# Crosslinking kinetics in emulsion copolymerization of methyl methacrylate/ethylene glycol dimethacrylate

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A newly developed kinetic model for network structure development during emulsion crosslinking copolymerization of vinyl and divinyl monomer is used to investigate the kinetics of emulsion crosslinking copolymerization of methyl methacrylate and ethylene glycol dimethacrylate. The agreement of predicted with measured development of crosslinking density and that of monomer concentration in the polymer particles is found to be satisfactory. It is shown that the crosslinking density is fairly high even from very early stages of polymerization and that the produced polymeric networks tend to be highly heterogeneous. The kinetics of crosslinking and resulting network structure are essentially different from those for polymerizations in homogeneous media such as bulk and solution polymerization.

**(Keywords: polymeric network; gel; mathematical model; crosslinking density distribution; free-radical copolymerization)**

## INTRODUCTION

The kinetics of crosslinking in emulsion polymerization have received very little attention from academic and industrial researchers, considering the ever-growing importance of polymeric networks in commercial products made by emulsion polymerization processes. The physical and chemical properties of polymeric networks depend on the kinetics of polymerization, therefore an understanding of the mechanism and kinetics of network formation and growth is essential for the effective design of network structures.

Based on the pioneering work of Flory and Stockmayer[1–4], various statistical models have been developed for network formation[5–11]. In these mean-field approaches, the combination of molecules based on the most probable distribution is assumed, therefore these models cannot account for the heterogeneity of network structure, which has already been recognized experimentally[12–19]. Since free-radical polymerization is kinetically controlled, the history of the generated network structure must be accounted for. Although it may be possible to describe such non-equilibrium polymerizations by statistical methods[20,21], a kinetic model would be suitable for the comprehensive description of network structure development. Furthermore, kinetic models are easily applied to control various polymerization reactors including batch, semibatch and continuous stirred tank reactors.

Recently, a new kinetic theory for free-radical copolymerization with long chain branching and crosslinking has been proposed[22–28]. This kinetic theory accounts for the history of the generated network structure as well as for all of the important elementary reactions in free-radical copolymerization. This theory proves the existence and permits calculation of the crosslinking density distribution, although most statistical models inevitably employ the assumption that the crosslinking density is the same for all chains. By application of this theory, a kinetic model for emulsion crosslinking copolymerization was also developed[29]. In this paper, this newly developed model is applied to investigate the kinetics of network formation in emulsion crosslinking copolymerization of methyl methacrylate and ethylene glycol dimethacrylate.

## THEORETICAL

### *Network structure development*

In order to describe the crosslinked structure development, the structural change of a primary polymer molecule is considered. The process of the crosslinking reaction is shown schematically in *Figure 1*. As proposed in earlier papers[23–30], the crosslinking points are divided into two types: the crosslinking points that are formed during the formation of the primary polymer molecule are defined as the instantaneous crosslinking points, and those formed after the primary polymer molecule is formed are defined as the additional crosslinking points, as shown in *Figure 1*. Since a crosslinking point is defined as a unit that bears a tribranching point, the crosslinking density is given by the sum of these two types of crosslinking density. Therefore, at total monomer conversion $x=n$ ($n$ is used to designate the conversion at present time), the total number of crosslinking points on a given primary polymer molecule that was formed at $x=b$ ($b$ is used for the conversion at which the primary polymer molecule is born), is given by the sum of the crosslinking points formed during the formation of the

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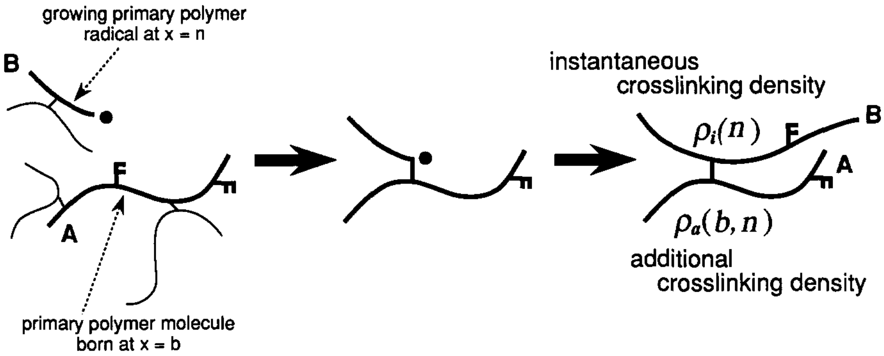

