Evidence of unequal vinyl group reactivity in copolymerization/crosslinking reactions of mono- and divinyl comonomers

Antonios G. Mikos, Christos G. Takoudis and Nikolaos A. Peppas*
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA
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A kinetic model was developed for the copolymerization/crosslinking reaction of a monovinyl and a divinyl monomer. The general form of the model incorporates initiation, propagation, chain transfer and termination reactions and considers the situation of different reactivities of the vinyl groups of the divinyl monomer. Experimental data on the copolymerization of styrene with *m*- and *p*-divinylbenzene obtained by Hild and Okasha were used to evaluate this model.

(Keywords: kinetic modelling; crosslinking reaction; gelation; divinyl monomer; polystyrene)

INTRODUCTION

Polymer networks can be produced either by addition or by condensation polymerizations. Copolymerization/crosslinking reactions of a monomer containing a single double bond (e.g. monovinyl monomer) with a monomer containing two double bonds (e.g. divinyl monomer) are typical polyaddition reaction schemes. The divinyl monomer behaves as a comonomer and a crosslinking agent.

The basic reactions of the copolymerization/crosslinking of a monovinyl ($CH_2{=}CH{-}A$) and a divinyl monomer ($CH_2{=}CH{-}B{-}CH{=}CH_2$) are shown in *Figure 1*. A copolymerization reaction leads to linear polymer chains with pendant vinyl groups. These pendant vinyl groups react with living polymer chains producing highly branched polymer chains and eventually an infinite network. The copolymerization and crosslinking reactions occur simultaneously rather than consecutively. In general, the crosslinking reaction may be either intermolecular or intramolecular. However, intramolecular crosslinking reactions may be neglected at low concentrations of the divinyl monomer[1].

The classical gelation theory[2,3] proposed by Flory and Stockmayer is applicable to monovinyl–divinyl monomer reactions only if all vinyl groups have equal reactivities. Therefore, this theory cannot be applied to many systems, such as styrene–divinylbenzene, because of unequal vinyl group reactivities of the two monomers[4–9]. Furthermore, during the reaction the reactivities of the pendant vinyl groups might change due to a shielding effect by the rest of the macromolecule. Thus, the reactivities of the vinyl groups of the divinyl monomer must be considered to be dependent on each other, i.e. the reactivity of the remaining vinyl group of the divinyl monomer changes once one vinyl group has reacted.

In a previous publication[10] we developed a kinetic model for copolymerization/crosslinking reactions of a monovinyl monomer with a divinyl monomer with independent vinyl group reactivities and we investigated the effect of various polymerization parameters on the gelation process and the structure of the polymer gel.

However, there is evidence[11] that the reactivity of the second vinyl group of a divinyl monomer may be different from that of the first vinyl group. Therefore, kinetic modelling of copolymerization/crosslinking reactions of a monovinyl monomer with a divinyl monomer with dependent vinyl group reactivities is needed to describe such systems. The predictions of this kinetic model are compared with experimental data[9] for the copolymerization/crosslinking of styrene with either *m*- or *p*-divinylbenzene.

KINETIC MODELLING

Polymerization mechanism

The copolymerization/crosslinking mechanism for monovinyl–divinyl reactions includes four steps: initiation, propagation and crosslinking, termination and chain transfer to monomer. In the development of the kinetic mechanism it is assumed that all the polymerization reactions are irreversible, the crosslinking reactions are intermolecular and the terminal group of a living polymer chain determines its reactivity.

All possible steps involved in the copolymerization/crosslinking mechanism of a monovinyl and a divinyl monomer may be described in the reaction scheme presented below. Here, I is the initiator, A is the initiated radical, M_1 is the monovinyl monomer and M_2 is the divinyl monomer. The term 'primary polymer chains' is used to designate polymer chains that would result if all crosslinks were severed[2]. The symbol $P_{p,q,r}$ designates a living polymer chain with a monovinyl monomer terminal group. The symbols $Q_{p,q,r}$ and $R_{p,q,r}$ represent living polymer chains with divinyl monomer terminal groups corresponding to a pendant vinyl group and a crosslink, respectively. Finally, the symbol $M_{p,q,r}$ corresponds to a dead polymer chain. Three subscripts are used to describe a polymer chain; they refer to the

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* To whom correspondence should be addressed.

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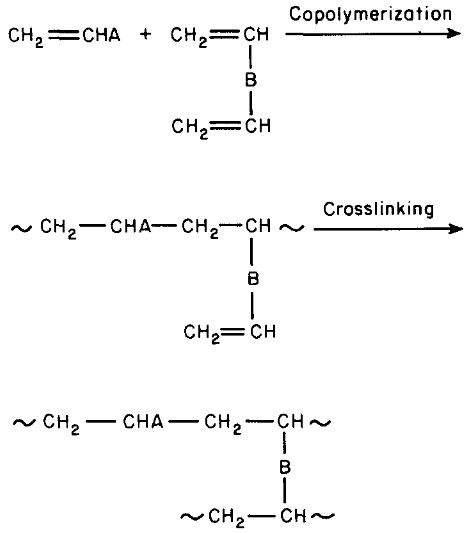

Figure 1 Basic steps of the monovinyl–divinyl monomer copolymerization/crosslinking reaction

number of monovinyl units p, pendant vinyl groups q, and crosslinks per chain r.

Initiation. In the initiation step, seven possible reactions are included:

$$I \xrightarrow{k_d} 2A$$

$$M_1 + A \xrightarrow{k_{i_1}} P_{1,0,0}$$

$$M_2 + A \xrightarrow{k_{i_2}} Q_{0,1,0}$$

$$P_{p,q,r} + A \xrightarrow{k_{i_3}} P_{p,q-1,r+1} + R_{0,0,1}$$

$$Q_{p,q,r} + A \xrightarrow{k_{i_3}} Q_{p,q-1,r+1}(R_{p,q-1,r+1}) + R_{0,0,1}$$

$$R_{p,q,r} + A \xrightarrow{k_{i_3}} R_{p,q-1,r+1} + R_{0,0,1}$$

$$M_{p,q,r} + A \xrightarrow{k_{i_3}} M_{p,q-1,r+1} + R_{0,0,1}$$

The term $R_{p,q-1,r+1}$ shown in parentheses designates the product of the reaction of the terminal pendant vinyl group of the living polymer chain $Q_{p,q,r}$.

