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Gel formation by chain-crosslinking photopolymerization of methyl methacrylate and ethylene glycol dimethacrylate

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Photoinitiated free-radical crosslinking copolymerization of methyl methacrylate and ethylene glycol dimethacrylate has been investigated in toluene at a monomer concentration of 35 w/v%. The photoinitiators used were benzoin, benzoin methyl ether, benzoin ethyl ether and 2,2-dimethoxy-2-phenyl-acetophenone. Conversion of monomer and pendant vinyl groups and the size of the pregel polymers were measured as a function of the reaction time up to the onset of macrogelation. Approximately 30% of the pendant vinyl groups were found to be consumed by cyclization reactions. The fraction of units in cycles is independent of the EGDM concentration. As a result of the cyclization reactions, the accessibility of the radical centres and pendant vinyl groups for other polymer molecules is strongly reduced. Consequently, both termination and crosslinking reactions are controlled by the segmental diffusion of the polymer radicals. Calculations indicate a 1–2 orders of magnitude decrease in the average reactivity of pendant vinyls for intermolecular reactions compared to the monomeric vinyls. This drastic decrease in pendant reactivity is mainly responsible for the delay in the gel point. Contrary to gelation theories, the size distribution curves of the pregel polymers change from monomodal to bimodal distributions as polymerization proceeds. This finding confirms the coagulation-type gelation mechanism of compact primary particles and indicates the shape polydispersity of the pregel polymers. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: photopolymerization; microgel formation; cyclization)

INTRODUCTION

Bulk photopolymerization of multifunctional monomers is one of the most efficient methods of synthesizing strongly crosslinked polymers with a high mechanical strength and excellent resistance to solvent penetration[1–3]. Such materials have found application as dental materials, aspherical lenses, nonlinear optical materials and coatings. To predict the final properties of these materials, their structural characteristics are extremely important, and these in turn depend on the history of the network formation process. Previous researches indicate the existence of spatial inhomogeneities in such materials. For instance, the appearance of multiple glass transitions[4,5], the existence of trapped radicals[6–8] and residual unsaturation in the final networks[9] are indications of the presence of regions more crosslinked than the surrounding environment in the material. Such inhomogeneities in the final materials are undesirable for applications because structural inhomogeneity results in a dramatic reduction in the strength of the crosslinked polymers.

The reason for the inhomogeneous nature of highly crosslinked networks is nonidealities in their formation process such as unequal vinyl group reactivity, cyclization, and multiple crosslinking. For example, in chain-crosslinking copolymerization, the growing chains in the pre-gel stage are rich in divinyl monomer (DVM) units because of the higher reactivity of the DVM. Furthermore, these chains are highly diluted by the monomer at low conversions so that cyclization predominates in the early stages of the reaction. As a consequence, the growing chains become internally crosslinked and their structure approaches that of microgels[10–12]. Thus, the appearance of microgels during the network formation processes can be compared with the formation of primary molecules as intermediates in classical gelation theories[13]. The interparticular reactions, namely crosslinking and multiple crosslinking, are responsible for the agglomeration of microgels leading to macrogelation. Previous experimental work from our group showed that a large number of multiple crosslinks form between two microgels after they link together in the reaction mixture by a single crosslink[14]. Thus one may expect that, in the final network, the microgels, or their agglomerates formed by extensive multiple crosslinkages, are more

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highly crosslinked than the later formed portions of the network.

Whereas the properties of final networks or partially formed networks have been thoroughly investigated in the last decade, there have not been many reports on the pre-gel period of photopolymerization, i.e. the period in which highly crosslinked regions start to form. This is mainly due to the rapid polymerization of multifunctional monomers in bulk and the almost immediate onset of macrogelation. In the present work, conversion of the monomers and pendant vinyl groups as well as the molecular weight and size distribution of the soluble polymers were determined experimentally in the pre-gel regime of photocopolymerization of methyl methacrylate (MMA)/ethylene glycol dimethacrylate (EGDM) monomers. In order to focus on the pre-gel period of the reactions, we magnified this period by adding an inert diluent into the copolymerization system. Under these conditions, one may expect that the data obtained correspond to the early stages of bulk photopolymerization, where the unreacted monomers act as a diluent of the reaction system. U.v. photopolymerizations were carried out at 35 w/v% monomer concentration in toluene, using 0.3 wt% of a photoinitiator. The photoinitiators used were benzoin (B), benzoin methyl ether (BME), benzoin ethyl ether (BEE) and 2,2-dimethoxy-2-phenyl-acetophenone (DMPA). These molecules are known to undergo α-cleavage to produce benzoyl and substituted benzyl radicals[15,16], as shown in *Scheme 1*.

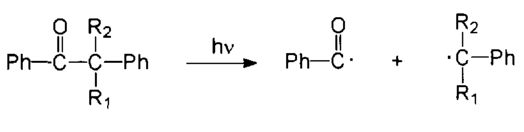
It is the purpose of this paper to present new measurements which will enable us to estimate the magnitude of cyclization and reduced pendant reactivity depending on the reaction conditions. In this way, we hope to develop a deeper insight into the formation mechanism of globular structures in chain-crosslinking copolymerization and their influence on polymerization kinetics.

KINETIC MODELLING

There are several theories of network formation to describe the relations between the molecular weight of polymers and the conversion or reaction time during crosslinking. These theories include statistical[17–23] and kinetic methods[24–34], and simulation in n-dimensional space, such as the percolation method[35–37]. In the past half century, statistical and kinetic approaches have been extensively used to describe polymeric gelation. These approaches consider the average properties of the reaction system and, therefore, they cannot deal exactly and directly with long-range correlations such as cyclization or with the resulting heterogeneities. On the other hand, the percolation theory that belongs to a non-mean-field theory can take heterogeneities into account, but at present the result of this theory is unrealistic due to the difficulty of introducing realistic mobilities. The critical region seems to be the main domain of application of percolation techniques to polymer networks. The experimental data obtained in the present study were organized and studied within the framework of a kinetic model which includes constants for cyclization and pendant reactivity.