**Figure 1** Schematic drawing of the process of crosslinking. At $x=n$, the crosslinking density of the primary polymer molecules that were formed at $x=b$ is given by equation (1)

primary polymer molecule (instantaneous crosslinking density, $\rho_i(b)$) and the additional crosslinking points added in the conversion interval $b$ to $n$ (additional crosslinking density, $\rho_a(b,n)$):

$$\rho(b,n)=\rho_i(b)+\rho_a(b,n) \tag{1}$$

Fundamental equations for each type of crosslinking density can be derived from simple balance equations[24,27,28]. For batch emulsion copolymerization, they are given by[29]:

$$\frac{\partial\rho_a(b,n)}{\partial n}=\left(\frac{k_p^{*0}(n)}{k_p(n)}\right)\left\{\frac{F_2(b)-\rho_a(b,n)-\rho_c(b,n)}{([M]_n V(n))/N_0}\right\} \tag{2}$$

$$\rho_i(b)=\left(\frac{k_p^{*0}(b)}{k_p(b)}\right)\left(\frac{N_0 b}{[M]_b V(b)}\right)\{\bar{F}_2(b)-\bar{\rho}_a(b)-\bar{\rho}_c(b)\} \tag{3}$$

where $k_p^{*0}$ and $k_p$ are the pseudo-kinetic rate constants[22–29] for crosslinking and propagation reactions, respectively. $F_2$ is the instantaneous mole fraction of divinyl monomer bound in the polymer chains, $\rho_c$ is the cyclization density which is the mole fraction of pendant double bonds wasted by cyclization reactions, $N_0$ is the total number of moles of monomer initially charged, $[M]$ is the monomer concentration in the polymer particles, and $V$ is the volume of the polymer particles. The over-bars in equation (3) designate the accumulated values at a given conversion. Therefore, the right-hand side of equation (2) is the ratio between the crosslinking reaction rate of the primary polymer molecules formed at $x=b$ and the propagation rate of the reaction system. On the other hand, the right-hand side of equation (3) shows the ratio of the total crosslinking reaction rate in the system to the propagation rate.

On the basis of the present kinetic model for emulsion crosslinking copolymerization, it was shown[29] that (1) the average crosslinking density is fairly high even from very early stages of polymerization, and (2) polymer networks tend to be heterogeneous. Quite often, the crosslinking density of the primary polymer molecules formed at earlier stages of polymerization possess fairly high crosslinking densities.

Before quantitative comparison with experimental results is made, however, a mathematical model for cyclization reactions is required. In our formalism, it is convenient to divide the cyclization reactions into two groups, namely primary and secondary cyclization[25,27,28]. With primary cyclization the cycle forms within one primary polymer molecule, while with secondary cyclization it is formed between two or more primary polymer molecules. For primary cyclization, the following assumptions were employed[28,29]: (1) the conformation of each primary polymer molecule follows the Gaussian distribution with an appropriate scaling law for its size, disregarding the correlation due to already existing crosslinks and cycles; (2) the chain length of the primary polymer molecule is sufficiently large. On the basis of these assumptions, the primary cyclization density of the primary polymer molecules that were formed at $x=b$ is given by[25,27,28]:

$$\rho_{cp}(b)=k_{cp}F_2(b) \tag{4}$$

where $k_{cp}$ is a rate constant for the primary cyclization reactions.

For secondary cyclizations we assume that the average number of secondary cycles per crosslink, $\eta$, is constant as a simple approximation[27]. Under these assumptions, the elastic crosslinking density[27], which was defined as the sum of the crosslinking density and secondary cyclization, is given by[29]:

$$\frac{\partial\rho_{el,a}(b,n)}{\partial n}=\left[\frac{k_{p,e}^{*0}(n)}{k_p(n)}\right]\left\{\frac{[1-k_{cp}(b)]F_2(b)-\rho_{el,a}(b,n)}{([M]_n V(n))/N_0}\right\} \tag{5}$$

$$\rho_{el,i}(b)=\left[\frac{k_{p,e}^{*0}(b)}{k_p(b)}\right]\left[\frac{N_0 b}{[M]_b V(b)}\right]\{[1-k_{cp}(b)]\bar{F}_2(b)-\bar{\rho}_{el,a}(b)\} \tag{6}$$

$$\rho_{el}(b,n)=\rho_{el,i}(b)+\rho_{el,a}(b,n) \tag{7}$$

where $k_p^{*0}=(1+\eta)k_p^{*0}$.