Propagation and crosslinking. The propagation and crosslinking step can be written in terms of 18 distinct reactions:

$$P_{p,q,r} + M_1 \xrightarrow{k_{p_{11}}} P_{p+1,q,r}$$

$$P_{p,q,r} + M_2 \xrightarrow{k_{p_{12}}} Q_{p,q+1,r}$$

$$P_{p,q,r} + P_{x,y,z} \xrightarrow{k_{p_{13}}} R_{p,q,r+1} + P_{x,y-1,z+1}$$

$$P_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{p_{13}}} R_{p,q,r+1} + Q_{x,y-1,z+1}(R_{x,y-1,z+1})$$

$$P_{p,q,r} + R_{x,y,z} \xrightarrow{k_{p_{13}}} R_{p,q,r+1} + R_{x,y-1,z+1}$$

$$P_{p,q,r} + M_{x,y,z} \xrightarrow{k_{p_{13}}} R_{p,q,r+1} + M_{x,y-1,z+1}$$

$$Q_{p,q,r} + M_1 \xrightarrow{k_{p_{21}}} P_{p+1,q,r}$$

$$Q_{p,q,r} + M_2 \xrightarrow{k_{p_{22}}} Q_{p,q+1,r}$$

$$Q_{p,q,r} + P_{x,y,z} \xrightarrow{k_{p_{23}}} R_{p,q,r+1} + P_{x,y-1,z+1}$$

$$Q_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{p_{23}}} R_{p,q,r+1} + Q_{x,y-1,z+1}(R_{x,y-1,z+1})$$

$$Q_{p,q,r} + R_{x,y,z} \xrightarrow{k_{p_{23}}} R_{p,q,r+1} + R_{x,y-1,z+1}$$

$$Q_{p,q,r} + M_{x,y,z} \xrightarrow{k_{p_{23}}} R_{p,q,r+1} + M_{x,y-1,z+1}$$

$$R_{p,q,r} + M_1 \xrightarrow{k_{p_{31}}} P_{p+1,q,r}$$

$$R_{p,q,r} + M_2 \xrightarrow{k_{p_{32}}} Q_{p,q+1,r}$$

$$R_{p,q,r} + P_{x,y,z} \xrightarrow{k_{p_{33}}} R_{p,q,r+1} + P_{x,y-1,z+1}$$

$$R_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{p_{33}}} R_{p,q,r+1} + Q_{x,y-1,z+1}(R_{x,y-1,z+1})$$

$$R_{p,q,r} + R_{x,y,z} \xrightarrow{k_{p_{33}}} R_{p,q,r+1} + R_{x,y-1,z+1}$$

$$R_{p,q,r} + M_{x,y,z} \xrightarrow{k_{p_{33}}} R_{p,q,r+1} + M_{x,y-1,z+1}$$

Termination. Termination by combination occurs as follows:

$$P_{p,q,r} + P_{x,y,z} \xrightarrow{k_{tc_{11}}} M_{p+x,q+y,r+z}$$

$$P_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{tc_{12}}} M_{p+x,q+y,r+z}$$

$$P_{p,q,r} + R_{x,y,z} \xrightarrow{k_{tc_{13}}} M_{p+x,q+y,r+z}$$

$$Q_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{tc_{22}}} M_{p+x,q+y,r+z}$$

$$Q_{p,q,r} + R_{x,y,z} \xrightarrow{k_{tc_{23}}} M_{p+x,q+y,r+z}$$

$$R_{p,q,r} + R_{x,y,z} \xrightarrow{k_{tc_{33}}} M_{p+x,q+y,r+z}$$

Termination by disproportionation occurs as follows:

$$P_{p,q,r} + P_{x,y,z} \xrightarrow{k_{td_{11}}} M_{p,q,r} + M_{x,y,z}$$

$$P_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{td_{12}}} M_{p,q,r} + M_{x,y,z}$$

$$P_{p,q,r} + R_{x,y,z} \xrightarrow{k_{td_{13}}} M_{p,q,r} + M_{x,y,z}$$

$$Q_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{td_{22}}} M_{p,q,r} + M_{x,y,z}$$

$$Q_{p,q,r} + R_{x,y,z} \xrightarrow{k_{td_{23}}} M_{p,q,r} + M_{x,y,z}$$

$$R_{p,q,r} + R_{x,y,z} \xrightarrow{k_{td_{33}}} M_{p,q,r} + M_{x,y,z}$$

Chain transfer. Chain transfer to the monomer is also important and may be represented by 18 different reactions:

$$\mathrm{P}_{p,q,r}+\mathrm{M}_1 \xrightarrow{k_{\mathrm{f}_{11}}} \mathrm{M}_{p,q,r}+\mathrm{P}_{1,0,0}$$

$$\mathrm{P}_{p,q,r}+\mathrm{M}_2 \xrightarrow{k_{\mathrm{f}_{12}}} \mathrm{M}_{p,q,r}+\mathrm{Q}_{0,1,0}$$

$$\mathrm{P}_{p,q,r}+\mathrm{P}_{x,y,z} \xrightarrow{k_{\mathrm{f}_{13}}} \mathrm{M}_{p,q,r}+\mathrm{P}_{x,y-1,z+1}+\mathrm{R}_{0,0,1}$$

$$\mathrm{P}_{p,q,r}+\mathrm{Q}_{x,y,z} \xrightarrow{k_{\mathrm{f}_{13}}} \mathrm{M}_{p,q,r}+\mathrm{Q}_{x,y-1,z+1}(\mathrm{R}_{x,y-1,z+1})+\mathrm{R}_{0,0,1}$$

$$\mathrm{P}_{p,q,r}+\mathrm{R}_{x,y,z} \xrightarrow{\mathrm{f}_{13}} \mathrm{M}_{p,q,r}+\mathrm{R}_{x,y-1,z+1}+\mathrm{R}_{0,0,1}$$

$$\mathrm{P}_{p,q,r}+\mathrm{M}_{x,y,z} \xrightarrow{k_{\mathrm{f}_{13}}} \mathrm{M}_{p,q,r}+\mathrm{M}_{x,y-1,z+1}+\mathrm{R}_{0,0,1}$$

$$\mathrm{Q}_{p,q,r}+\mathrm{M}_1 \xrightarrow{k_{\mathrm{f}_{21}}} \mathrm{M}_{p,q,r}+\mathrm{P}_{1,0,0}$$