A kinetic scheme for chain-crosslinking photopolymerization of vinyl/divinyl monomers can be written as follows. The polymerization system involves three types of vinyl groups: those on vinyl and divinyl monomers and those on polymer chains, i.e., pendant vinyls. Accordingly, the polymerization system can be considered as a special case of terpolymerization in which one of the vinyl groups (pendant vinyls) is created during the course of the reaction when the vinyl on the divinyl monomer reacts. The pendant vinyl groups thus formed can then react by cyclization, crosslinking or multiple crosslinking reactions, or remain pendant. With cyclization the cycle is formed when the macroradical attacks the pendant vinyl groups in the same kinetic chain, while with multiple crosslinking it is formed if the radical attacks double bonds pendant on other chains already chemically connected to the growing radical[25,38] (*Figure 1*). It should be noted that cyclization and multiple crosslinking were recently re-defined as primary and secondary cyclizations, respectively[28]. In the following text the classical definitions will be used.

The divinyl monomer can be found in the polymer as units bearing pendant vinyl groups, cycles, crosslinks or multiple crosslinks. Since, according to the classical theory of gelation[17], only one crosslink per weight-average primary molecule is necessary for the onset of macrogelation, the content of pendant vinyls is a highly sensitive indicator of the formation of cycles and multiple crosslinks in finite species. Here, we define the pendant conversion, x_3, as the fraction of divinyl monomer units with both vinyl groups reacted, i.e., the fraction of fully reacted divinyl monomer units in the polymer. Theories neglecting cyclization predict that every divinyl monomer unit in the polymer should initially bear a pendant vinyl group, i.e., $\lim_{x \to 0} x_3 = 0$ where x is the monomer conversion. Since crosslinking is a second-order reaction, deviation from zero indicates the existence of cyclization. On the other hand, the rate of change of pendant conversion x_3 with monomer conversion x or with reaction time t is a measure of the extent of multiple crosslinkages. The greater the slope of x_3 vs the x or t curve, the higher the number of multiple crosslinks formed per crosslink. Thus, the occurrence of multiple crosslinking will be reflected in a greater



B : R_1 = H , R_2 = OH
BME : R_1 = H , R_2 = OCH_3
BEE : R_1 = H , R_2 = OCH_2CH_3
DMPA : R_1 = R_2 = OCH_3

Scheme 1

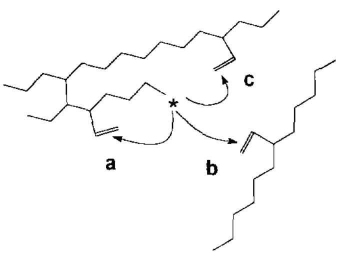


Figure 1 Schematic picture of cyclization (a), crosslinking (b) and multiple crosslinking (c) in free-radical crosslinking copolymerization

decrease in polymer unsaturation as conversion proceeds than would otherwise occur.

Let k_{cyc} be the fraction of pendant vinyls in cycles at zero conversion and k_{mc} be the average number of multiple crosslinkages per crosslink; then, based on the kinetic equations given previously[24-34], the following rate equations for the weight-average molecular weight $\bar{M}_{\mathrm{w}}$ and the pendant conversion x_3 can be written:

$$\frac{\mathrm{d}(x\bar{M}_{\mathrm{w}})}{\mathrm{d}x} = \bar{M}_{\mathrm{w}}^{\bullet}\left[1 + \frac{r_{21}\bar{r}_{32}(1 - x_3)\bar{F}_2}{1 + (2r_{21} - 1)f_2}\left(\frac{x}{1 - x}\right)\frac{\bar{M}_{\mathrm{w}}}{\bar{M}_{\mathrm{u}}}\right]^2$$

$$; \bar{M}_{\mathrm{w}}(0) = M_{\mathrm{w},0}^{\bullet} \qquad (1)$$

$$; \bar{M}_{\mathrm{w}}(x_{\mathrm{c}}) = \infty$$

$$\frac{\mathrm{d}x_3}{\mathrm{d}x} = \frac{r_{21}}{1 + (2r_{21} - 1)f_2}\left[\frac{\bar{r}'_{32}(1 - x_3)}{(1 - x)} - \frac{2f_2}{\bar{F}_2}\frac{(x_3 - k_{\mathrm{cyc}})}{x}\right];$$

$$x_3(0) = k_{\mathrm{cyc}} \qquad (2)$$

where r_{21} is the reactivity ratio of vinyls on divinyl to monovinyl monomers, $\bar{r}_{32}$ and $\bar{r}'_{32}$ are the actual and apparent reactivity ratios of pendant vinyl to monomeric vinyl on divinyl monomer, respectively f_2 and $\bar{F}_2$ are the accumulated mole fractions of divinyl monomer in the reaction mixture and in the copolymer, respectively, $\bar{M}_{\mathrm{u}}$ is the molecular weight of the repeating unit, $\bar{M}_{\mathrm{w}}^{\bullet}$ is the weight-average molecular weight of the primary chains and x_{c} is the critical conversion at the gel point. It should be noted that the apparent reactivity ratio of pendant to monomeric vinyl $\bar{r}'_{32}$ includes both the contributions of crosslinking and multiple crosslinking reactions, and is related to the actual reactivity ratio through the equation

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

The mole fraction of the divinyl monomer in the reaction mixture f_2 is given by the Skeist equation[39]:

$$\frac{\mathrm{d}f_2}{\mathrm{d}x} = \frac{f_2 - F_2}{1 - x} \qquad ; f_2(0) = f_{20} \qquad (4)$$

where f_{20} is the initial mole fraction of the divinyl monomer in the monomer mixture.

