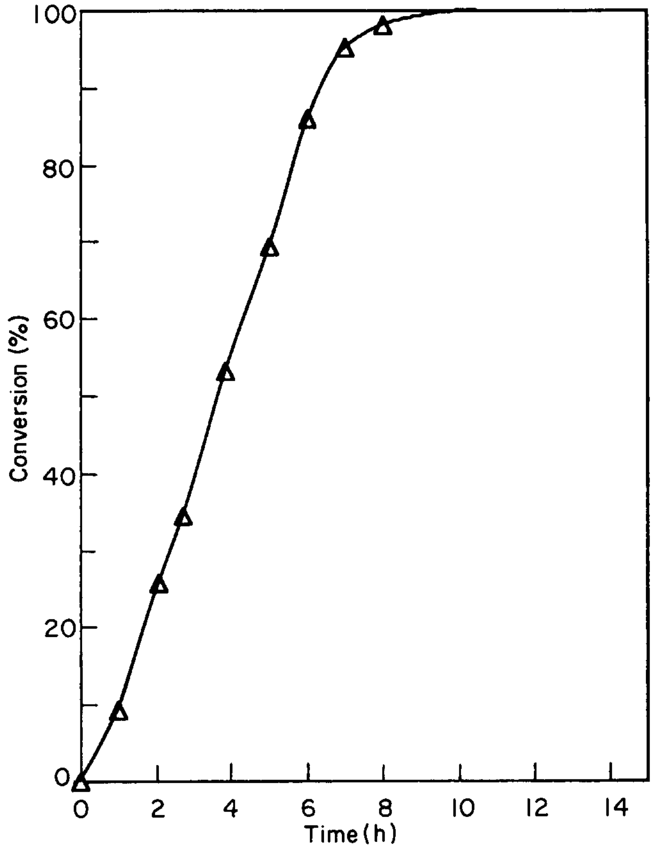


Figure 4 Conversion–time curve for unseeded semi-continuous emulsion polymerization of styrene–butadiene (62–38 wt%). TDM (%): 0.5. Monomer feed rate (% h^{-1}): 14.3

where DP_{np}^{gel} is the number average chain length of the primary chains which belong to the gel.

For calculation, the kinetic rate constants and reactivity ratios were the following:

$$k_{p_1} = 1.05 \times 10^7 \exp(-3560/T)\,\mathrm{l\,mol^{-1}\,s^{-1}} \quad \text{(ref. 12)}$$

$$k_{p_2} = 1.02 \times 10^8 \exp(-4650/T)\,\mathrm{l\,mol^{-1}\,s^{-1}} \quad \text{(ref. 13)}$$

$$r_1 = 0.79 \qquad r_2 = 1.38 \qquad \text{(ref. 14)}$$

where r_{i3}, the reactivity ratio of the pendent vinyl group of butadiene, is the only adjustable parameter used both for the ID model and the model developed by Hamielec *et al.*

The transfer rate constant on TDM:

$$\frac{k_{Tr_1}}{k_{p_1}} = \frac{k_{Tr_2}}{k_{p_2}} = 2 \qquad \text{(this work)}$$

Termination rate constants k_t are likely to span over several orders of magnitude because of the gel effect that usually takes place in emulsion polymerization where the polymer fraction is as high as 0.7–0.9. We set the ratio k_t/k_p to 100, a typical value calculated by a number of authors[15–17]. Moreover, under our conditions it turned out that the termination rate is essentially controlled by the transfer reaction to the mercaptan.

RESULTS AND DISCUSSION

Rates of polymerization R_p were computed from conversion–time curves. The monomer concentration within the polymer particles can be found using the Morton equation[18] when the reaction is conducted under flooded conditions and particles are allowed to swell at equilibrium. Otherwise (under starved conditions) the monomer concentration is readily obtained by a balance between the rate of polymerization and monomer feed rate. Equation (1) gives the total radical concentration $[R^0]$, used directly in the expressions mentioned above. When the number of polymer particles is known, $[R^0]$ can be transformed into $\bar{n}$, the average number of radicals per particle. A typical kinetic curve is shown in *Figure 4*, while values of $\bar{n}$ plotted *versus* conversion are given in *Figure 5*. It is seen that $\bar{n}$ lies between 0.5 and 1, close to the ideal case of Smith–Ewart case II.