$$\mathrm{Q}_{p,q,r}+\mathrm{M}_2 \xrightarrow{k_{\mathrm{f}_{22}}} \mathrm{M}_{p,q,r}+\mathrm{Q}_{0,1,0}$$

$$\mathrm{Q}_{p,q,r}+\mathrm{P}_{x,y,z} \xrightarrow{k_{\mathrm{f}_{23}}} \mathrm{M}_{p,q,r}+\mathrm{P}_{x,y-1,z+1}+\mathrm{R}_{0,0,1}$$

$$\mathrm{Q}_{p,q,r}+\mathrm{Q}_{x,y,z} \xrightarrow{k_{\mathrm{f}_{23}}} \mathrm{M}_{p,q,r}+\mathrm{Q}_{x,y-1,z+1}(\mathrm{R}_{x,y-1,z+1})+\mathrm{R}_{0,0,1}$$

$$\mathrm{Q}_{p,q,r}+\mathrm{R}_{x,y,z} \xrightarrow{k_{\mathrm{f}_{23}}} \mathrm{M}_{p,q,r}+\mathrm{R}_{x,y-1,z+1}+\mathrm{R}_{0,0,1}$$

$$\mathrm{Q}_{p,q,r}+\mathrm{M}_{x,y,z} \xrightarrow{k_{\mathrm{f}_{23}}} \mathrm{M}_{p,q,r}+\mathrm{M}_{x,y-1,z+1}+\mathrm{R}_{0,0,1}$$

$$\mathrm{R}_{p,q,r}+\mathrm{M}_1 \xrightarrow{k_{\mathrm{f}_{31}}} \mathrm{M}_{p,q,r}+\mathrm{P}_{1,0,0}$$

$$\mathrm{R}_{p,q,r}+\mathrm{M}_2 \xrightarrow{k_{\mathrm{f}_{32}}} \mathrm{M}_{p,q,r}+\mathrm{Q}_{0,1,0}$$

$$\mathrm{R}_{p,q,r}+\mathrm{P}_{x,y,z} \xrightarrow{k_{\mathrm{f}_{33}}} \mathrm{M}_{p,q,r}+\mathrm{P}_{x,y-1,z+1}+\mathrm{R}_{0,0,1}$$

$$\mathrm{R}_{p,q,r}+\mathrm{Q}_{x,y,z} \xrightarrow{k_{\mathrm{f}_{33}}} \mathrm{M}_{p,q,r}+\mathrm{Q}_{x,y-1,z+1}(\mathrm{R}_{x,y-1,z+1})+\mathrm{R}_{0,0,1}$$

$$\mathrm{R}_{p,q,r}+\mathrm{R}_{x,y,z} \xrightarrow{k_{\mathrm{f}_{33}}} \mathrm{M}_{p,q,r}+\mathrm{R}_{x,y-1,z+1}+\mathrm{R}_{0,0,1}$$

$$\mathrm{R}_{p,q,r}+\mathrm{M}_{x,y,z} \xrightarrow{k_{\mathrm{f}_{33}}} \mathrm{M}_{p,q,r}+\mathrm{M}_{x,y-1,z+1}+\mathrm{R}_{0,0,1}$$

It is apparent that this detailed kinetic mechanism includes the specific case of the copolymerization/crosslinking reaction of a monovinyl monomer with a divinyl monomer with independent vinyl group reactivities.

Reaction rates

Based on the kinetic mechanism, one may derive the rate equations for the concentrations of the various polymerizing species, as well as the moments of the molecular weight distribution of the crosslinked polymer. (We shall use italics to denote concentrations of the species of the same symbols.)

The rate equation for initiator I is:

$$r_{\mathrm{I}}=-k_{\mathrm{d}}I \qquad (1)$$

The rate expression for initiated radicals A is given by:

$$r_{\mathrm{A}}=2fk_{\mathrm{d}}I-(k_{\mathrm{i}_1}M_1+2k_{\mathrm{i}_2}M_2+k_{\mathrm{i}_3}M_3)A \qquad (2)$$

Here, f is the initiator efficiency and M_3 is the concentration of pendant vinyl groups, defined as:

$$M_3\equiv\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty}q(P_{p,q,r}+Q_{p,q,r}+R_{p,q,r}+M_{p,q,r}) \qquad (3)$$

The rate expression for monovinyl monomer M_1 may be written as follows:

$$r_{\mathrm{M}_1}=-[k_{\mathrm{i}_1}A+(k_{\mathrm{p}_{11}}+k_{\mathrm{f}_{11}})P+(k_{\mathrm{p}_{21}}+k_{\mathrm{f}_{21}})Q+(k_{\mathrm{p}_{31}}+k_{\mathrm{f}_{31}})R]M_1 \qquad (4)$$

The terms P, Q and R are the concentrations of total living polymer with monovinyl terminal, divinyl terminal corresponding to a pendant vinyl group, and divinyl terminal corresponding to a crosslink, respectively. These terms are defined by

$$P\equiv\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty}P_{p,q,r} \qquad (5)$$

$$Q\equiv\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty}Q_{p,q,r} \qquad (6)$$

$$R\equiv\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty}R_{p,q,r} \qquad (7)$$

The equation for the divinyl monomer M_2 is similarly expressed as:

$$r_{\mathrm{M}_2}=-2[k_{\mathrm{i}_2}A+(k_{\mathrm{p}_{12}}+k_{\mathrm{f}_{12}})P+(k_{\mathrm{p}_{22}}+k_{\mathrm{f}_{22}})Q+(k_{\mathrm{p}_{32}}+k_{\mathrm{f}_{32}})R]M_2 \qquad (8)$$