The accumulated elastic crosslinking density is given by:

$$\frac{d(x\bar{\rho}_{el}(x))}{dx}=2\left[\frac{k_{p,e}^{*0}(x)}{k_p(x)}\right]\left[\frac{N_0 x}{[M]_x V(x)}\right]\left\{[1-k_{cp}(x)]\bar{F}_2(x)-\frac{\bar{\rho}_{el}(x)}{2}\right\} \tag{8}$$

If $k_{cp}$ is known, the accumulated elastic crosslinking density, $\bar{\rho}_{el}$ can be determined experimentally by measuring the number of unreacted pendant double bonds on the polymer chains. The magnitude of $k_{cp}$ depends on the molecular conformation of the primary polymer molecules. It may be reasonable to assume that the chain conformation of the primary polymer molecules in the polymer particles is similar to that in a monomer mixture, and therefore $k_{cp}$ may be determined from the experimental results in bulk polymerization. It is expected that the effect of the primary cyclization is small for polymerization without solvent[27,31–33]. For the bulk copolymerization of methyl methacrylate and ethylene glycol dimethacrylate, it is reported that the $k_{cp}$ value is very small[28,32], i.e. $k_{cp} \approx 0.03$, and therefore the effect of primary cyclization is neglected in the present experimental system.

The crosslinking densities used so far are defined with respect to monomeric unit, namely:

$$\rho = \frac{(\text{no. of crosslinked units})}{(\text{total no. of monomeric units bound in the polymer chain})} \tag{9}$$

On the other hand, from the point of view of the elastic properties of polymer networks, the crosslinking density defined as the fraction of units which are crosslinked may be important, namely:

$$\rho^{f} = \frac{(\text{no. of crosslinked units})}{(\text{total no. of units bound in the polymer chain})} \tag{10}$$

The relationship between these two types of crosslinking density is given by[25–28]:

$$\rho^{f}(b, n) = \frac{\rho(b, n)}{1 + \rho_{i}(b)} \tag{11}$$

*Monomer concentration in the polymer particles*

Taking into account the elastic free energy change due to the crosslinked network structure as well as free energy contributions of mixing and interfacial tension, the monomer concentration in the polymer particles can be estimated by the following equation[29]:

$$G = -\phi_{p}^{5/3}\left\{\chi_{1} + \frac{1}{\phi_{p}} + \frac{\ln(1-\phi_{p})}{\phi_{p}^{2}}\right\} - C\left(1 - \frac{\phi_{p}^{2/3}}{2}\right) \tag{12}$$

where $G$ and $C$ are given by:

$$G \equiv \frac{2\bar{M}_{M}\gamma}{RTr_{0}d_{M}} \tag{13}$$

$$C \equiv \left(\frac{d_{P}}{d_{M}}\right)\bar{\rho}_{el}^{f} \tag{14}$$

In the above equations, $\chi_1$ is the interaction parameter for the particular monomer–polymer pair, $\bar{M}_M$ is the average molecular weight of monomeric unit of the monomer mixture in the polymer particles, $\gamma$ is the interfacial tension, $r_0$ is the radius of the unswollen polymer particle, $d_M$ and $d_P$ are the densities of monomer and polymer, respectively, and $\phi_p$ is the volume fraction of polymer in the polymer particles. If $\phi_p$ can be calculated, the monomer concentration in the polymer particles is obtained.

The problem with the application of equation (12) to real systems is that the interfacial tension $\gamma$ is not available. In order to calculate $\phi_p$, we used the following method for convenience[29]. It is known that the volume fraction of monomer in polymer particles remains approximately constant until the end of interval II (as long as the separate monomer phase exists) for a number of monomers with linear polymerization, i.e. for $C=0$. This implies that the free energy contribution of interfacial tension, $G$, can be approximated as a constant until the end of interval II for linear polymerization. For linear polymerization, since $\phi_p$ is known for various types of monomer, it is possible to calculate $G$. Therefore, by applying the value of $G$ for the corresponding monovinyl monomer (methyl methacrylate in the present case), it is possible to use equation (12) and to estimate the effect of crosslinked network structure on the equilibrium monomer concentration in the polymer particles.