Figure 6 shows the drift in composition encountered in a semi-continuous styrene–butadiene copolymerization. This illustrates the greater reactivity of butadiene compared to styrene.

The evolution of the gel weight fraction *versus* conversion is shown in *Figure 7* for semi-continuous seeded copolymerization of styrene and butadiene with a low content of chain transfer agent (0.1% TDM). Theoretical curves from the ID model and from the generalized theory of Flory (GF model) were obtained by setting r_{i3} at 2.5×10^{-4}. Both models predict gel formation and a large increase in gel weight fraction at early conversion, then a levelling off and a sudden increase at the end of the conversion. The effect of N_{crit} does not seem to be as critical as we would expect; the two curves with $N_{crit} = 2$ and 3 are very close together and lead to the same value of gel fraction at final conversion. On the other hand, it is surprising to see how close the theoretical curves of the ID and GF models lie, although the design of these two models are quite different. Interestingly, both models indicate that at 100% conversion, a small fraction of polymer remains in the sol, which is consistent with *Figure 2b* where it is shown that linear primary chains are still formed at high conversion.

Effective crosslink densities obtained through equation (29) are compared with theoretical densities from the ID model, whereas total crosslink densities from equation

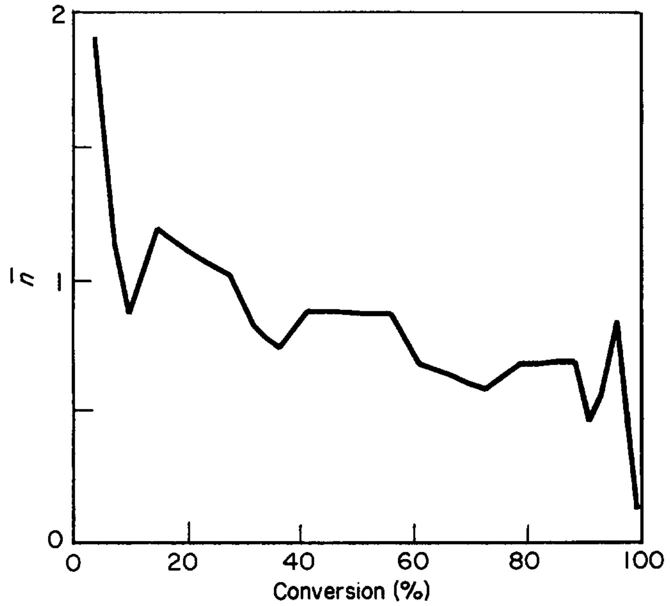


Figure 5 Average number of radicals $\bar{n}$ per particle *versus* conversion. Same conditions as in *Figure 4*

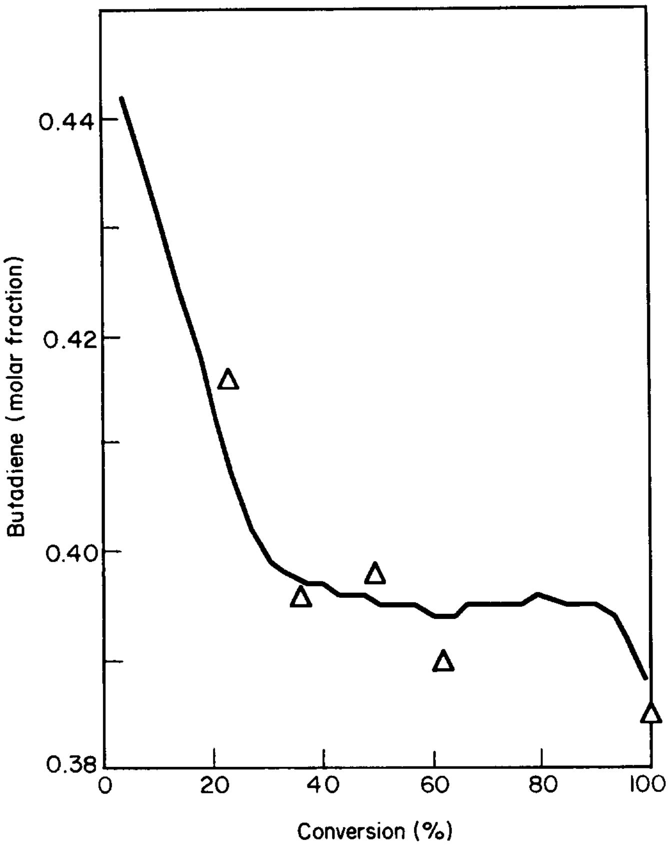


Figure 6 Average copolymer composition *versus* conversion. Same conditions as in *Figure 4*. Comparison with experimental data (Δ)

