# Crosslinking kinetics in polyacrylamide networks

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Kinetics of network formation in free-radical copolymerization of acrylamide and *N*,*N*′-methylenebisacrylamide in aqueous solution (56.6 g comonomer per litre) at 25°C have been studied. It was found that as high as 80% of pendant double bonds are consumed immediately on polymerization and are wasted in primary cyclization. Primary cyclization is responsible for the delay in the onset of gelation at low mole fractions of divinyl monomer. The effects of decreased reactivity of pendant double bonds and secondary cyclization become significant as the mole fraction of divinyl monomer increases. The decreased reaction rate between huge molecules due to steric hindrance in the pre-gelation period contributes to microgel formation, and consequently to formation of spatially inhomogeneous networks.

**(Keywords: acrylamide; *N*,*N*′-methylenebisacrylamide; polyacrylamide; gels; crosslinking; cyclization; intramolecular reaction)**

## INTRODUCTION

It is well known that the Flory gelation model[1] functions best at low mole fractions of divinyl monomer, with the error increasing rapidly with increasing levels of divinyl monomer. The deviation from the Flory model has been attributed to the intramolecular reaction[2], namely cyclization, and to decreased reactivity of pendant double bonds[3]. In considering cyclization, it may be convenient to divide these reactions into two types, namely primary and secondary cyclization[4] (see *Figure 1*). With primary cyclization the cycle is formed within one primary polymer molecule, while with secondary cyclization it is formed between two or more primary polymer molecules. In the bulk copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA), it was found that secondary cyclization and the decreased reactivity of pendant double bonds are mainly responsible for the delay of the onset of gelation[4]. However, it is quite natural to suspect that the relative contributions of these three effects, namely decreased reactivity of pendant double bonds, primary cyclization and secondary cyclization, change with polymerization conditions.

Polyacrylamide gels are usually synthesized by copolymerization of acrylamide (AAm) and *N*,*N*′-methylenebisacrylamide (Bis) in aqueous solution. Various studies have shown that polyacrylamide gels are inhomogeneous[5], namely they possess regions having very different degrees of crosslinking density. Since Flory's idealized model[1] assumes that the crosslinking density is the same for all chains, copolymerization of AAm and Bis may be considered as a highly non-ideal system. In this paper, we clarify what kinds of non-ideality govern the copolymerization of AAm and Bis in aqueous solution. Also to be discussed is the formation mechanism of spatially inhomogeneous networks.

## PRELIMINARY CONSIDERATIONS

### *Process of crosslinking*

Network formation in free-radical polymerization is a non-equilibrium process, namely it is kinetically controlled, and therefore each primary polymer molecule experiences a different history of crosslinking and cyclization. Based on the chemical kinetics, it is possible to estimate the crosslinking density as a function of its birth time[6–10]. The existence of crosslinking density distribution shows that the polymer networks synthesized by free-radical polymerization are inherently inhomogeneous on a microscopic scale. The variance of the crosslinking density distribution becomes significant when the following non-ideal effects are important[8–10]:

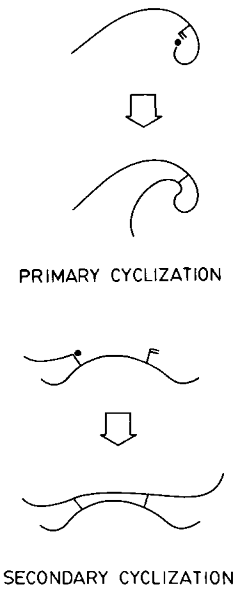

**Figure 1** Classification of cyclization processes

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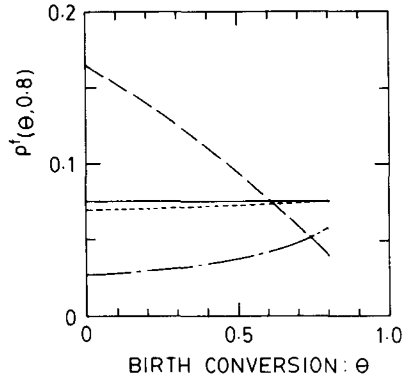

**Figure 2** Effect of monomeric double-bond reactivity on the crosslinking density of primary polymer molecules at total monomer conversion $x=0.8$. $\theta$ is the total monomer conversion at which the given primary polymer molecule was born. Initial mole fraction of divinyl monomer $f_{20}=0.05$. $(r_1^d, r_2^d)$= ——, (1.0, 1.0); --------, (1.14, 1.7); — — —, (0.5, 2.0); —·—, (2.0, 0.5)

(i) differences in the reactivities of monomeric double bonds;

(ii) decreased reactivity of pendant double bonds relative to monomeric double bonds; and

(iii) cyclization reactions.