## EXPERIMENTAL

The monovinyl monomer, methyl methacrylate (MMA), was purified by distillation after being washed with 10% aqueous potassium hydroxide to remove inhibitor. The divinyl monomer, ethylene glycol dimethacrylate (EGDMA), was washed in a similar way to remove inhibitor. Sodium lauryl sulfate and potassium persulfate of extra pure grade were used without further purification as emulsifier and initiator, respectively.

The reactor used was a 400 ml cylindrical glass vessel with a dished bottom, equipped with a four-bladed paddle-type impeller. Four baffle plates were set on the vessel wall at 90° intervals. After the desired amounts of water, emulsifier and monomer mixture were fed to the reactor, the dissolved oxygen was removed by bubbling nitrogen gas for 30 min. The polymerization was started by injecting aqueous initiator solution which had also been deaerated by bubbling nitrogen gas. The polymerization was carried out at 50°C using a water bath with thermostat. The impeller speeds were kept constant at 450 rev $\text{min}^{-1}$ during polymerization.

Concentrations used were 200 g $l^{-1}$ water for the total monomer, 1.0 g $l^{-1}$ water for sodium lauryl sulfate, and 0.625 g $l^{-1}$ water for potassium persulfate.

Total monomer conversion was determined gravimetrically using methanol as precipitant. The concentration of each monomer was determined by gas chromatography. The number of pendant double bonds was measured by the combustion flask method for the determination of the amount of halide in organic compounds[34,35] after the bromination of the polymer samples in chloroform solution.

## RESULTS AND DISCUSSION

### *Kinetics of copolymerization*

The conversion–time histories for initial mole fraction of divinyl monomer $f_{20} = 0.0128$, 0.0259 and homopolymerization of MMA are shown in *Figure 2*. (In this paper, $f_{20}$ is used to designate the initial mole fraction of divinyl monomer in the monomer mixture.)

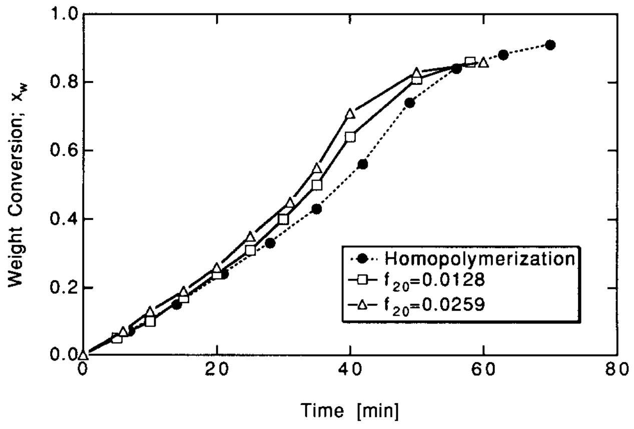

**Figure 2** Conversion–time histories for the copolymerization of MMA/EGDMA ($f_{20} = 0.0128$ and 0.0259) and homopolymerization of MMA

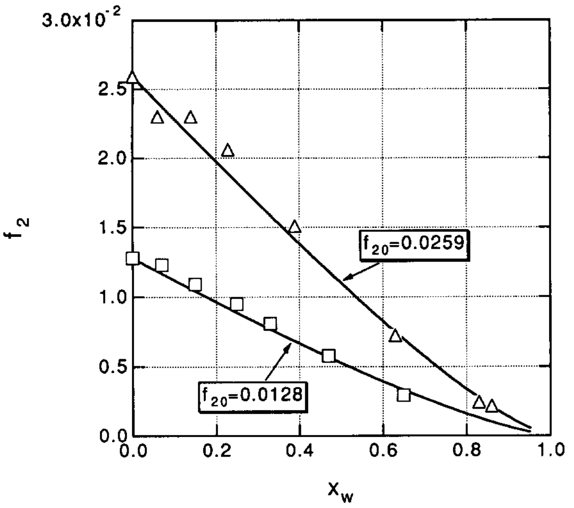

**Figure 3** Calculated and experimental compositional change of monomer mixture during polymerization ($r_1 = 0.43$, $r_2 = 2.0$)

The polymerization rate is essentially the same at low conversions; however, it increases as $f_{20}$ becomes larger at high conversions, possibly due to the decrease in bimolecular termination rate, i.e. the gel effect. It was reported that significantly more and smaller polymer particles are produced in emulsion polymerizations that contain divinyl monomers[36]; however, an increase in the number of polymer particles was not observed for the low $f_{20}$ investigated.