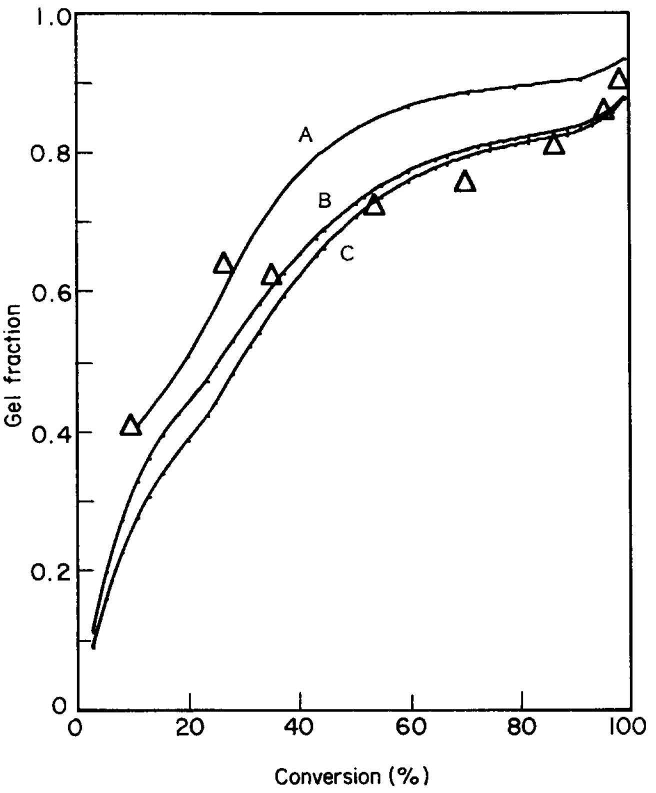


Figure 7 Gel fraction *versus* conversion in a seeded semi-continuous emulsion polymerization of styrene–butadiene (70–30 wt%). TDM (%): 0.1. Monomer feed rate (% h^{-1}): 16.7. Comparison of experimental data (Δ) with (A) GF model and ID model with (B) $N_{crit} = 2$ and (C) $N_{crit} = 3$. The reactivity ratio $r_{i3} = 2.5 \times 10^{-3}$

(30) are compared with calculated data from the GF model (*Figure 8*).

In both cases the agreement between experimental and theoretical curves can be considered as good; it shows that the crosslink densities increase steadily as the reaction proceeds. For a better understanding of these curves, it must be kept in mind that in semi-continuous processes the polymer content in particles can be as high as 80% throughout the reaction, depending upon the rates of polymerization and monomer feeding. So the ratio of monomer to polymer will control the rate of copolymerization of the pendent double bond of butadiene while the ratio of monomer to chain transfer agent will control the primary chain distribution. This is well illustrated in *Figures 9* and *10* where the amount of TDM was varied from 0.15 to 1.1% in a series of semi-continuous emulsion polymerizations of styrene and butadiene (62–38 wt%). As expected, gel fraction decreases as the TDM content is increased, which is well predicted by the two models. Again the two kinetic models give us general trends that are actually observed experimentally for the effective crosslink density ρ_c, as well as for the total crosslink density ρ_t. As we increase the TDM level, the polymer network gets more and more crosslinked but the efficiency of those crosslinks diminishes. This slight increase in ρ_t is simply explained by looking at *Figure 11*, where the instantaneous crosslink density of the primary chain is simulated.

Increasing the TDM level delays the gel point and yields a more densely crosslinked gel because of the drift of crosslink density of the primary chains. However, this gel is characterized by a large number of dangling chains with no elastic properties.