Moreover, the instantaneous and accumulated mole fractions of the divinyl monomer units in the copolymer, F_2 and $\bar{F}_2$ respectively, can be calculated from the following equations:

$$F_2 = \frac{2r_{21}f_2}{1 + (2r_{21} - 1)f_2} \qquad (5)$$

$$\bar{F}_2 = \frac{1}{x}[f_{20} - (1 - x)f_2] \qquad (6)$$

The independent variable conversion x in the above equations can be replaced with time t using the rate equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{\mathrm{p}}(R_{\mathrm{i}}/k_{\mathrm{t}})^{0.5}(1 - x) \qquad (7)$$

where k_{p} and k_{t} are the instantaneous rate constants for propagation and termination respectively, R_{i} is the rate of initiation which, for a photopolymerization, can be expressed as[40]

$$R_{\mathrm{i}} = 2\phi I_0(1 - \mathrm{e}^{-\epsilon[A]b}) \qquad (7a)$$

where ϕ is the quantum yield of the initiator, ϵ is the extinction coefficient of the initiator, b is the thickness of the reaction vessel, $[A]$ is the concentration of the photoinitiator and I_0 is the incident light intensity in terms of light quanta per unit volume and time.

The instantaneous propagation rate constant k_{p} relates to the propagation rate constant for the homopolymerization of MMA, k_{pl}, through the equation

$$k_{\mathrm{p}} = k_{\mathrm{pl}}[1 + (2r_{21} - 1)f_2] \qquad (7b)$$

In chain-crosslinking polymerizations it is known that the propagation rate constants of the elementary reactions are reaction controlled up to about 80% of the monomer conversions[41,42]. Thus, it is reasonable to assume a constant k_{p} in the pregel regime. However, the termination rate constant k_{t} becomes diffusion controlled right down to zero conversion[43]. For a constant initiation rate, the ratio of the termination rate constant of macroradicals at conversion x to that at $x = 0$, $k_{\mathrm{t}}/k_{\mathrm{t0}}$, can be calculated from equation (7) as follows:

$$\frac{k_{\mathrm{t}}}{k_{\mathrm{t0}}} = \left(\frac{(\mathrm{d}x/\mathrm{d}t)_0}{(\mathrm{d}x/\mathrm{d}t)/(1 - x)}\right)^2 \qquad (8)$$

Moreover, the termination rate constant of zero conversion polymeric radicals, k_{t0}, may also be not constant and may depend on the crosslinker content in the monomer mixture. In order to extract k_{t0} from the initial rates, we define a relative initial termination rate constant $k_{\mathrm{t0,\,rel}}$[43]. This is the ratio of k_{t0} for the crosslinking polymerization to that for the linear polymerization at the same reaction condition. $k_{\mathrm{t0,\,rel}}$ can be calculated from equations (7) and (7b) as

$$k_{\mathrm{t0,\,rel}} = \frac{k_{\mathrm{t0}}}{k_{\mathrm{t0,l}}} = \left\{[1 + (2r_{21} - 1)f_{20}]\frac{(\mathrm{d}x/\mathrm{d}t)_{0,\mathrm{l}}}{(\mathrm{d}x/\mathrm{d}t)_0}\right\}^2 \qquad (9)$$

where the subscript 0,l indicates the initial rates for linear polymerization.

Due to the depletion of the monomer and the initiator and the diffusion controlled termination reactions, the weight-average molecular weight of the primary chains $\bar{M}_{\mathrm{w}}^{\bullet}$ is not constant but a function of conversion. The variation of $\bar{M}_{\mathrm{w}}^{\bullet}$ with conversion can be calculated for a constant initiation rate as follows[44]:

$$\frac{\bar{M}_{\mathrm{w}}^{\bullet}}{M_{\mathrm{w},0}^{\bullet}} = \frac{(\mathrm{d}x/\mathrm{d}t)}{(\mathrm{d}x/\mathrm{d}t)_0} \qquad (10)$$

where the subscript 0 denotes the initial values at the start of the reaction.

Up to the gel point, all the molecules present in free-radical crosslinking copolymerization are finite. Thus, the equations given above can be solved for the molecular weights and pendant conversions if the rate constants and kinetic parameters are known. In this study, we used the above equations to calculate the average reactivity of the pendant vinyl groups as follows: since $\bar{M}_{\mathrm{w}}$ diverges at the gel point, the value of $\bar{r}_{32}$ satisfying $\bar{M}_{\mathrm{w}}(x_{\mathrm{c}}) = \infty$ was obtained numerically using simultaneous solution of equations (1)–(6). The drift in the primary chain length was included into the calculations by fitting equation (10) to experimental time–conversion data.

Note that the derivation of the equations given above makes the following assumptions: (1) steady-state approximation for the concentration of each radical species; the reactivities are independent of the type of radical end; (2) cyclization, crosslinking and multiple crosslinking reactions occur at constant rates; (3) every polymer radical possesses only one radical centre; and (4) the mole fraction of pendant vinyl groups is independent of the chain length of the polymer molecules.

EXPERIMENTAL

Materials

Commercially available methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDM) monomers, and the photoinitiators benzoin (B), benzoin methyl ether (BME), benzoin ethyl ether (BEE) and 2,2-dimethoxy-2-phenyl-acetophenone (DMPA) were purified by usual methods. The polymerization solvent toluene (Merck p.a.) was twice distilled before use.

Methods

Photoinitiated copolymerization of MMA and EGDM was carried out in toluene at 27 ± 0.1°C. The initiators used were B, BME, BEE and DMPA. The conversion of the monomers up to the onset of macrogelation was followed by dilatometry. The dilatometers, constructed in this laboratory, consisted of a blown glass bulb, approximately 25 ml in volume, connected to a 30 cm length of 1.5 mm precision-bore capillary tubing with a ground-glass joint. The thickness of the dilatometers was less than 6 mm to ensure the applicability of the thin-film approximation and uniform light intensity across the sample. The reaction mixture was flushed with nitrogen 20 min prior to the polymerization. Polymerization was initiated with u.v. light of intensity 3.8×10^{-9} einsteins generated using a medium mercury lamp. The meniscus of the polymerizing solution was measured throughout the experiment with a millimetric paper to 0.2 mm. The polymerization technique used has been described in detail elsewhere[45]. The reproducibility of the kinetic data was checked by repeating the experiments. The deviation in the initial slopes of time vs conversion data between two runs was always less than 3%. Different series of experiments were carried out using the photoinitiators listed above. In each series, the initial concentrations of the monomers and the initiator were held constant at 3.5 M (35 w/v%) and 0.3 wt% (with respect to the monomers) respectively, while the crosslinker concentration was varied over wide range.