Recently Baselga *et al.*[11] argued that differences in the reactivity of monomeric double bonds are responsible for inhomogeneous polyacrylamide networks. They determined the reactivity ratios from the change in copolymer composition during copolymerization, and found the reactivity ratio of the double bond on acrylamide, $r_1^d=1.14$, and that on *N,N'*-methylenebisacrylamide, $r_2^d=1.7$. *Figure 2* shows the crosslinking density of a primary polymer molecule at total monomer conversion $x=0.8$ as a function of monomer conversion $\theta$ when the given primary polymer molecule was born, namely $\rho^f(\theta, 0.8)$ is the crosslinking density at $x=0.8$ for the primary polymer molecule that was born at $x=\theta$. As is shown in *Figure 2*, the crosslinking density is the same for all primary polymer molecules regardless of their birth time when $r_1^d=r_2^d=1.0$, and, as the reactivity ratios $r_1^d$ and $r_2^d$ deviate from unity, the crosslinking density can differ appreciably with birth time. However, fairly large differences in the reactivities of monomeric double bonds would be necessary to account for the formation of inhomogeneous networks. The reactivity ratios, $r_1^d=1.14$ and $r_2^d=1.7$, clearly do not give a significant range of crosslinking densities and therefore differences in the reactivities of monomeric double bonds for the acrylamide system studied by Baselga *et al.* cannot explain the existence of inhomogeneous networks.

### *Process of cyclization*

One of the important features of a cyclization reaction is that it is controlled not by a conventional rate law which uses average concentrations of functional groups, but by conformational statistics of the sequence of bonds. As was shown in *Figure 1*, we differentiate primary and secondary cyclization. The mathematical importance of the difference between primary and secondary cyclization is that primary cyclization is solely a function of the birth time of a primary polymer molecule, while secondary cyclization is a function of both birth time and present time.

Based on the 'random-flight model', the primary cyclization density for the primary polymer molecule that was born at monomer conversion $x=\theta$ is given by the following equation if the chain length is sufficiently long[8]:

$$\rho_{cp}(\theta)=k_{cp}F_2(\theta) \tag{1}$$

where $F_2(\theta)$ is the instantaneous mole fraction of divinyl monomer bound in polymer chains at $x=\theta$. The above equation shows that the primary cyclization density is proportional to the mole fraction of divinyl monomer bound in polymer chains. Equation (1) can also be derived if one assumes that primary cyclization is formed solely with a small number of monomer units. The parameter $k_{cp}$ may be determined by extrapolating the pendant double-bond conversion $x_{pd}$ to zero monomer conversion $x=0$, since crosslinkages and secondary cycles do not exist at $x=0$, although it is unclear whether $k_{cp}$ may have a constant value throughout the polymerization. The applicability of equation (1) will be discussed later.

Secondary cyclization can be defined clearly in the pre-gelation period. However, it is ambiguous in the post-gelation period, since from a physical point of view it is impossible to distinguish it from crosslinking. Secondary cyclization may be recognized as an adjustable parameter or a correction factor in order to connect structural properties (such as crosslinking density) to mass properties (such as gel point, average molecular weight of sol fraction and weight fraction of gel in the post-gelation period). We will call the sum of crosslinking density $\rho$ and secondary cyclization $\rho_{cs}$ the elastic crosslinking density[8–10], $\rho_{el}$. (Please note that the elastic crosslinking density is not necessarily equal to the elastically effective crosslinking density.)

Although secondary cyclization is also governed by chain conformational statistics like primary cyclization, it may be convenient to consider the average number of secondary cycles per crosslink[8,10], $\eta$, since it is necessary to have a crosslinkage in order for secondary cyclization to occur. As the simplest approximation, we will assume $\eta$ to be constant. With this approximation, the accumulated mole fraction of the pendant double bonds which is consumed by crosslinking and secondary cyclization, $\bar{\rho}_{el,a}$ (which was called the elastic crosslinking density of additional type in earlier papers[8,10]), is given by:

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

where $k_{p,e}^{*0}=(1+\eta)k_p^{*0}$, $k_p^{*0}$ and $k_p$ are the pseudo-kinetic rate constants for the crosslinking reaction and for the propagation reaction[6–10], and $\bar{F}_2$ is the accumulated mole fraction of divinyl monomer bound in polymer chains.