Several equations may be written for the rates of the various types of living polymer, as follows. Living polymer $\mathrm{P}_{p,q,r}$:

$$\begin{aligned}r_{\mathrm{P}_{p,q,r}}&=(k_{\mathrm{p}_{11}}P_{p-1,q,r}+k_{\mathrm{p}_{21}}Q_{p-1,q,r}+k_{\mathrm{p}_{31}}R_{p-1,q,r})M_1\\&-[k_{\mathrm{i}_3}A+(k_{\mathrm{p}_{13}}+k_{\mathrm{f}_{13}})P+(k_{\mathrm{p}_{23}}+k_{\mathrm{f}_{23}})Q\\&+(k_{\mathrm{p}_{33}}+k_{\mathrm{f}_{33}})R][qP_{p,q,r}-(q+1)P_{p,q+1,r-1}]\\&-[(k_{\mathrm{p}_{11}}+k_{\mathrm{f}_{11}})M_1+2(k_{\mathrm{p}_{12}}+k_{\mathrm{f}_{12}})M_2+(k_{\mathrm{p}_{13}}+k_{\mathrm{f}_{13}})M_3\\&+(k_{\mathrm{tc}_{11}}+k_{\mathrm{td}_{11}})P+(k_{\mathrm{tc}_{12}}+k_{\mathrm{td}_{12}})Q+(k_{\mathrm{tc}_{13}}+k_{\mathrm{td}_{13}})R]P_{p,q,r}\end{aligned} \qquad (9)$$

Total living polymer P:

$$\begin{aligned}r_{\mathrm{P}}&=[k_{\mathrm{i}_1}A+(k_{\mathrm{p}_{21}}+k_{\mathrm{f}_{21}})Q+(k_{\mathrm{p}_{31}}+k_{\mathrm{f}_{31}})R]M_1\\&-[2(k_{\mathrm{p}_{12}}+k_{\mathrm{f}_{12}})M_2+(k_{\mathrm{p}_{13}}+k_{\mathrm{f}_{13}})M_3\\&+(k_{\mathrm{tc}_{11}}+k_{\mathrm{td}_{11}})P+(k_{\mathrm{tc}_{12}}+k_{\mathrm{td}_{12}})Q+(k_{\mathrm{tc}_{13}}+k_{\mathrm{td}_{13}})R]P\end{aligned} \qquad (10)$$

Living polymer $\mathrm{Q}_{p,q,r}$:

$$\begin{aligned}r_{\mathrm{Q}_{p,q,r}}&=2(k_{\mathrm{p}_{12}}P_{p,q-1,r}+k_{\mathrm{p}_{22}}Q_{p,q-1,r}+k_{\mathrm{p}_{32}}R_{p,q-1,r})M_2\\&-(k_{\mathrm{i}_3}A+(k_{\mathrm{p}_{13}}+k_{\mathrm{f}_{13}})P+(k_{\mathrm{p}_{23}}+k_{\mathrm{f}_{23}})Q\\&+(k_{\mathrm{p}_{33}}+k_{\mathrm{f}_{33}})R]q(Q_{p,q,r}-Q_{p,q+1,r-1})\\&-[(k_{\mathrm{p}_{21}}+k_{\mathrm{f}_{21}})M_1+2(k_{\mathrm{p}_{22}}+k_{\mathrm{f}_{22}})M_2+(k_{\mathrm{p}_{23}}+k_{\mathrm{f}_{23}})M_3\\&+(k_{\mathrm{tc}_{12}}+k_{\mathrm{td}_{12}})P+(k_{\mathrm{tc}_{22}}+k_{\mathrm{td}_{22}})Q+(k_{\mathrm{tc}_{23}}+k_{\mathrm{td}_{23}})R]Q_{p,q,r}\end{aligned} \qquad (11)$$

Total living polymer Q:

$$\begin{aligned}r_{\mathrm{Q}}={}&2[k_{\mathrm{i}_2}A+(k_{\mathrm{p}_{12}}+k_{\mathrm{f}_{12}})P+(k_{\mathrm{p}_{32}}+k_{\mathrm{f}_{32}})R]M_2\\&-[k_{\mathrm{i}_3}A+(k_{\mathrm{p}_{13}}+k_{\mathrm{f}_{13}})P+(k_{\mathrm{p}_{23}}+k_{\mathrm{f}_{23}})Q+(k_{\mathrm{p}_{33}}+k_{\mathrm{f}_{33}})R\\&+(k_{\mathrm{p}_{21}}+k_{\mathrm{f}_{21}})M_1+(k_{\mathrm{p}_{23}}+k_{\mathrm{f}_{23}})M_3\\&+(k_{\mathrm{tc}_{12}}+k_{\mathrm{td}_{12}})P+(k_{\mathrm{tc}_{22}}+k_{\mathrm{td}_{22}})Q+(k_{\mathrm{tc}_{23}}+k_{\mathrm{td}_{23}})R]Q\qquad(12)\end{aligned}$$

Living polymer $\mathrm{R}_{p,q,r}$:

$$\begin{aligned}r_{\mathrm{R}_{p,q,r}}={}&(k_{\mathrm{p}_{13}}P_{p,q,r-1}+k_{\mathrm{p}_{23}}Q_{p,q,r-1}+k_{\mathrm{p}_{33}}R_{p,q,r-1})M_3\\&-[k_{\mathrm{i}_3}A+(k_{\mathrm{p}_{13}}+k_{\mathrm{f}_{13}})P+(k_{\mathrm{p}_{23}}+k_{\mathrm{f}_{23}})Q+(k_{\mathrm{p}_{33}}+k_{\mathrm{f}_{33}})R]\\&\times[qR_{p,q,r}-(q+1)R_{p,q+1,r-1}-Q_{p,q+1,r-1}]\\&-[(k_{\mathrm{p}_{31}}+k_{\mathrm{f}_{31}})M_1+2(k_{\mathrm{p}_{32}}+k_{\mathrm{f}_{32}})M_2+(k_{\mathrm{p}_{33}}+k_{\mathrm{f}_{33}})M_3\\&+(k_{\mathrm{tc}_{13}}+k_{\mathrm{td}_{13}})P+(k_{\mathrm{tc}_{23}}+k_{\mathrm{td}_{23}})Q+(k_{\mathrm{tc}_{33}}+k_{\mathrm{td}_{33}})R]R_{p,q,r}\qquad(13)\end{aligned}$$