The polymer samples for pendant vinyl group measurements were obtained by a gravimetric technique. For this purpose, a 15 ml three-neck flask of 0.7 mm thickness containing a magnetic stirrer bar fitted with a nitrogen inlet and pipette outlet was filled with the liquid mixture. After degassing of the mixture, polymerization was initiated with the u.v. light of the mercury lamp at 27 ± 0.1°C. After predetermined polymerization times, the content of the flask was poured into 100 ml of methanol and allowed to settle. The precipitated polymer was filtered and dried *in vacuo* to constant weight. Measurement of the number of pendant vinyls on MMA/EGDM copolymers was carried out using a bromination method with pyridine sulfate dibromide (PSDB) reagent in the presence of mercury acetate as catalyst[46]. The method is based on the reaction of pendant vinyl groups with bromine produced *in situ* from the PSDB reagent and back-titration of the excess bromine. For the calculation of pendant conversion, the reactivities of monomeric vinyls were assumed to be equal[28,47].

Gel point measurements were carried out using two different methods. First, the gravimetric technique was used to follow the polymerization reactions; the gel point was determined as the midpoint between the last time at which a soluble polymer was obtained and that at which the polymer was not soluble in toluene. For ascertaining the insoluble gel component of samples, the latter were treated with an approximately 50-fold excess of toluene at room temperature. The formation of insoluble polymer was detected visually from the appearance of gel particles in toluene. Second, dilatometers containing a steel sphere of 4.8 mm diameter were used for the gel point measurements. The midpoint between the last time at which the sphere moved magnetically and that at which it stopped moving was taken as the gel point. We found remarkable consistency in the gel points determined using both methods. Each gel point reported in this paper is an average of at least four measurements. Standard deviations were 7%.

Apparent molecular weights and the size distribution of the pregel polymers were obtained by size exclusion chromatography (Waters, Model M-6000A), equipped with a refractive index detector, using two polystyrene gel columns (500, 10 000 A) at a flow rate of 1.0 ml min^{-1} in THF at 40°C, and using polystyrene standards.

RESULTS AND DISCUSSION

Monomer conversions

Figures 2A and *2B* show plots of fractional monomer conversion, x, vs polymerization time, t, up to the onset of macrogelation for different crosslinker concentrations.

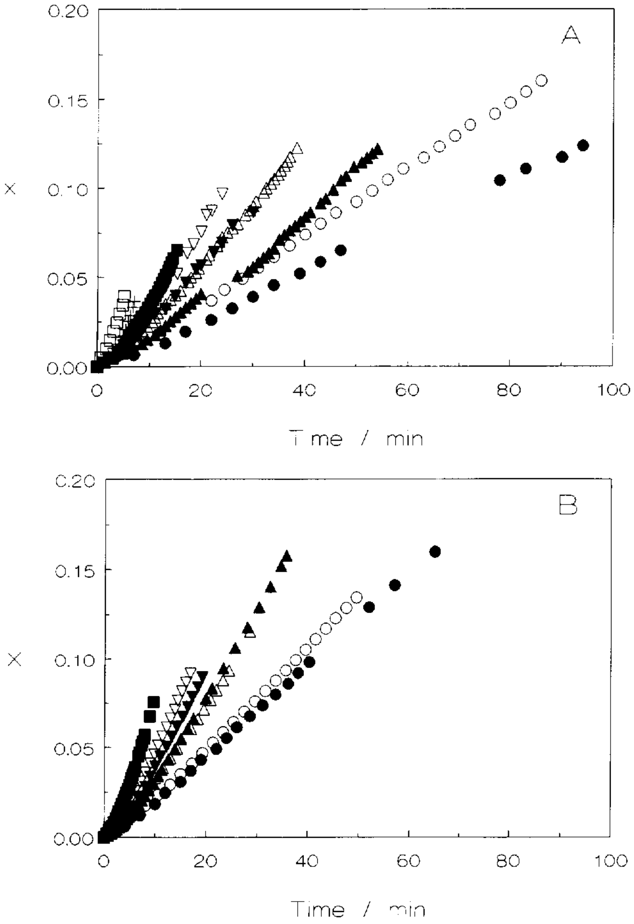


Figure 2 Monomer conversion x vs time histories in MMA–EGDM copolymerization in the presence of benzoin (A) and 2,2-dimethoxy-2-phenylacetophenone (B) as the photoinitiator. EGDM mol% = 0 (●), 3.6 (O), 6.4 (▲), 9.3 (△), 12.1 (▼), 15.1 (▽), 25 (■), 50 (□) and 75 (+)

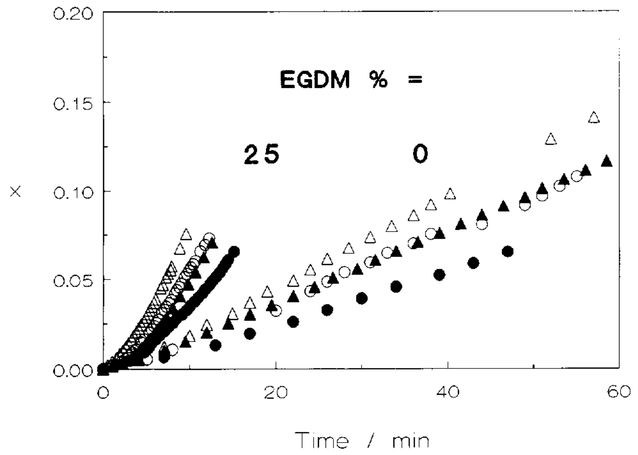


Figure 3 Monomer conversion x *versus* time histories in MMA–EGDM copolymerization for the photoinitiators benzoin (●), benzoin methyl ether (○), benzoin ethyl ether (▲) and 2,2-dimethoxy-2-phenylacetophenone (△). The EGDM concentrations were 0 and 25 mol%