The pendant double-bond conversion $x_{pd}$ is given by:

$$\begin{aligned} x_{pd}&=(\bar{\rho}_{el,a}+\bar{\rho}_{cp})/\bar{F}_2 \\ &=(\bar{\rho}_{el,a}/\bar{F}_2)+k_{cp} \end{aligned} \tag{3}$$

where $\bar{\rho}_{cp}$ is the accumulated primary cyclization density.

### *Reactivity ratios*

There are complications in the formulation of the copolymer composition equation for vinyl/divinyl copolymerization. Although various composition equations for vinyl/divinyl copolymerization have been proposed[2], all equations involve unrealistic assumptions. Difficulties mainly arise from the complicated behaviour of the pendant double bonds, namely they may react intermolecularly and intramolecularly. The intramolecular reactions (cyclization) do not follow a conventional rate law, and the reactivity of a pendant double bond may not be the same as that for monomer double bonds, and therefore it is very difficult to estimate the monomer consumption by just reacted pendant double bonds. Strictly, in order to know the copolymer composition, it is necessary to know the kinetic behaviour of pendant double bonds completely[9,10], i.e. a knowledge of the reactivity ratios $r_1$ and $r_2$ is insufficient to calculate the change in copolymer composition during polymerization. Therefore, application of the Mayo–Lewis equation[12] or its integrated form known as the Meyer–Lowry equation[13] is not exact, since monomer consumption by just reacted pendant double bonds is not considered. However, quite often the copolymerization parameters $r_1$ and $r_2$ have been obtained without taking into account the behaviour of pendant double bonds. It is worth noting here that those parameters should be recognized as empirical parameters, which may not reflect true chemical reactivities.

For the copolymerization of AAm and Bis, since the chemical structures of vinyl groups are the same, the reactivity ratios are expected to be $r_1=0.5$ and $r_2=2.0$. Please note that since a divinyl monomer possesses two double bonds, the reactivity ratios defined with respect to monomer unit, $r_1$ and $r_2$, are related to those defined with respect to double bonds, $r_1^d$ and $r_2^d$, as follows:

$$r_1 = r_1^d/2 \tag{4}$$

$$r_2 = 2r_2^d \tag{5}$$

On the other hand, Baselga *et al.*[11] estimated the reactivity ratios by application of the Meyer–Lowry equation to their copolymer composition data, and found that $r_1=0.57$ and $r_2=3.4$. Unfortunately, they did not mention the confidence intervals for their parameters, so that it is difficult to decide whether their reactivity ratios should be considered different from the expected values. We decided to use reactivity ratios, $r_1=0.5$ and $r_2=2.0$, for the calculation of copolymer composition based on the following reasons. (i) Baselga *et al.*'s[11] experimental data could be fitted equally well using reactivity ratios $r_1=0.5$ and $r_2=2.0$, as is shown in *Figure 3*. (ii) Especially, for mole fractions of divinyl monomer less than 15%, which we have used for our experiments, there is practically no difference in the calculated copolymer composition using $r_1=0.5, r_2=2.0$ and $r_1=0.57, r_2=3.4$.

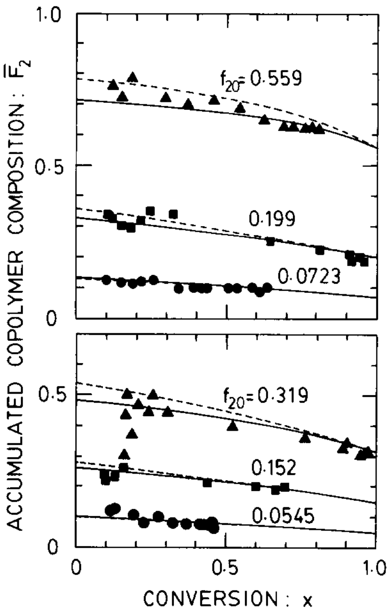

Figure 3 Calculated and experimental compositional drift of the accumulated AAm/Bis copolymer. Experimental data are taken from ref. 11. Calculated values: ——, $r_1=0.5$, $r_2=2.0$; --------, $r_1=0.57$, $r_2=3.4$