Total living polymer R:

$$\begin{aligned}r_{\mathrm{R}}={}&[k_{\mathrm{i}_3}A+(k_{\mathrm{p}_{13}}+k_{\mathrm{f}_{13}})P+(k_{\mathrm{p}_{23}}+k_{\mathrm{f}_{23}})Q]M_3\\&+[k_{\mathrm{i}_3}A+(k_{\mathrm{p}_{13}}+k_{\mathrm{f}_{13}})P+(k_{\mathrm{p}_{23}}+k_{\mathrm{f}_{23}})Q+(k_{\mathrm{p}_{33}}+k_{\mathrm{f}_{33}})R]Q\\&-[(k_{\mathrm{p}_{31}}+k_{\mathrm{f}_{31}})M_1+2(k_{\mathrm{p}_{32}}+k_{\mathrm{f}_{32}})M_2\\&+(k_{\mathrm{tc}_{13}}+k_{\mathrm{td}_{13}})P+(k_{\mathrm{tc}_{23}}+k_{\mathrm{td}_{23}})Q+(k_{\mathrm{tc}_{33}}+k_{\mathrm{td}_{33}})R]R\qquad(14)\end{aligned}$$

Finally, the rate expression for dead polymer $\mathrm{M}_{p,q,r}$ is given by

$$\begin{aligned}r_{\mathrm{M}_{p,q,r}}={}&[k_{\mathrm{f}_{11}}M_1+2k_{\mathrm{f}_{12}}M_2+k_{\mathrm{f}_{13}}M_3]P_{p,q,r}\\&+[k_{\mathrm{f}_{21}}M_1+2k_{\mathrm{f}_{22}}M_2+k_{\mathrm{f}_{23}}M_3]Q_{p,q,r}\\&+[k_{\mathrm{f}_{31}}M_1+2k_{\mathrm{f}_{32}}M_2+k_{\mathrm{f}_{33}}M_3]R_{p,q,r}\\&-[k_{\mathrm{i}_3}A+(k_{\mathrm{p}_{13}}+k_{\mathrm{f}_{13}})P+(k_{\mathrm{p}_{23}}+k_{\mathrm{f}_{23}})Q+(k_{\mathrm{p}_{33}}+k_{\mathrm{f}_{33}})R]\\&\times[qM_{p,q,r}-(q+1)M_{p,q+1,r-1}]\\&+\tfrac{1}{2}k_{\mathrm{tc}_{11}}\sum_{x=0}^{p}\sum_{y=0}^{q}\sum_{z=0}^{r}P_{x,y,z}P_{p-x,q-y,r-z}\\&+k_{\mathrm{tc}_{12}}\sum_{x=0}^{p}\sum_{y=0}^{q}\sum_{z=0}^{r}P_{x,y,z}Q_{p-x,q-y,r-z}\\&+k_{\mathrm{tc}_{13}}\sum_{x=0}^{p}\sum_{y=0}^{q}\sum_{z=0}^{r}P_{x,y,z}R_{p-x,q-y,r-z}\\&+\tfrac{1}{2}k_{\mathrm{tc}_{22}}\sum_{x=0}^{p}\sum_{y=0}^{q}\sum_{z=0}^{r}Q_{x,y,z}Q_{p-x,q-y,r-z}\\&+k_{\mathrm{tc}_{23}}\sum_{x=0}^{p}\sum_{y=0}^{q}\sum_{z=0}^{r}Q_{x,y,z}R_{p-x,q-y,r-z}\\&+\tfrac{1}{2}k_{\mathrm{tc}_{33}}\sum_{x=0}^{p}\sum_{y=0}^{q}\sum_{z=0}^{r}R_{x,y,z}R_{p-x,q-y,r-z}\\&+(k_{\mathrm{td}_{11}}P+k_{\mathrm{td}_{12}}Q+k_{\mathrm{td}_{13}}R)P_{p,q,r}+(k_{\mathrm{td}_{12}}P+k_{\mathrm{td}_{22}}Q\\&+k_{\mathrm{td}_{23}}R)Q_{p,q,r}+(k_{\mathrm{td}_{13}}P+k_{\mathrm{td}_{23}}Q+k_{\mathrm{td}_{33}}R)R_{p,q,r}\qquad(15)\end{aligned}$$

The moments of the molecular weight distribution, $\psi_{i,j,k}$, of crosslinked copolymer for the total polymer can be calculated from the previous rate expressions:

$$\psi_{i,j,k}\equiv\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty}p^iq^jr^k(P_{p,q,r}+Q_{p,q,r}+R_{p,q,r}+M_{p,q,r})\qquad(16)$$

Here i, j and k are integers. By definition,

$$\psi_{0,1,0}\equiv M_3\qquad(17)$$

Based on the definition of the distribution moments, one may obtain the rate equations for the first few moments. The rate equation for the concentration of total polymer is:

$$\begin{aligned}r_{\psi_{0,0,0}}={}&(k_{\mathrm{i}_1}M_1+2k_{\mathrm{i}_2}M_2+k_{\mathrm{i}_3}M_3)A\\&+[k_{\mathrm{f}_{11}}M_1+2k_{\mathrm{f}_{12}}M_2+k_{\mathrm{f}_{13}}M_3]P\\&+[k_{\mathrm{f}_{21}}M_1+2k_{\mathrm{f}_{22}}M_2+k_{\mathrm{f}_{23}}M_3]Q\\&+[k_{\mathrm{f}_{31}}M_1+2k_{\mathrm{f}_{32}}M_2+k_{\mathrm{f}_{33}}M_3]R\\&-\tfrac{1}{2}k_{\mathrm{tc}_{11}}P^2-k_{\mathrm{tc}_{12}}PQ-k_{\mathrm{tc}_{13}}PR\\&-\tfrac{1}{2}k_{\mathrm{tc}_{22}}Q^2-k_{\mathrm{tc}_{23}}QR-\tfrac{1}{2}k_{\mathrm{tc}_{33}}R^2\qquad(18)\end{aligned}$$

The rate equation for the concentration of monovinyl units in the polymer is:

$$r_{\psi_{1,0,0}}=[k_{\mathrm{i}_1}A+(k_{\mathrm{p}_{11}}+k_{\mathrm{f}_{11}})P+(k_{\mathrm{p}_{21}}+k_{\mathrm{f}_{21}})Q+(k_{\mathrm{p}_{31}}+k_{\mathrm{f}_{31}})R]M_1\qquad(19)$$