The initiators used were benzoin and 2,2-dimethoxy-2-phenyl acetophenone (DMPA) respectively. Acceleration of the rate of polymerization with increasing EGDM content can be seen from the figures. Moreover, compared to benzoin, higher rates were achieved with DMPA as the photoinitiator of copolymerization. *Figure 3* compares conversion vs time data for the initiators benzoin (B), benzoin methyl ether (BME), benzoin ethyl ether (BEE) and DMPA. Polymerization rate increases in the order B < BME or BEE < DMPA. Since quantum efficiencies for initiation by the initiators used do not differ to any significant extent, higher rates of polymerization are, according to equation (7a), due to the greater amount of light absorbed under photolysis conditions, and to the increase in the rate constants for the α-cleavage by substitution in α position[48]. In this connection it should be pointed out that benzoyl and benzyl radicals formed according to *Scheme 1* are equally effective as initiators in the polymerization of methyl acrylate and MMA[49]. Since benzoyl radicals are generated in the case of each initiator, the different reactivities may be attributed to the enhanced reactivity of nucleophilic benzyl radicals by substitution, i.e. increased reactivity in the order

$$\mathrm{Ph\dot{C}HOH} < \mathrm{Ph\dot{C}HOMe} \quad \text{or}$$

$$\mathrm{Ph\dot{C}HOEt} < \mathrm{Ph\dot{C}(OMe)_2}$$

By using the numerical fit of the experimental time–conversion data, the reduced initial rates, $(\mathrm{d}x/\mathrm{d}t)_0/(\mathrm{d}x/\mathrm{d}t)_{0,l}$, were calculated and are shown in *Figure 4* for the photoinitiator benzoin as a function of the EGDM concentration. The reduced initial rates are defined as the ratio of the initial rate in the presence to that in the absence of the crosslinker under the same experimental conditions. Calculated results for EGDM contents higher than 20% were not included in the figure because of the large scatter in the data points, probably due to the high polymerization rates. A significant rate enhancement can be seen at zero monomer conversion. Since the initial concentrations of both the monomers and the initiator were fixed in the experiments, the reduced initial rates are equivalent to the reduced molecular weight of the primary chains, i.e.

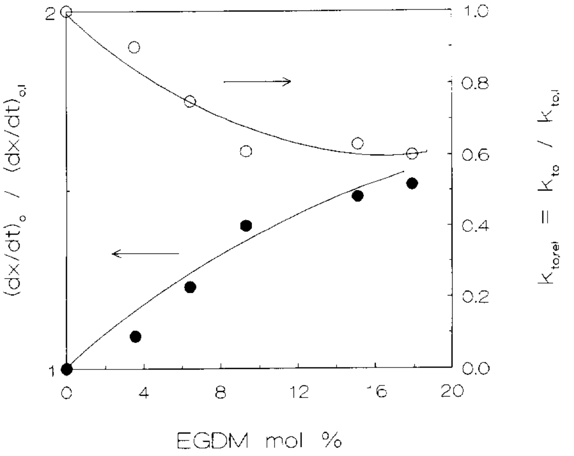


Figure 4 Variation of the reduced initial rate $(\mathrm{d}x/\mathrm{d}t)_0/(\mathrm{d}x/\mathrm{d}t)_{0,1}$ (●) and relative termination rate constants $k_{t0,\mathrm{rel}}$ (○) with EGDM concentration. The photoinitiator was benzoin

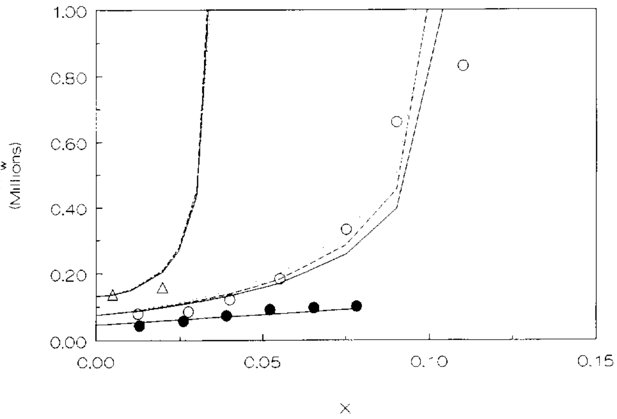


Figure 5 Variation of the weight-average molecular weight of the pregel polymers $\bar{M}_\mathrm{w}$ with the monomer conversion x in MMA–EGDM copolymerization in the presence of benzoin. EGDM mol% = 0 (●), 9.3 (○) and 50 (△). The curves for crosslinked systems were calculated using the kinetic model for $a = 0$ (solid curves), 2 (dashed curves) and 5 (dotted curves). The parameters used in the calculations were $r_{21} = 1$, $k_\mathrm{cyc} = 0.3$ and $\bar{r}'_{32} = \bar{r}^0_{32}$

$$\frac{(\mathrm{d}x/\mathrm{d}t)_0}{(\mathrm{d}x/\mathrm{d}t)_{0,l}} = \frac{\bar{M}^\bullet_{\mathrm{w},0}}{\bar{M}^\bullet_{\mathrm{w},0,1}} \tag{11}$$

where $\bar{M}^\bullet_{\mathrm{w},0}$ and $\bar{M}^\bullet_{\mathrm{w},0,1}$ are the weight-average molecular weights of the primary chains at zero monomer conversion in the presence and absence of the crosslinker respectively. Thus, the increase of the initial rates shown in *Figure 4* also indicates an increase of the initial primary chain length with increasing crosslinker concentration. Similar results were also obtained for the other initiators used. This indirect evidence of the variation of the initial primary chain length with crosslinker concentration was examined with the molecular weight averages obtained from the g.p.c. curves. In *Figure 5*, weight-average molecular weights obtained from g.p.c. curves are given as a function of the monomer conversion x for different crosslinker concentrations from 0 to 50 mol% EGDM. The curves for crosslinked systems were calculated using the kinetic model as discussed in the following sections. By extrapolating to zero monomer conversion, the apparent molecular weights of the primary chains were estimated. Although the g.p.c. curves cannot be treated to give quantitative estimates of the molecular weights, the results indicate an increase of the molecular weight with the crosslinker content and, thus, support our previous finding.