In another series of copolymerizations where the monomer composition was changed (styrene–butadiene, 72–28 wt%), both models were applied leading to

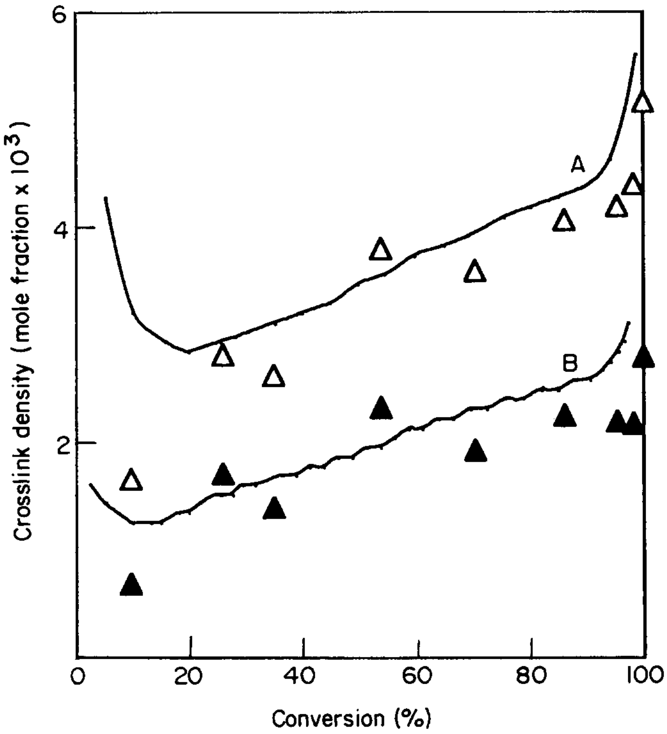


Figure 8 Crosslink density of the polymer network *versus* conversion. Same conditions as in *Figure 7*. Calculated data using equations (29) (▲) and (30) (Δ), respectively, from experimental swelling ratios. Solid curves are obtained from kinetic models: (A) GF model; (B) ID model

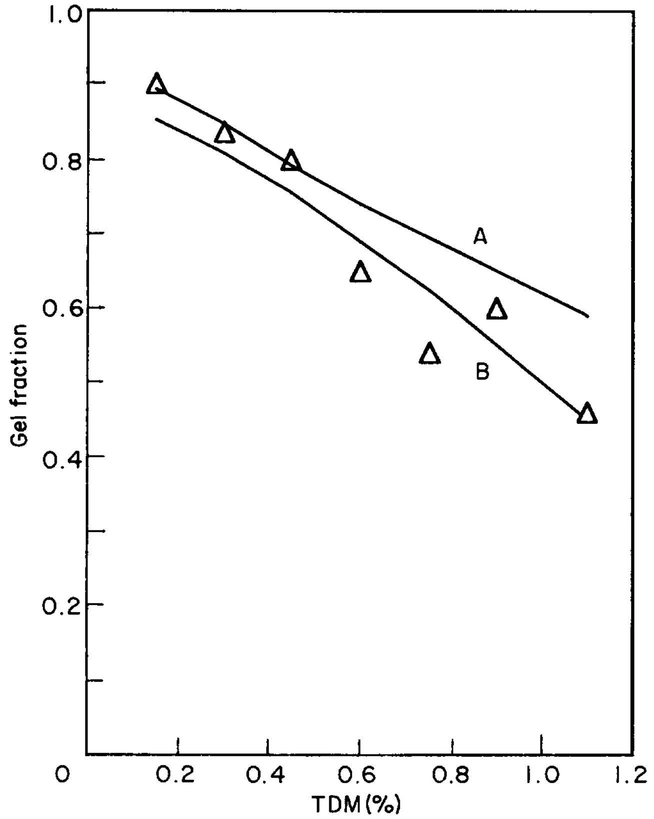


Figure 9 Effect of TDM level (%) on the final polymer gel fraction in a series of semi-continuous emulsion polymerization of styrene–butadiene (62–38 wt%). Monomer feed rate ($\% \, h^{-1}$): 14.3. Comparison with kinetic models: (A) ID model; (B) GF model. The reactivity ratio $r_{i3} = 2.5 \times 10^{-3}$