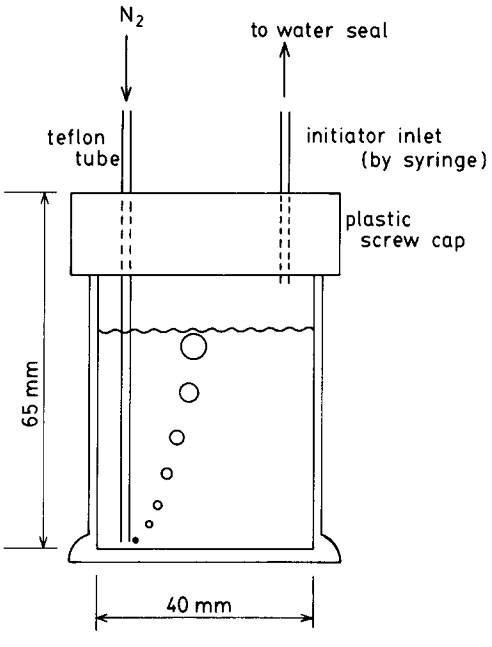

Figure 4 Schematic drawing of the reactor used for batch polymerization

## EXPERIMENTAL

Acrylamide (AAm) and *N,N'*-methylenebisacrylamide (Bis) were high-purity Aldrich products (electrophoresis grade). As initiator, the redox system potassium persulphate (PS)/triethanolamine (TEA) was employed. PS was purchased from BDH Chemicals, and TEA was from Fisher Scientific.

AAm, Bis and TEA were dissolved in ion-exchanged water, and poured into the glass reactor shown in *Figure 4*. The glass reactor was kept in a water bath maintained at 25°C. After deaeration by bubbling $N_2$ for 20 min, PS, also dissolved in ion-exchanged water and kept at 25°C with $N_2$ bubbling, was injected by syringe. From preliminary experiments, more than 10 min of $N_2$ bubbling was necessary for sufficient reproducibility. $N_2$ bubbling was continued throughout polymerization in order to mix the reactants, i.e. if no mixing was provided, insoluble microgel-like particles tended to sediment and gel molecules were formed only in the lower part of the reactor. Since the diameter of the reactor is not small enough, a temperature rise was observed. However, the maximum temperature rise was less than 3°C, and the effect on the kinetics is considered tolerable.

The polymerization was stopped by adding acetone containing 0.3 wt% of 4-methoxyphenol at a desired time, with complete mixing with the break-up of gel molecules if they were present. The polymer was separated by centrifugation, and washed three times with acetone containing 4-methoxyphenol. The washed polymers were dried at 60°C under vacuum for more than three days. Conversion was determined gravimetrically. Complete removal of monomer was checked by liquid chromatography for several samples. The number of pendant double bonds was measured by bromometry (bromate/bromide titration). When the size of ruptured gels was not small enough, they were ground with a mortar and pestle in order to reduce titration time. The end-point was determined when the solution remained colourless for more than 15 min.

Concentrations used were $56.6\,\mathrm{g\,l^{-1}}$ for comonomers, $2.48\times10^{-3}\,\mathrm{mol\,l^{-1}}$ for PS and $4.23\times10^{-4}\,\mathrm{mol\,l^{-1}}$ for TEA. The weight-average chain length ($\bar{P}_w$)for homopolymer of AAm was measured by low-angle laser light scattering photometry using a Chromatix KMX-6 LALLS photometer. A value of $\bar{P}_{w,\mathrm{homo}} = 1.07\times10^5$ was obtained. When $0.094\,\mathrm{mol\,l^{-1}}$ of isopropyl alcohol (IPA) was added as a chain transfer agent, $\bar{P}_{w,\mathrm{homo}}$ decreased to $2.83\times10^4$.

## RESULTS AND DISCUSSION

### *Polymerization kinetics*

The conversion–time histories for initial mole fraction of divinyl monomer $f_{20}=0.07$ and homopolymerization of AAm are shown in *Figure 5*. The gel point was assumed to occur when the acceleration in polymerization rate occurred, and more conveniently it was monitored by measuring the sharp temperature increase in the reactor. The presence of 7 mol% of Bis increases noticeably the overall polymerization rate even in the pre-gelation period. Since the reactivity of Bis is higher than AAm, the increase of reaction rate is understandable; however, such a large increase (the ratio of polymerization rate at zero monomer conversion on a weight basis is about 3.5) cannot be attributed to the addition of monomer with higher reactivity. This large increase would be better explained by the dramatic increase in radical concentration caused by a large decrease in the bimolecular termination rate of polymer radicals. As reported by Bansil and Gupta[14], polyacrylamide gels with $f_{20}>0.02$ become turbid. In our experiments, it was clearly observed that the reaction system becomes turbid right from the start of polymerization, and that these particles tend to sediment if no mixing is used. These insoluble microgel-like particles seem to be responsible for the increase in polymerization rate. If all double bonds are equally reactive, Flory's model, using $\bar{P}_{wp}=1.07\times10^5$ for the weight-average chain length of the primary polymer molecules, predicts the following double-bond conversion at the gel point, $p_c$:

$$p_c=(1+f_{20})/(2f_{20}\bar{P}_{wp})=7.14\times10^{-5} \qquad (6)$$

It is expected that various non-idealities not accounted for by Flory's model delay the gel point. However, it may be possible to assume that gelation occurs on a microscopic scale at fairly low conversions, and consequently insoluble microgels are formed. Since the mobility of radical centres located on a microgel is restricted, the bimolecular termination rate may decrease considerably. These microgels were connected with each other with tie polymer chains, and gelation, on a macroscopic scale, was observed at a weight conversion $x_{cw}\approx0.2$.

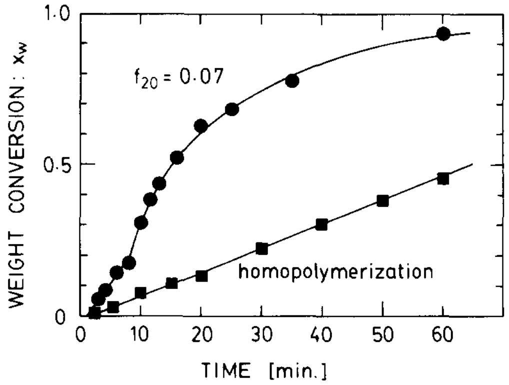

**Figure 5** Conversion–time histories for the copolymerization of AAm/Bis ($f_{20}=0.07$) and homopolymerization of AAm

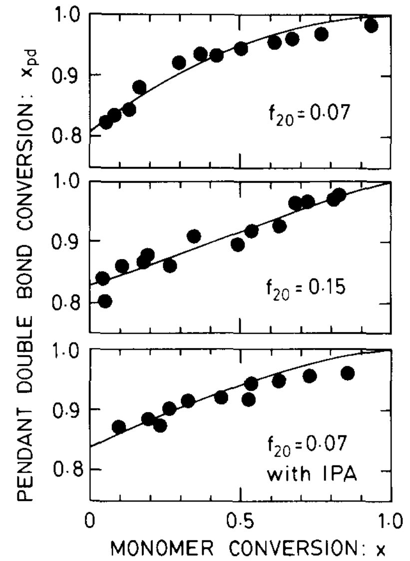

**Figure 6** Pendant double-bond conversion *versus* monomer conversion measured by bromate/bromide titration and calculated (——) using equation (2) and parameters in *Table 1*

### *Kinetics of pendant double-bond consumption*

The number of pendant double bonds *versus* monomer conversion was measured for three experimental conditions, namely $f_{20}=0.07, 0.15$ and 0.07 with $0.094\,\mathrm{mol\,l^{-1}}$ of IPA. The pendant double-bond conversion $x_{pd}$ *versus* monomer conversion is shown in *Figure 6*. The lines were calculated using equation (2). The parameters used ($k_{cp}$ and $k^{*0}_{p,e}/k_p$) are summarized in *Table 1*. The agreement of calculations with experimental data seems satisfactory at least for conversions less than 50%. At high conversions, $k^{*0}_{p,e}/k_p$ may decrease because of the tighter structure of the gel, i.e. trapping of pendant double bonds[15].

The intercept at zero conversion in *Figure 6* gives the degree of primary cyclization ($=k_{cp}$). At least 80% of the pendant double bonds are found to be consumed by primary cyclization at zero monomer conversion. A simple model for primary cyclization given by equation (1) shows that $k_{cp}$ is independent of monomer compositions ($f_{20}$), and the chain length of the primary polymer molecule, if (i) the molecular conformation does not change, and (ii) the primary polymer chain length is large enough. The $y$ intercept of *Figure 6* ($=k_{cp}$) seems nearly independent of $f_{20}$ and the chain length of primary polymer molecules, and this result supports equation (1). Several experimental results of the effect of the initial