Variation of the initial rates or molecular weights of the primary chains with the EGDM concentration suggests that the termination rate constant of zero conversion polymer radicals, k_{t0}, should depend on the crosslinker content of the initial monomer mixture. The relative initial termination rate constant of the radicals, $k_{t0,\mathrm{rel}}$, calculated using equation (9), is also shown in *Figure 4* as a function of the EGDM concentration. For calculations, the reactivities of the monomeric vinyls are taken as equal[28,47]. $k_{t0,\mathrm{rel}}$ decreases continuously as the amount of crosslinker in the reaction mixture increases. Since we are dealing here with zero-conversion polymer radicals, i.e., the polymer radicals in the absence of preformed polymers, the variation of k_{t0} with EGDM content can be possible only by a change of the macroradical coil dimensions, which may occur as a result of a first-order intramolecular reaction such as cyclization.

In *Figure 6A*, the rate of polymerization, $\mathrm{d}x/\mathrm{d}t$, calculated using a polynomial fit of the experimental x vs t data, is shown as a function of the monomer conversion x. In *Figure 6B*, the rates have been converted to the termination rate constants using equation (8). No gel effect can be seen in the absence of the crosslinker up to 10% monomer conversion. As the amount of crosslinker increases, the decrease in k_t with conversion becomes more dominant as a result of the increasing gel effect.

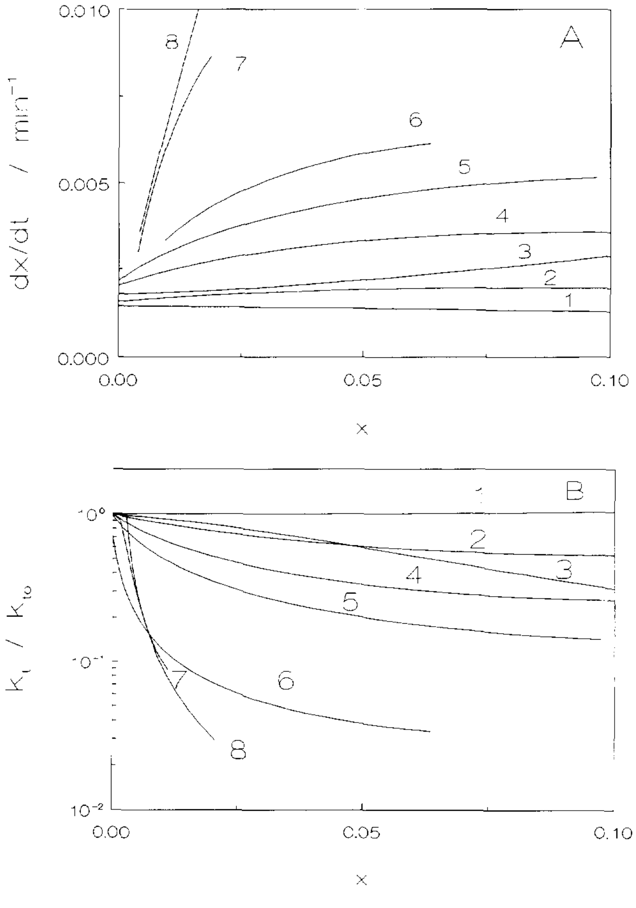


Figure 6 Rate of polymerization $\mathrm{d}x/\mathrm{d}t$ (A) and relative termination rate constant k_t/k_{t0} (B) shown as a function of the monomer conversion x in MMA–EGDM copolymerization, using benzoin as photoinitiator. EGDM mol% = 0 (1), 3.5 (2), 6.4 (3), 9.3 (4), 15.1 (5), 25 (6), 75 (7) and 100 (8)

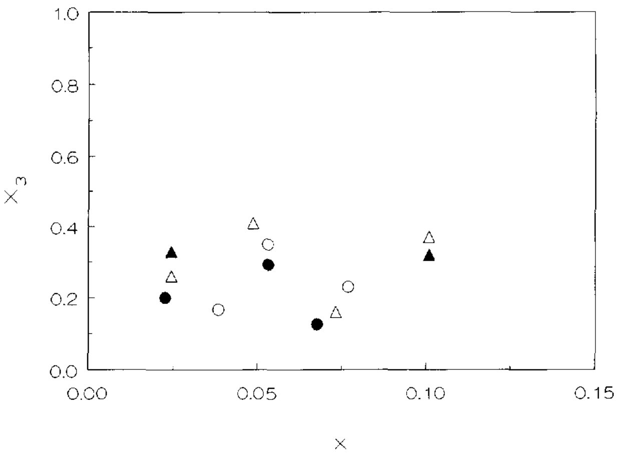


Figure 7 Pendant conversion x_3 vs monomer conversion x in MMA–EGDM copolymerization. The photoinitiators used were benzoin (empty symbols) and benzoin methyl ether (filled symbols). EGDM mol% = 9.3 (○, ●) and 15.1 (△, ▲)

Cyclization

Figure 7 shows the plot of pendant conversion x_3 *versus* monomer conversion x for different crosslinker concentrations. Some scatter of the data points originates from the uncertainty of the method of measurements, which is estimated to be ±0.1. We obtain a limiting value for pendant conversion of about 0.3, indicating that 30% of pendant double bonds are consumed by the cyclization reaction. The fraction of units in cycles is independent of the EGDM concentration. However, since increasing EGDM concentration also increases the number of divinyl monomer units on the polymer molecules, the higher the EGDM content, the higher is the number of cycles on polymer chains, and therefore the more compact are the primary particles. It is difficult to derive the extent of multiple crosslinkages from the experimental data in *Figure 7* because of the experimental error involved in the data points. However, the slight change in polymer unsaturation with conversion indicates that the multiple crosslink reactions are not important under the experimental conditions. The results on cyclization are in accord with the reaction rate data of the previous section. Increasing crosslinker content increases the compactness of the structures formed; this will result in a decrease in the mobility of chain segments and therefore suppresses diffusion-controlled termination of radicals owing to steric reasons. These phenomena are reflected in the enhancement of the rate of polymerization shown in *Figure 2*.