The rate equation for the concentration of pendant vinyl groups in the polymer is:

$$\begin{aligned}r_{\psi_{0,1,0}}={}&2[k_{\mathrm{i}_2}A+(k_{\mathrm{p}_{12}}+k_{\mathrm{f}_{12}})P+(k_{\mathrm{p}_{22}}+k_{\mathrm{f}_{22}})Q+(k_{\mathrm{p}_{32}}+k_{\mathrm{f}_{32}})R]M_2\\&-[k_{\mathrm{i}_3}A+(k_{\mathrm{p}_{13}}+k_{\mathrm{f}_{13}})P+(k_{\mathrm{p}_{23}}+k_{\mathrm{f}_{23}})Q+(k_{\mathrm{p}_{33}}+k_{\mathrm{f}_{33}})R]M_3\qquad(20)\end{aligned}$$

Finally, the rate equation for the concentration of crosslinks is:

$$r_{\psi_{0,0,1}}=2[k_{\mathrm{i}_3}A+(k_{\mathrm{p}_{13}}+k_{\mathrm{f}_{13}})P+(k_{\mathrm{p}_{23}}+k_{\mathrm{f}_{23}})Q+(k_{\mathrm{p}_{33}}+k_{\mathrm{f}_{33}})R]M_3\qquad(21)$$

Invoking the quasi-steady-state approximation for the initiated radical A, equation (22) is obtained:

$$(k_{\mathrm{i}_1}M_1+2k_{\mathrm{i}_2}M_2+k_{\mathrm{i}_3}M_3)A=2fk_{\mathrm{d}}I\qquad(22)$$

Thus, equation (18) becomes:

$$\begin{aligned}r_{\psi_{0,0,0}}={}&2fk_{\mathrm{d}}I+[k_{\mathrm{f}_{11}}M_1+2k_{\mathrm{f}_{12}}M_2+k_{\mathrm{f}_{13}}M_3]P\\&+[k_{\mathrm{f}_{21}}M_1+2k_{\mathrm{f}_{22}}M_2+k_{\mathrm{f}_{23}}M_3]Q\\&+[k_{\mathrm{f}_{31}}M_1+2k_{\mathrm{f}_{32}}M_2+k_{\mathrm{f}_{33}}M_3]R\\&-\tfrac{1}{2}k_{\mathrm{tc}_{11}}P^2-k_{\mathrm{tc}_{12}}PQ-k_{\mathrm{tc}_{13}}PR\\&-\tfrac{1}{2}k_{\mathrm{tc}_{22}}Q^2-k_{\mathrm{tc}_{23}}QR-\tfrac{1}{2}k_{\mathrm{tc}_{33}}R^2\qquad(23)\end{aligned}$$

Gel point

The copolymerization/crosslinking reaction results eventually in the formation of a polymer network. The gel point corresponds to the incipient formation of the polymer network.

The moments of the molecular weight distribution of the crosslinked copolymer can be used to calculate important structural parameters of the polymer network[10], such as the average number of effective crosslinks per linear chain, ν_{e}, where effective crosslinks are those resulting from intermolecular crosslinking reactions:

$$\nu_{\mathrm{e}}=\psi_{0,0,1}/\psi_{0,0,0}\qquad(24)$$

The time corresponding to the gel point, namely the gelation time, can be calculated by solving the proposed kinetic model. It corresponds to an average number of crosslinks per primary polymer chain equal to 2:

$$\nu_e = 2 \tag{25}$$

RESULTS AND DISCUSSION

The kinetic model just presented can be solved for the copolymerization/crosslinking reaction of monovinyl–divinyl comonomers to predict the rates, conversions, molecular weights and number of effective crosslinks as a function of time before and after the gel point. Of particular interest to us is the prediction of the structural characteristics of networks prepared by copolymerization of styrene with either *m*-divinylbenzene or *p*-divinylbenzene. Recently, Hild and Okasha[9] offered experimental data for these reactions, carried out in a batch solution polymerization reactor at 60°C. To evaluate the applicability of the model in such reactions, the experimental conditions and data of Hild and Okasha[9] are used and compared to the predictions of the model.

The initiator and the solvent used were azobisisobutyronitrile (AIBN) and benzene, respectively. The initial concentration of initiator was $I_0 = 0.08\,\mathrm{mol\,l^{-1}}$, whereas that of styrene was $M_{1_0} = 4\,\mathrm{mol\,l^{-1}}$. Also, the initial concentrations of *m*- and *p*-divinylbenzene were $M_{2_0} = 0.08\,\mathrm{mol\,l^{-1}}$ and $M_{2_0} = 0.086\,\mathrm{mol\,l^{-1}}$, respectively. The relative amount of the divinyl monomer was expressed by the value of the crosslinking ratio X, which is defined as the ratio of the initial divinyl to monovinyl monomer concentration. In most cases low values of crosslinking ratio are sufficient to cause gelation (e.g. $X \simeq 0.001$)[12]. However, the initial concentration of the initiator and the polymerization temperature may also affect the gelation process[10].

It must be noted that the kinetic model developed here neglects intramolecular cyclization reactions. Therefore, it is valid for low values of the crosslinking ratio. Consequently, it is reasonable to assume that the concentrations of the living polymer chains with a divinyl monomer terminal group are approximately equal to zero:

$$Q \simeq 0 \quad \text{and} \quad R \simeq 0 \tag{26}$$

For the polymerization systems considered, the termination by disproportionation can be ignored because the termination reaction of two polymer radicals occurs by coupling[13]. The chain transfer to monomer reactions can be neglected because the transfer constant to the monomer at 60°C is[13] 6×10^{-5}. The chain transfer to solvent reaction is also neglected as the solvent used by Hild and Okasha[9] (benzene) is known to have a very low chain transfer constant, equal to[14] 2.3×10^{-6}. Nevertheless, the proposed kinetic model can be easily extended to include the chain transfer to solvent reactions.

Invoking now the quasi-steady-state approximation for the total living polymer with a styrene terminal group P, equations (10), (12), (14) and (22) lead to

$$P = \left(\frac{2fk_d I}{k_{tc_{11}}}\right)^{1/2} \tag{27}$$

The values of the kinetic constants, corresponding to the homopolymerization of styrene, are[14]: $k_d = 0.85 \times 10^{-5}\,\mathrm{s^{-1}}$, $k_{p_{11}} = 145\,\mathrm{l\,mol^{-1}\,s^{-1}}$, $k_{tc_{11}} = 2.9 \times 10^{7}\,\mathrm{l\,mol^{-1}\,s^{-1}}$. The reactivity ratios r_{12} of styrene with the first double bond of the *m*- and *p*-divinylbenzene are[9] 0.88 and 1.18, respectively.