somewhat different results. The GF model is closer to experimental values (*Figure 12*). It is to be noted that the reactivity ratio has to be changed from $r_{i3} = 2.5 \times 10^{-3}$ to 3.33×10^{-3} to get a better fit with experimental data. It is a familiar feature of vinyl–divinyl copolymerization that when the fraction of divinyl monomer increases, the pendent double bonds become less reactive due to steric hindrance. At this point it is worth mentioning previous studies on butadiene and butadiene–styrene emulsion polymerization, which used the original theory of Flory–Stockmayer[19,20]. To make reliable comparisons we had to use the Arrhenius parameter to extrapolate data obtained in references 19 and 20, from 15–60° up to 75°C (i.e. the reference temperature for this work). As in this work, we also assumed that only the 1,2 pendent vinyl groups are active in copolymerization. Results reported in *Table 1* show that the values for reactivity ratios are quite similar, ranging from 2×10^{-3} to 2.5×10^{-3}.

In other words, as long as the drift in crosslinking density is limited (as in references 19 and 20, where polymerizations were stopped at low conversion), the original theory of Flory–Stockmayer still holds; on the other hand, for high conversion polymerization, one has to take into account the dramatic change in crosslinking rate and turn to more realistic modelling.

CONCLUSIONS

Modelling based on primary chain distribution functions turns out to be a quite powerful tool to derive most of the important parameters in vinyl/divinyl copolymeriza-

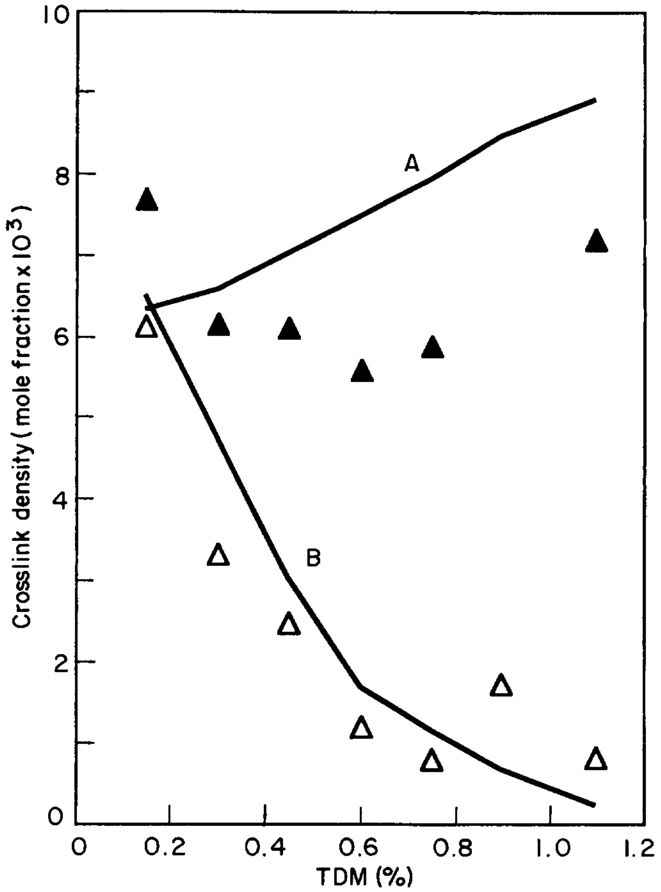


Figure 10 Effect of TDM level (%) on the crosslink density of the polymer network. Same conditions as in *Figure 9*. Calculated data using equations (29) (Δ) and (30) (▲), respectively, from experimental swelling ratios. Solid curves are obtained from kinetic models: (A) GF model; (B) ID model