**Table 1** Experimental conditions, gel point and estimated parameters

| Experiment number | $f_{20}$ | [IPA] ($\mathrm{mol\,l^{-1}}$) | $k_{cp}$ | $k^{*0}_{p,e}/k_p$ | Gel point $x_c$ | |
|---|---|---|---|---|---|---|
| | | | | | Weight conv. | Molar conv. |
| R1 | 0.07 | 0 | 0.81 | 3.8 | 0.20 | 0.19 |
| R2 | 0.15 | 0 | 0.83 | 1.9 | 0.25 | 0.23 |
| R3 | 0.07 | 0.094 | 0.84 | 2.7 | 0.25 | 0.24 |

| Experiment number | $\bar{\rho}_a(x_c)=1/(2\bar{P}_{wp})$ | $\bar{\rho}_{el,a}(x_c)$ | $\eta$ | $k^{*0}_p/k_p$ |
|---|---|---|---|---|
| R1 | $4.67\times10^{-6}$ | $7.54\times10^{-3}$ | $1.61\times10^{3}$ | $2.35\times10^{-3}$ |
| R2 | $4.67\times10^{-6}$ | $9.24\times10^{-3}$ | $1.98\times10^{3}$ | $9.60\times10^{-4}$ |
| R3 | $1.77\times10^{-5}$ | $5.94\times10^{-3}$ | $3.35\times10^{2}$ | $8.05\times10^{-3}$ |

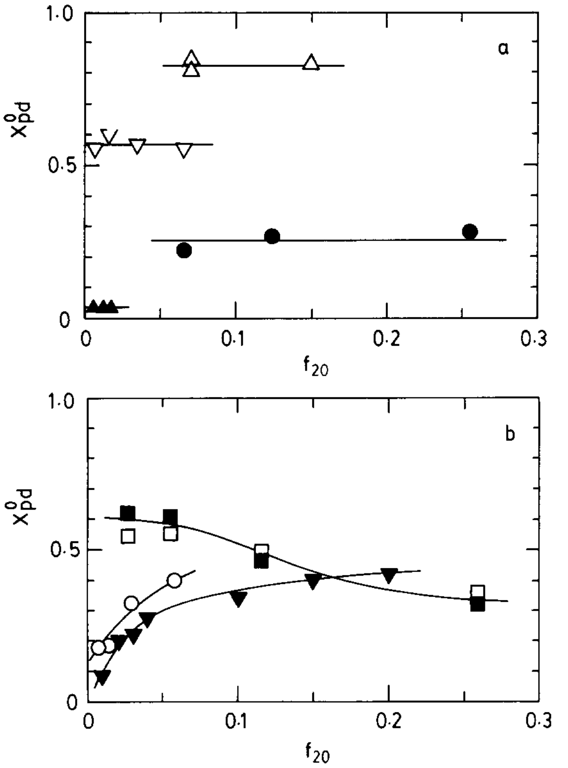

**Figure 7** Effect of initial mole fraction of divinyl monomer on primary cyclization at zero monomer conversion. Styrene/*p*-divinylbenzene: ●, bulk polymerization[2,15]; ○, 15 vol% in toluene[16]; ▽, 10 vol% in cyclohexane[16]. Styrene/EGDMA: ■, bulk polymerization[17]; □, 60 vol% in toluene[17]; ▼, 15 vol% in toluene[18,19]. MMA/EGDMA: ▲, bulk polymerization[4]. AAm/Bis: △, 56.6 g l$^{-1}$ in water (this work)

mole fraction of divinyl monomer $f_{20}$ on primary cyclization at zero monomer conversion reported are summarized in *Figures 7a* and *7b*. In some cases $k_{cp}$ ($=x^0_{pd}$) appears to be independent of $f_{20}$, as shown in *Figure 7a*; however, dependence of $f_{20}$ has also been reported (*Figure 7b*). It is worth noting, however, that the results for styrene/EGDMA at low $f_{20}$ are conflicting depending on who the researchers were (compare ■, □ and ▼). The problem may partly be caused by inaccuracy of the analytical methods for pendant double-bond conversion measurement used, especially when the amount of divinyl monomer is small. Furthermore, if the molecular conformation changes with addition of divinyl monomer, a dependence on $f_{20}$ is reasonable. Independence on chain length was also reported by Landin and Macosko[4] for MMA/EGDMA at $f_{20}=0.0114$.

Primary cyclization appears to be fairly significant. Lower monomer concentrations are believed to promote the effect of cyclization (please note that our monomer concentration is less than 6 wt%). For *N,N'*-methylenebisacrylamide (Bis), even gel-free homopolymerization was reported for a very low monomer concentration with special redox initiator[20–22], and cyclopolymerization of Bis was proposed. It is unclear whether cyclization formed within one Bis unit is significant or not in our experiments; however, it might contribute somewhat to the high $k_{cp}$ values found.