The reactor volume can be assumed constant during the polymerization. Hence, the rate of change of any species is equal to the corresponding reaction rate. The initial initiator and monomer concentrations used in the calculations are those used by Hild and Okasha[9]. The initial condition of any distribution moment of the crosslinked copolymer is zero:

$$\psi_{i,j,k}(0) = 0 \tag{28}$$

Equations (1) and (4) can be solved by invoking the long-chain approximation, to yield:

$$\ln\left(\frac{M_{1_0}}{M_1}\right) = 2k_{p_{11}}\left(\frac{2fI_0}{k_d k_{tc_{11}}}\right)^{1/2}\left[1 - \exp\left(-\frac{k_d t}{2}\right)\right] \tag{29}$$

Therefore, the initiator efficiency f can be determined from the experimental data by plotting $\ln(M_{1_0}/M_1)$ vs. $[1 - \exp(-k_d t/2)]$. Using the previously mentioned values of the kinetic constants and the experimental data of Hild and Okasha[9], we have calculated the initiator efficiency for the styrene/*m*-divinylbenzene reaction to be equal to 0.45 and that for the styrene/*p*-divinylbenzene system to be 0.77.

The calculated monomer conversions until gelation are compared with the experimental data[9] in *Figures 2* and *3* for the copolymerization/crosslinking reaction of styrene with *m*- and *p*-divinylbenzene, respectively. It is seen that the predictions of the kinetic model are in good agreement with experimental results. Although autoacceleration of the polymerization reaction might have been expected due to formation of highly branched polymer chains, it is apparent from *Figures 2* and *3* that such a behaviour (gel effect) is not observed up to the gel point.

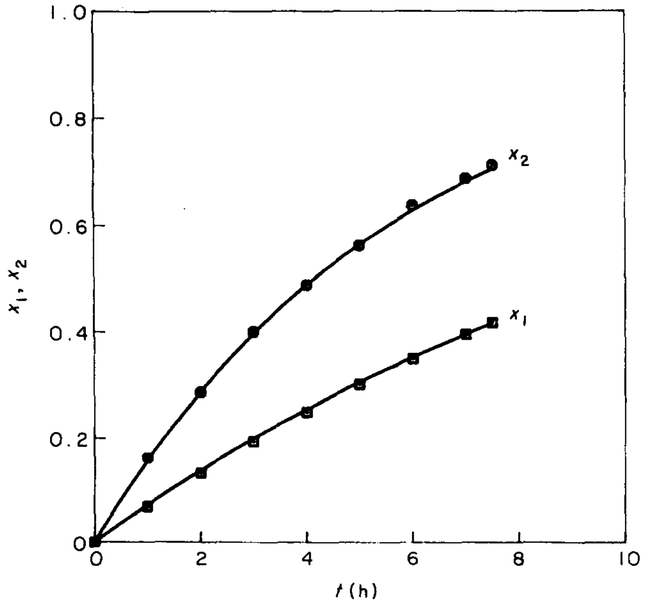

Figure 2 Calculated conversions of styrene x_1 and *m*-divinylbenzene x_2 during the copolymerization/crosslinking reaction of styrene with *m*-divinylbenzene; the experimental data for the styrene (□) and the *m*-divinylbenzene (○) conversions were obtained by Hild and Okasha[9] ($T = 60°\mathrm{C}$, $I_0 = 0.08\,\mathrm{mol\,l^{-1}}$, $M_{1_0} = 4\,\mathrm{mol\,l^{-1}}$ and $M_{2_0} = 0.08\,\mathrm{mol\,l^{-1}}$)

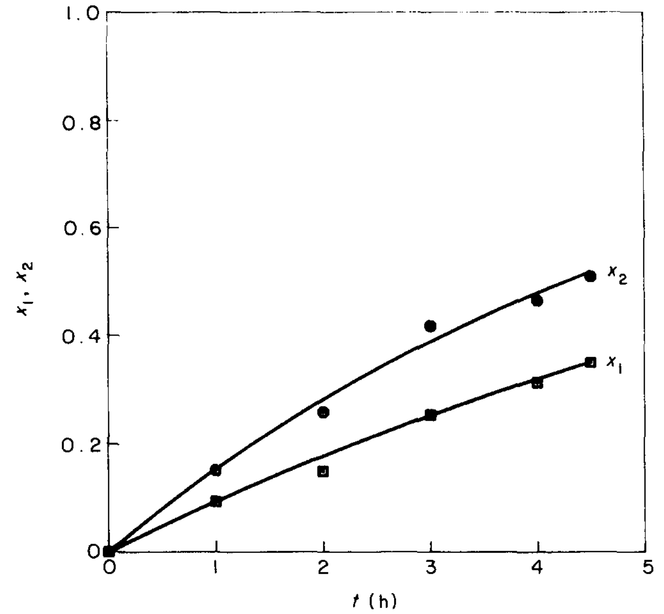

Figure 3 Calculated conversions of styrene x_1 and *p*-divinylbenzene x_2 during the copolymerization/crosslinking reaction of styrene with *p*-divinylbenzene; the experimental data for the styrene (□) and the *p*-divinylbenzene (○) conversions are obtained by Hild and Okasha[9] ($T = 60°\text{C}$, $I_0 = 0.08\,\text{mol}\,\text{l}^{-1}$, $M_{1_0} = 4\,\text{mol}\,\text{l}^{-1}$ and $M_{2_0} = 0.086\,\text{mol}\,\text{l}^{-1}$)

According to the values of the reactivity ratios of the first double bond, it is concluded that *m*-divinylbenzene is incorporated in the polymer faster than *p*-divinylbenzene. Consequently, one might expect that for the same polymerization conditions the gel time for the reaction of styrene with *m*-divinylbenzene would be smaller than the corresponding time for the styrene/*p*-divinylbenzene reaction. Yet, it is found[9] that the gel times for the copolymerization/crosslinking reaction of styrene with *m*- and *p*-divinylbenzene are 7.5 and 4.5 h, respectively. Thus, the reactivity of the second double bond is considerably smaller than that of the first one (at least for *m*-divinylbenzene). The crosslinking ratio in both cases was 0.02 and, therefore, any possible delay of gelation due to intramolecular crosslinking reactions can be neglected.