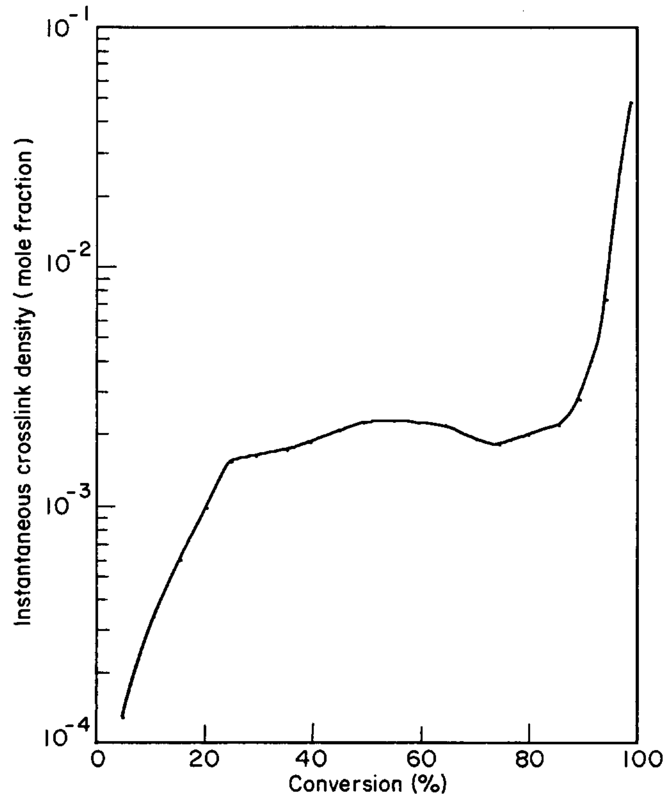


Figure 11 Simulation of instantaneous crosslink density of the primary chain. Same conditions as in *Figure 9*

Table 1 Reactivity on pendent double bond of butadiene

Reference	Monomer composition	Temperature (°C)	Model	r_{i3} ($\times 10^3$)[a]
19	Butadiene	40–60	Flory	2.00
20	Butadiene–styrene (71/29 wt%)	5–25	Flory	2.25
This work	Butadiene–styrene ((25–35)–(75–65) wt%)	75	ID GF	2.50

[a] Apparent reactivity ratio extrapolated to the reference temperature (75°C) using the Arrhenius parameters found in references 19 and 20. The residual unsaturations in the main chain are supposed to be unreactive

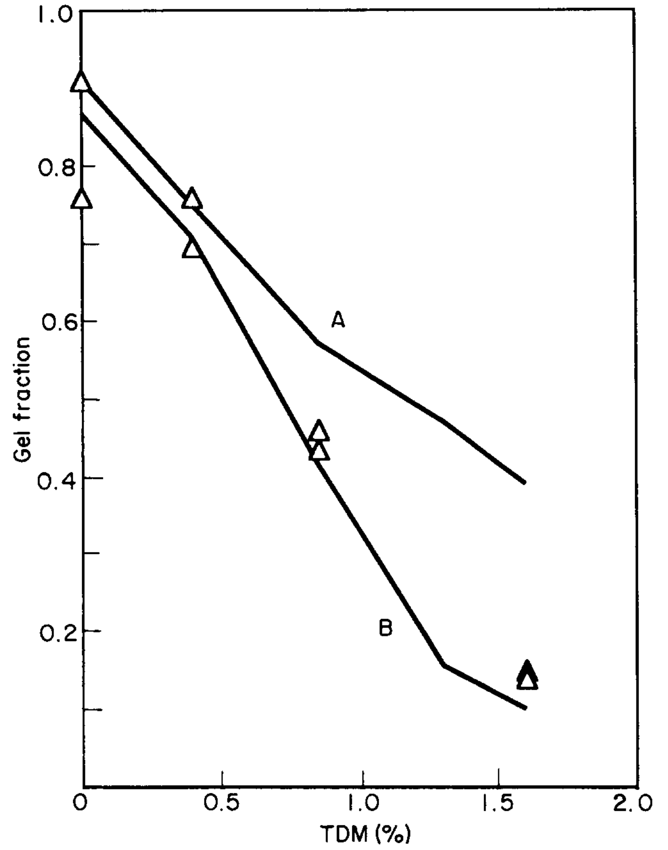


Figure 12 Effect of TDM level (%) on the final polymer gel fraction in a series of semi-continuous emulsion polymerization of styrene–butadiene (72–28 wt%). Monomer feed rate (% h^{-1}): 14.3. Comparison with kinetic models: (A) ID model; (B) GF model. The reactivity ratio $r_{i3} = 3.33 \times 10^{-3}$

tion, such as the crosslink densities of the polymer network or the branching frequency of the soluble chains. At any conversion along the reaction, macroradicals as well as deactivated primary chains are thus characterized in terms of molecular weight and number of crosslinked units per chain. Radical deactivation, such as bimolecular coupling, disproportionation or transfer reaction, are included in the derivation of these functions. This theoretical framework has been extended to transfer reactions on the polymer backbone, which generate pendent macroradicals; the latter eventually can recombine and form a three-dimensional network.