The compositional drifts of the monomer mixture, determined by gas chromatography, are shown in *Figure 3*. If the reactivities of all monomeric double bonds are equal, the reactivity ratios are expected to be 0.5 and 2.0. On the basis of the assumption that the monomer composition in the polymer particles is the same as that in the monomer droplets, the reactivity ratios of $r_1 = 0.43$ and $r_2 = 2.0$ appear to be satisfactory for the purpose of estimating the copolymer composition. In this paper, therefore, these apparent reactivity ratios are used.

### *Network structure development*

In the model calculations, it was assumed that all polymer particles are produced instantaneously at conversion $x = 0$. The nucleation mechanism, which is still controversial[37], may play a role in the development of network formation at the initial stage of polymerization; however, since the number of polymer particles becomes constant at less than 0.08 conversion in our experiments, the effect of nucleation period on the network structure development may be negligible. In the model calculations, the following parameters are used: $\chi_1 = 0.373$ (ref. 38); the conversion at which monomer droplets disappear, $x_c$ for the homopolymerization of MMA is 0.3 (ref. 39); the ratio of densities, $d_M/d_P = 0.775$; and $k_{cp} = 0$.

*Figure 4* shows the average elastic crosslinking density development. The average elastic crosslinking density was estimated experimentally by determining the number of unreacted pendant double bonds. By adjusting the parameter for the reactivity of pendant double bonds, $k_{p,e}^{*0}/k_p = 0.7$ and 0.6, the agreement with experimental data is satisfactory. Both experimental and calculated results show that the crosslinking density is fairly high even from a very early stage of polymerization. The average crosslinking density decreases slightly until the end of interval II, which results from the decrease in the crosslinking reaction rate relative to the propagation rate.

Aside from the intrinsic reactivity of the pendant double bonds, the reactivity of the pendant double bonds for crosslinking reactions may be affected by steric hindrance[40] and the excluded-volume effect[41]. The reported values of $k_{p,e}^{*0}/k_p$ for the bulk copolymerization of MMA and EGDMA[28,32] are larger than 10 for $f_{20} = 0.01$–$0.02$, which is much larger than the emulsion copolymerization. This large difference may be attributed to the difference of the molecular sizes of polymer radicals in the reaction system. In the case of bulk copolymerization, initiator radicals are generated inside the polymer–monomer mixture including gel molecules, and smaller polymer radicals with high mobility exist in much greater number than larger ones; therefore, both steric hindrance and the excluded-volume effect may have little effect on the overall crosslinking reaction rate and this makes polymer networks tighter. A tighter network structure enhances the tendency towards secondary cyclizations, which makes $k_{p,e}^{*0}/k_p$ values even larger. (Note that the effect of secondary cyclization is included in the parameter $k_{p,e}^{*0}/k_p$.) On the other hand, initiator radicals are generated in the water phase in emulsion polymerization, and the chain length of the primary polymer radicals is larger. The approach of growing polymer radicals to the pendant double bonds located in the network polymers may be hindered significantly. Higher polymer concentrations with longer primary polymer chains in emulsion polymerization may also contribute to the enhancement of steric effects as well as the decrease in the mobility of polymer chains.

*Figure 5* shows the experimental and calculated results for the monomer concentration in the polymer particles during polymerization. Note that no adjustable parameters are used in these calculations. For both the monomer concentrations and the conversion at which interval II ends, $x_c$ values agree satisfactorily with experimental results. Since the change in the average crosslinking density is small, the monomer concentration in the polymer particle is nearly constant until the end of interval II.

*Figure 6* shows the calculated crosslinking density distribution change during polymerization. Mainly due to a high crosslinking reaction rate at earlier stages of polymerization, the primary polymer molecules formed earlier possess very high crosslinking densities. Since the variance of the crosslinking density distribution is large,

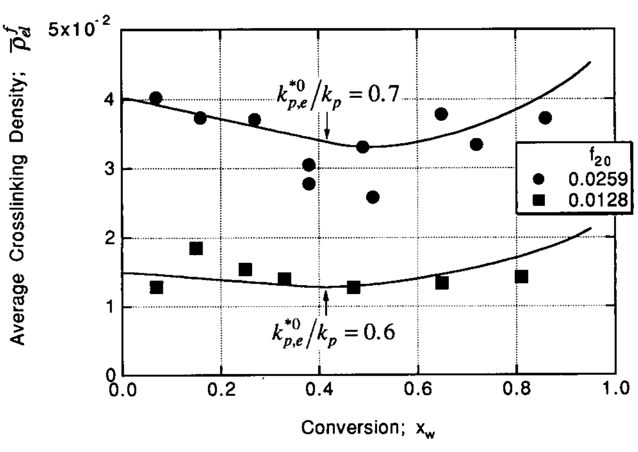

**Figure 4** Calculated and experimental average elastic crosslinking density development. The parameter for the reactivity of pendant double bonds, $k_{p,e}^{*0}/k_p$, used in the calculations is shown in the figure