The ratio $k^{*0}_{p,e}/k_p$ shows the apparent reactivity of pendant double bonds including secondary cyclization. An example of elastic crosslinking density distribution change during polymerization for $f_{20}=0.07$ without IPA is shown in *Figure 8*. In the figure, $\theta$ is the monomer conversion $x$ at which the given primary polymer molecule is born, and $\psi$ is the monomer conversion at present time. For example, at monomer conversion $\psi=0.8$, the crosslinking density of a primary polymer molecule that is just born at conversion $\theta=0.8$ is far smaller than that of a primary polymer molecule that was born at conversion $\theta=0.3$. From *Figure 8*, it may be reasonable to guess that the polymer network is inhomogeneous, at least on a microscopic scale.

Estimated values of $k^{*0}_{p,e}/k_p$ are larger than unity, while the observed gel point on a macroscopic scale is much larger than predicted by equation (6). This fact implies that the consumption of pendant double bonds by secondary cyclization is much greater than that by crosslinking. Assuming that the weight-average chain length of primary polymer molecules is the same as that for homopolymers of AAm synthesized under the same reaction conditions, it is possible to roughly estimate $\eta$ and $k^{*0}_p/k_p$ from the observed gel point. These estimates are also shown in *Table 1*. When $f_{20}$ is increased, network structure becomes tighter, and therefore apparent reaction rate for the crosslinking reaction decreases due to steric hindrance. With these high mole fractions of divinyl monomer, insoluble microgels are formed. The reaction rate between these microgels is likely to decrease, since there are many inaccessible double bonds and radical centres (see figure 6 of ref. 6). A tight structure also increases the effect of secondary cyclization. When the primary polymer chain length is made smaller using IPA ($\bar{P}_{w,\mathrm{homo}}=2.83\times10^4$), the probability that a growing primary polymer molecule can find two or more pendant double bonds decreases, and therefore the effect of secondary cyclization decreases. This effect was also reported by Landin and Macosko[4] for MMA/EGDMA.

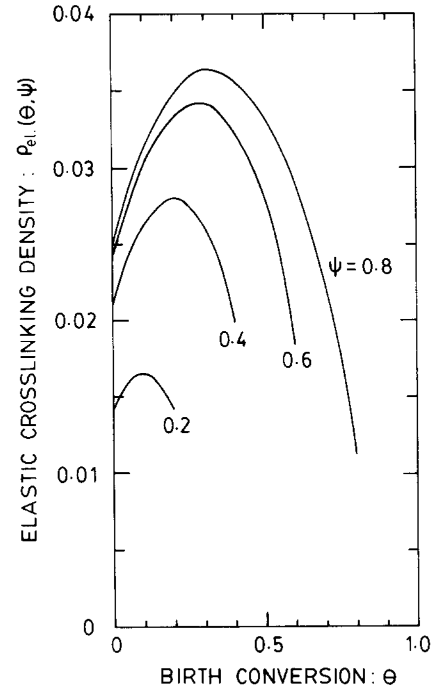

**Figure 8** Change of the calculated elastic crosslinking density distribution profile for $f_{20}=0.07$ without IPA. At a certain monomer conversion $\psi$, the primary polymer molecules with different birth time may bear completely different crosslinking density

Decreased secondary cyclization should reduce the gel tightness, and may contribute to an increase in the apparent reaction rate of crosslinking.

In free-radical polymerization, a crosslinkage is formed only via a polymer radical whose concentration is fairly low and whose lifetime is very short, and therefore steric effects caused by the presence of other chains as well as its own chain have a significant effect on the kinetics of network formation. When these physical effects are significant, it would be necessary to regard the apparent crosslinking reaction rate as structure-dependent as well as chain-length-dependent[10]. At least, it seems reasonable to consider that the reaction rate between huge molecules (or microgels) decreases as they grow in size and become tighter. Our experimental conditions under which insoluble microgels are formed may be rather unusual; however, from the point of view of the mobility of the chains, the formation of microgels may be a general feature of network formation in free-radical polymerization[23]. The formation mechanism of microgels may be as follows. Even if the reaction rate between huge molecules is hindered sterically, small molecules, which exist in far greater number, can diffuse into these huge molecules. Therefore, the structure of huge molecules may be tighter than that for smaller ones. A tight structure increases the probability of secondary cyclization, and thus it becomes even tighter. A tighter structure further decreases reaction rate between huge molecules. With continual repetition of these processes, microgels would be formed.