Our definition of gel material is probably oversimplified, or at least different from the usual definition in which the onset of gelation occurs when the weight average molecular weight goes to infinity. Our ID model does not specify a critical conversion point, i.e. the gel point, unlike the statistical treatments. it rather gives a deeper insight into gel formation by computing the weight fraction of highly branched macromolecules throughout polymerization. While these crosslinked chains are not counted as gel in the mean field theory, it is believed that even if the macromolecule sizes remain finite, they largely contribute to the viscoelastic properties of the polymer. Moreover, for practical reasons the quantification of these crosslinked chains, whether they are called clusters, microgels or nanogels, is very useful in some applications where their presence is troublesome, as well as in solving the problems encountered in gel permeation chromatography analysis, where microgels are known to plug columns.

Hence this ID model should complement the mean field approach. While the onset of macroscopic gel formation is generally well accounted for by Flory's theory, the ID model gives a lot of useful information on the chain cluster sizes before or in the vicinity of the gel point.

The distribution functions allow the effective crosslink density to be computed straightforwardly, discriminating between elastically active crosslinking points and crosslinks located on dangling chains, no matter what assumptions are made to calculate the gel weight fraction. Again this approach is complementary to the Flory–Stockmayer model of gelation, in which the crosslink density refers to the total concentration of crosslinking points whether they are effective or ineffective. Hence the simultaneous use of both models gives an extraordinary set of valuable information on the sol and gel structure.

The fact that the drift in the relative rate of crosslinking, R_p^*/R_p, is taken into account to calculate the network parameters renders the two models more reliable. Then the application of both models to high-conversion emulsion polymerization of styrene and butadiene demonstrates their ability to predict the major features of diene polymerization.

Kinetic models are now gaining in reliability and accuracy in the field of polymer engineering, and they are increasingly used to design and control new processes.

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APPENDIX

Computation of $N_p(m)$*—distribution functions of primary chains with* m *crosslinking points*

$N_p(m)$ is obtained by summing $N_p(n, m)$ over n, with $N_p(n, m)$ given by:

$$N_p(n,m) = \left(\frac{P_i P_{ab}^m}{\tau + \beta/2}\right)\left[\tau P_{aa}^n \frac{n^m}{m!} + \frac{\beta}{2} P_i P_{aa}^n \frac{n^{m+1}}{(m+1)!}\right]$$

$$N_p(m) = \sum_{n=1}^{\infty} N_p(n,m)$$

$$= \left(\frac{P_i P_{ab}^m}{\tau + \beta/2}\right)\left[\tau \frac{S(m)}{m!} + \frac{\beta}{2} P_i \frac{S(m+1)}{(m+1)!}\right]$$

$$S(m) = \sum_{n=1}^{\infty} n^m P_{aa}^n$$

An analytical form was found for $S(m)$ only for finite values of m, using the following recurring equation:

$$\sum_{n=1}^{\infty} n^m P_{aa}^n = \frac{\partial}{\partial \rho}\left(p \sum_{n=1}^{\infty} n^{m-1} P_{aa}^n\right) \qquad (\text{with } P_{aa} < 1)$$

which gives the following expressions for $S(m)$ with $m = 1$–7:

$$S(1) = \frac{1}{(1 - P_{aa})^2}$$

$$S(2) = \frac{1}{(1 - P_{aa})^3}(P_{aa} + 1)$$

$$S(3) = \frac{1}{(1 - P_{aa})^4}(P_{aa}^2 + 4P_{aa} + 1)$$

$$S(4) = \frac{1}{(1 - P_{aa})^5}(P_{aa}^3 + 11P_{aa}^2 + 11P_{aa} + 1)$$

$$S(5) = \frac{1}{(1 - P_{aa})^6}(P_{aa}^4 + 26P_{aa}^3 + 66P_{aa}^2 + 26P_{aa} + 1)$$

$$S(6) = \frac{1}{(1 - P_{aa})^7}(P_{aa}^5 + 57P_{aa}^4 + 302P_{aa}^3 + 302P_{aa}^2 + 57P_{aa} + 1)$$

$$S(7) = \frac{1}{(1 - P_{aa})^8}(P_{aa}^6 + 120P_{aa}^5 + 1191P_{aa}^4 + 2416P_{aa}^3 + 1191P_{aa}^2 + 120P_{aa} + 1)$$