Previous percolation-type simulations, called kinetic gelation models[6,50], predicted zero pendant vinyl group conversion at zero monomer conversion. This means that there is no cycle formation at the start of the reaction; as the reaction proceeds, the number of cycles increases rapidly and, after passing a maximum, decreases again. However, our experimental results show that these predictions are incorrect. In fact, since cyclization involves only the reactions of a polymer radical with its own chain, it is reasonable to expect maximum cycle formation at zero monomer conversion. Indeed, our present results show that the extrapolated value of pendant vinyl conversion to zero monomer conversion is always not zero, indicating the existence of cycles in the first-formed primary molecules.

Gel points

Experimentally determined gel points, in terms of both the reaction time t_c and monomer conversion x_c are collected in *Figures 8A* and *8B*, respectively, as a function of the EGDM concentration. The initiators used were benzoin (B), benzoin methyl ether (BME), benzoin ethyl ether (BEE) and 2,2-dimethoxy-2-phenyl acetophenone (DMPA). The expected inverse dependence of the gel point on crosslinker concentration is seen for EGDM contents less than 40%. At higher EGDM contents, the gel point becomes insensitive to the amount of crosslinker in the initial monomer mixture. Moreover, gelation with respect to time occurs earlier if the initiators are changed in the order B < BME or BEE < DMPA, i.e., increasing the rate of polymerization. Experimental data also suggest that the critical conversion at the gel point x_c is independent of the type of photoinitiator, within the limits of experimental error. This is actually expected due to the fact that, according to equation (1), the weight-average molecular weights do not depend on the rate of initiation.

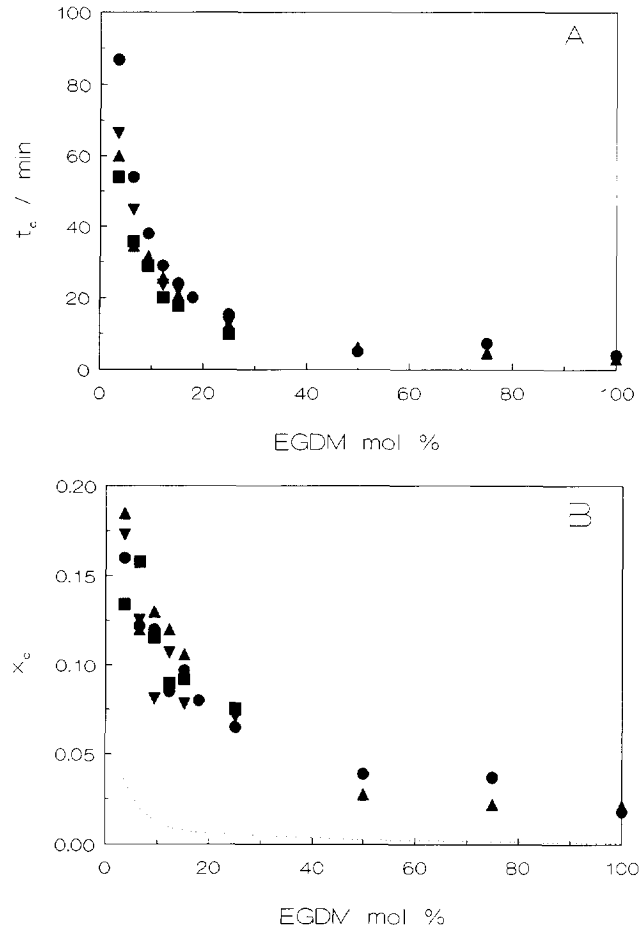


Figure 8 Gel points in terms of the reaction time t_c (A) and monomer conversion x_c (B) shown as a function of the EGDM concentration. The photoinitiators used were benzoin (●), benzoin methyl ether (▲), benzoin ethyl ether (▼) and 2,2-dimethoxy-2-phenylacetophenone (■). The dotted curve in (B) was calculated using the kinetic model for equal vinyl group reactivity. Cyclization and drift in the chain length were taken into account. Parameters used in the calculations were $r_{21} = \bar{r}_{32} = 1$ and $k_{cyc} = 0.3$

Pendant reactivity

Using the gel point data, the reactivity of pendant vinyl groups can be calculated. The value of $\bar{r}_{32}$ satisfying $\bar{M}_w = \infty$ at $x = x_c$ may be obtained numerically by simultaneous solution of equations (1)–(6). In the calculations the drift in the primary chain length was taken into account using equation (10), and the weight-average molecular weights of the primary chains at zero conversion $\bar{M}^{\bullet}_{w,0}$ were calculated from the $x = 0$ intercept of experimental M_w vs x plots.

Taking into account cyclization reactions but assuming that the reactivity of pendant vinyl groups is the same as that of the vinyl groups on the EGDM molecule, that is assuming $\bar{r}_{32} = 1$ (no substitution effect), the model predicts the gel points shown in *Figure 8B* as a dotted curve. It seems that the actual gel points exceed those predicted for $\bar{r}_{32} = 1$ by 1–2 orders of magnitude. The ratio of experimental to theoretical gel points for $\bar{r}_{32} = 1$ increases with increasing amounts of crosslinker. The model predicts actual gel points if the reactivity ratio $\bar{r}_{32}$ is much less than unity. The calculated $\bar{r}_{32}$ values are shown in *Figure 9* as a function of the EGDM concentration. The average reactivity of pendant vinyls strongly depends on the crosslinker concentration and decreases as the crosslinker concentration increases. At 5–15 mol% EGDM, the average pendant reactivity is 1–2 orders of magnitude lower than the monomeric vinyl reactivity. At higher EGDM contents, pendant reactivity becomes insensitive to the amount of crosslinker. Thus, although both cyclization and reduced pendant reactivity coexist in free-radical crosslinking copolymerizations, the latter is mainly responsible for the delay in the gel point. The consumption of nearly 30% of the pendant vinyl groups by cyclization reactions and the drastically reduced reactivity of the residual vinyl groups suggest the formation of compact, mutually impenetrable microgel particles as intermediates in free-radical MMA–EGDM copolymerization.