These steric effects should be weaker when low mole fractions of divinyl monomer are used. However, if $k_{cp}$ is the same even for very low mole fractions of divinyl monomer, the effect of primary cyclization on the consumption of pendant double bonds should remain unchanged. Therefore, it may be expected that primary cyclization is a dominant non-ideality for very low $f_{20}$ at low monomer concentrations (please note that our monomer concentration is less than 6 wt%). In order to test this hypothesis, experiments with $f_{20}=1\times10^{-4}$ and $2\times10^{-4}$ were done. The conversion–time histories obtained are shown in *Figure 9*. Full symbols are used to designate the samples in which gel molecules were observed. All gels are clear for these low $f_{20}$, and microgels were not visually observed. The formation of gel molecules was determined, basically, by measuring the fluidity of the reaction mixture. At a desired time the screw cap of the reactor was opened. When a gel molecule is obviously formed, the contents will not flow out of the reactor. In the vicinity of the gel point, the reactor contents were poured into water in which 4-methoxyphenol had been added. After being shaken, the diluted reaction mixture was checked to see whether swollen gel comparable in size to that of the reactor was observed. The gas bubble method[24] did not work well for our polymerization conditions since, near the gel point, the gel molecule is too flexible and weak to trap a bubble.

If Flory's simplifying conditions are applicable, gel point $x_c$ is given by:

$$x_c = 1/(2f_{20}\bar{P}_{wp}) \qquad (f_{20} \ll 1) \tag{7}$$

If primary cyclization is the only cause of the delay of gelation, and equation (1) is applicable for primary cyclization, the gel point $x_c$ is given by:

$$x_c = 1/[2f_{20}\bar{P}_{wp}(1-k_{cp})] \qquad (f_{20} \ll 1) \tag{8}$$

It is reasonable to use $\bar{P}_{wp}=1.07\times10^5$, the value for the weight-average primary polymer chain length measured for the homopolymerization of AAm.

The observed and calculated gel points are shown in *Table 2*. The value $k_{cp}=0.79$ agrees fairly well with the results obtained from the measurements of pendant double-bond conversions at zero monomer conversion for $f_{20}=0.07$ and $0.15$ ($k_{cp}=0.81$ to $0.84$, see *Table 1*).

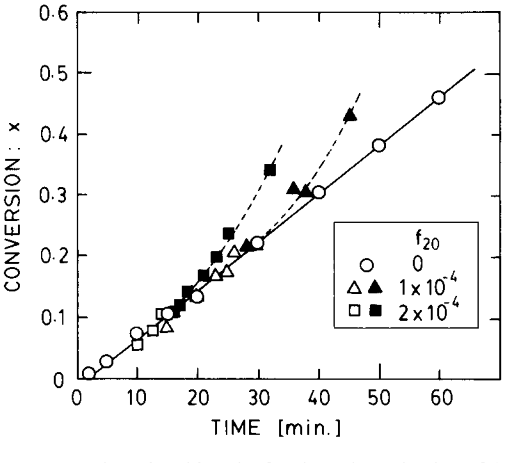

**Figure 9** Conversion–time histories for the polymerization of AAm/Bis and AAm. Full symbols are used to designate that a gel molecule was visually observed in the system

**Table 2** Observed and calculated gel point ($x_c$)

| $f_{20}$ | Observed | Equation (7) | Equation (8) with $k_{cp}=0.79$ |
|---|---|---|---|
| $1\times10^{-4}$ | 0.22 | 0.047 | 0.22 |
| $2\times10^{-4}$ | 0.11 | 0.023 | 0.11 |

It may be reasonable to regard primary cyclization as the main cause of the delay of the onset of gelation for copolymerizations with very low mole fractions of divinyl monomer and low monomer concentrations.

The effects of cyclization (primary and secondary) and steric hindrance on the crosslinking reaction change with polymerization conditions. Up to moderately high mole fractions of divinyl monomer, a general description of these effects may be as follows. At low monomer concentrations, the effect of primary cyclization is important, and secondary cyclization and steric hindrance become significant as the mole fraction of divinyl monomer ($f_{20}$) increases. At high monomer concentrations, the effect of primary cyclization may be small[4], since the probability of finding vinyl groups other than those on its own chain is large. The effects of secondary cyclization and steric hindrance on the crosslinking reaction become significant as $f_{20}$ increases. From these considerations, network defects in polyacrylamide gels may be smallest in the limits of high monomer concentration and very low mole fraction of divinyl monomer. This hypothesis was also proposed by Baselga *et al.*[25], who studied the elastic properties of polyacrylamide gels.

The existence of a crosslinking density distribution shows that polymer networks synthesized by free-radical polymerization are inherently inhomogeneous on a microscopic scale, and steric hindrance between huge molecules enhances this character and results in the formation of inhomogeneous networks on a macroscopic scale.

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