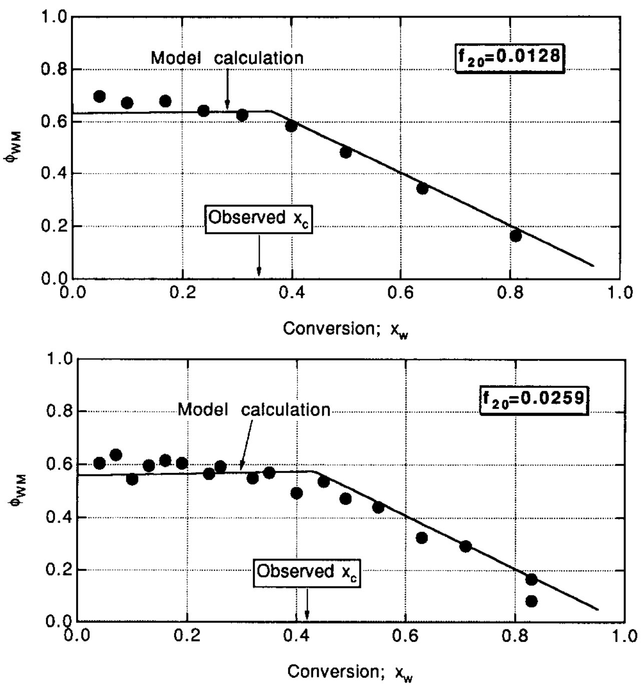

**Figure 5** Calculated and experimental monomer weight fraction in the polymer particles, $\phi_{WM}$

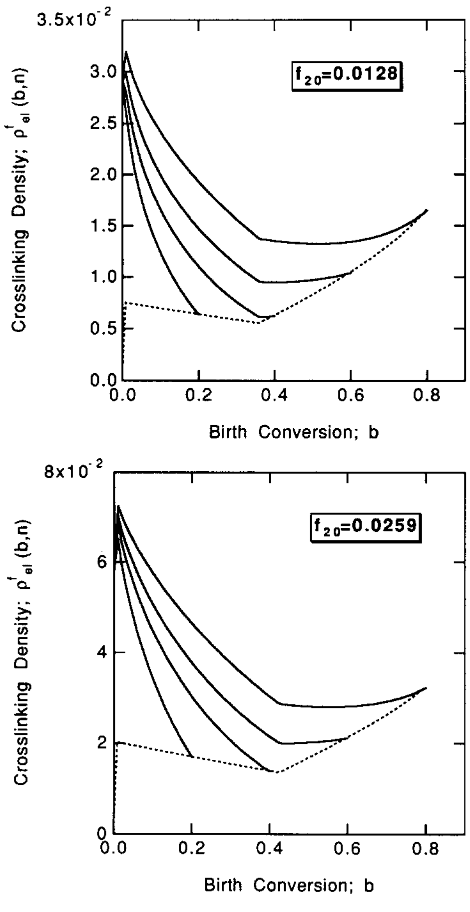

**Figure 6** Calculated crosslinking density distribution change during emulsion crosslinking copolymerization

the network structure inside these microspheres is expected to be heterogeneous. It is worth noting that the fact that the average crosslinking density does not change significantly during polymerization (see *Figure 4*) does not mean that the polymer network is homogeneously crosslinked, as shown clearly in *Figure 6*.

## CONCLUSIONS

A newly developed kinetic model for network structure development during emulsion crosslinking copolymerization of vinyl and divinyl monomer has been applied to investigate the kinetics of emulsion crosslinking copolymerization of MMA and EGDMA. The agreement of predicted with measured development of crosslinking density and that of monomer concentration in polymer particles is found to be satisfactory. The reactivity of pendant double bonds towards crosslinking, including secondary cyclization, is found to be much smaller than that for bulk polymerization. It is shown both experimentally and theoretically that the crosslinking density is fairly high even from very early stages of polymerization. From the calculated crosslinking density distribution, the polymeric networks produced are expected to be highly heterogeneous.

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