The change of the average number of crosslinks per polymer chain, ν_e, during the styrene/*m*-divinylbenzene reaction is shown in *Figure 4*. Assuming that the reactivity of the second double bond of *m*-divinylbenzene is the same as that of the first double bond, that is $k_{p_{12}} = k_{p_{13}}$, it is seen that, at the gelation time of 7.5 h, the number of crosslinks is equal to 4.53, which leads to the conclusion that the reactivities of the double bonds of *m*-dinvinylbenzene are dependent on each other at 60°C. The model predicts a gelation time of 7.5 h using the correct value of $\nu_e = 2$ only if the reactivity ratio r_{13} of styrene with the second double bond of *m*-divinylbenzene is 2.26.

Figure 5 shows the change of the number of crosslinks per chain for the copolymerization/crosslinking reaction of styrene with *p*-divinylbenzene, assuming that the reactivities of the vinyl groups of *p*-divinylbenzene are independent of each other. The value of ν_e corresponding to the observed gel time of 4.5 h is 2.03. Therefore, it is concluded that at 60°C the reactivity of the second double bond of *p*-divinylbenzene does not change once the first bond has reacted. This finding should not be extrapolated to other temperatures because the reactivity of the second double bond is different from that of the first one[11] at 90°C.

It is therefore interesting that the new kinetic model can predict the experimental data for reactions of styrene with *m*- or *p*-divinylbenzene.

CONCLUSIONS

A kinetic model for copolymerization/crosslinking reactions of monovinyl and divinyl comonomers was developed and applied to the case of styrene and *m*- or *p*-

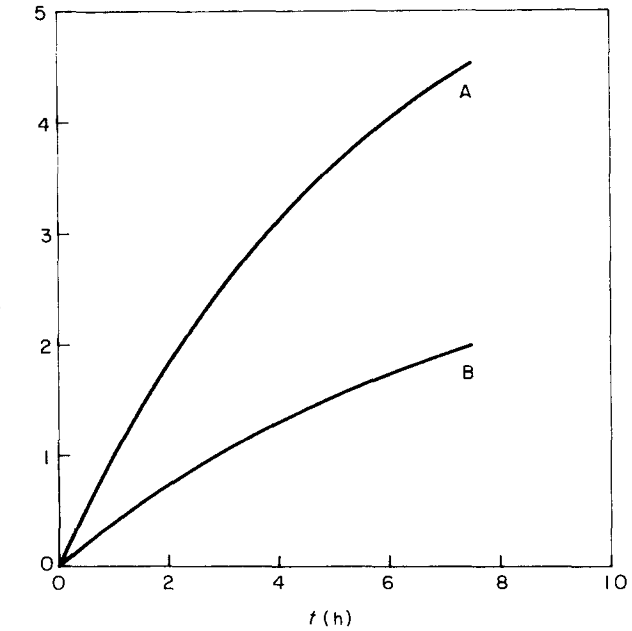

Figure 4 Change of the average number of crosslinks per polymer chain during the styrene/*m*-divinylbenzene reaction until gelation, assuming that the reactivities of the vinyl groups of the *m*-divinylbenzene are independent of each other (curve A) and dependent on each other (curve B) ($T = 60°\text{C}$, $I_0 = 0.08\,\text{mol}\,\text{l}^{-1}$, $M_{1_0} = 4\,\text{mol}\,\text{l}^{-1}$ and $M_{2_0} = 0.08\,\text{mol}\,\text{l}^{-1}$)

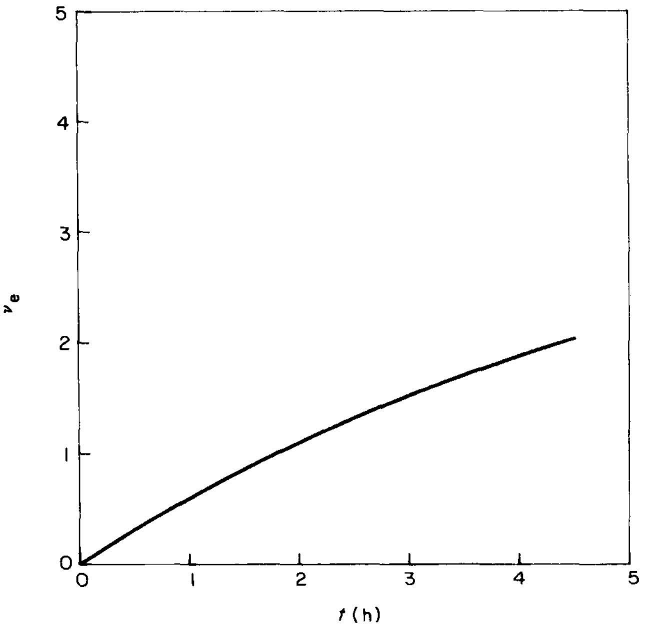

Figure 5 Change of the average number of crosslinks per polymer chain during the styrene/*p*-divinylbenzene reaction until gelation, assuming that the reactivities of the vinyl groups of the *p*-divinylbenzene are independent of each other ($T = 60°\text{C}$, $I_0 = 0.08\,\text{mol}\,\text{l}^{-1}$, $M_{1_0} = 4\,\text{mol}\,\text{l}^{-1}$ and $M_{2_0} = 0.086\,\text{mol}\,\text{l}^{-1}$)

divinylbenzene reaction. Using the data of Hild and Okasha[9], obtained by solution polymerization at 60°C, the monomer conversions could be predicted as a function of time.

For the reaction of styrene with *m*-divinylbenzene it was also shown that unequal reactivity of the two vinyl groups is exhibited at 60°C. However, for reactions of styrene with *p*-divinylbenzene at 60°C, the experimental results could be predicted by equal reactivity of the vinyl groups.

Finally, it was apparent from the previous analysis that the success of the kinetic model was pertinent to the evaluation of the correct values of the various kinetic constants. The reactivity ratios for the monovinyl–divinyl monomer copolymerization/crosslinking reactions are determined using the binary copolymerization equation, treating a divinyl monomer molecule as equivalent to two molecules of another monovinyl monomer. The validity of such a procedure might be questionable. The copolymerization equation of these reactions has been derived by Gibbs[15] and it has a complexity similar to that for ternary polymerization of three monovinyl monomers and it is only reduced to the binary copolymerization equation by assuming that the concentration of pendant vinyl groups does not change.

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