It must be pointed out that the kinetic model assumes constant rates for cyclization, crosslinking and multiple crosslinking reactions throughout the copolymerization. This assumption may not be valid in free-radical

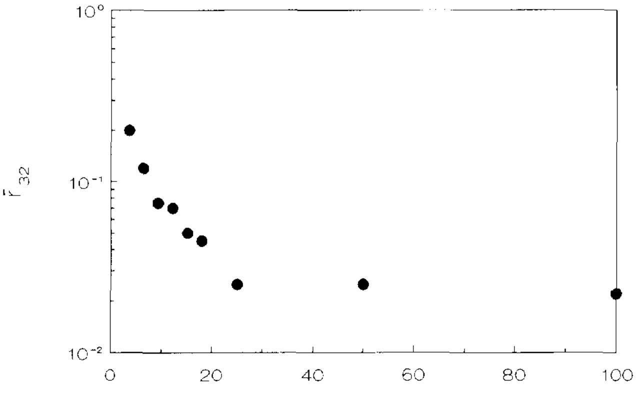


Figure 9 Variation of the average reactivity ratio of pendant to monomeric vinyls for intermolecular reactions, $\bar{r}_{32}$, with EGDM concentration in MMA–EGDM copolymerization, using benzoin as initiator. Calculations were for $r_{21} = 1$, $k_{cyc} = 0.3$ and $\bar{r}'_{32} = \bar{r}^0_{32}$

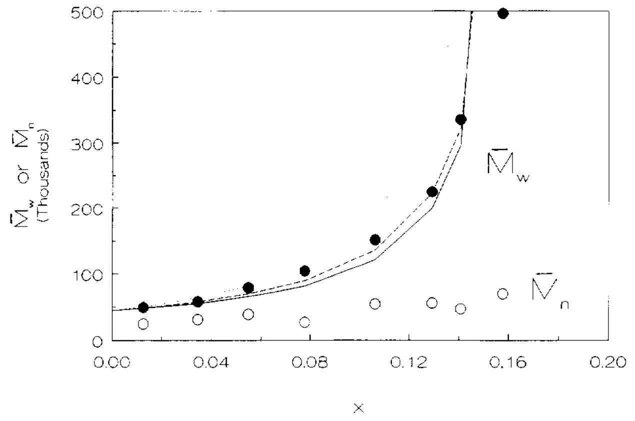


Figure 10 Weight- (●) and number-average (○) molecular weights vs conversion x in MMA–EGDM copolymerization at 6.4% EGDM concentration. The initiator was 2,2-dimethoxy-2-phenylacetophenone. The curves were calculated using the kinetic model for $a = 0$ (solid curves), 2 (dashed curves) and 5 (dotted curves). The parameters used in the calculations were $r_{21} = 1$, $k_{\mathrm{cyc}} = 0.3$ and $\bar{r}'_{32} = \bar{r}^0_{32}$

polymerizations due to the conversion dependence of the relative contributions of cyclization and multiple crosslinking reactions. One may expect that k_{mc} is zero at zero monomer conversion and increases as the reaction proceeds because multiple crosslinking becomes more probable the larger the molecules formed. Furthermore, an increasing number of multiple crosslinkages would lead to the formation of compact structures; thus the pendant reactivity represented by $\bar{r}_{32}$ should decrease as the reaction proceeds owing to the increasing extent of shielding of pendant vinyl groups. Accordingly, an increase in k_{mc} would lead to a decrease of the pendant reactivity $\bar{r}_{32}$. In order to account for decreasing pendant reactivity and increasing rate of multiple crosslinking reactions during the polymerization, the following empirical equation was recently proposed[51]:

$$\bar{r}_{32} = \bar{r}^0_{32}\exp(-ax) \tag{12}$$

where $\bar{r}^0_{32}$ is the reactivity ratio of pendant to monomeric vinyl at zero monomer conversion and a is an adjustable parameter. In order to evaluate the unknown parameters $\bar{r}^0_{32}$ and a, the model equations can be solved together with equation (12) to provide a best fit to the experimental $\bar{M}_w$ vs x data. *Figure 10* shows the variation of $\bar{M}_w$ and $\bar{M}_n$ with monomer conversion x at 6.4% EGDM concentration and in the presence of the photoinitiator DMPA. The curves were calculated using the kinetic model for $a = 0$, 2 and 5 (solid, dashed and dotted curves respectively). The curves in *Figure 5* also compare the calculation results with the experimental data. It seems that the calculations for $a = 0$ provide good agreement with the experimental data and the additional equation (12) is not necessary for the present copolymerization system. This is in contrast to the polymerization system of 1,4-DVB in dilute solutions[14,51], where both pendant reactivity and multiple crosslinking are strong functions of conversion. In the latter system, 1,4-DVB concentration was less than 5% (present monomer concentration is 35%). Under these reaction conditions, it was found that, on average, 100–800 multiple crosslinkages occur per intermolecular crosslink formed.[14] Thus, compared to the present system, 1,4-DVB polymerization leads to the formation of denser structures, probably because of the higher degree of monomer dilution.

Size distribution of sol molecules

Figure 11 shows a representative set of gel-permeation chromatograms (g.p.c.) for reaction products isolated at different reaction times up to the close vicinity of the gel point. The initial concentrations of EGDM were 0, 1, 6 and 9 mol% for series A, B, C and D respectively. As the polymerization time in MMA–EGDM copolymerization increases, the polydispersity ratios increase and the distribution curves change from single peaks to wider, bimodal distributions. The shape of the large elution volume peaks is essentially the same, irrespective of the polymerization time, while small elution volume-peaks are increased significantly as the reaction proceeds. Increasing crosslinker concentration results in strongly bimodal g.p.c. curves in the immediate vicinity of the gel point. For free-radical systems, bimodal distributions have been observed previously[52,53], but also, in some studies, monomodal g.p.c. curves have been reported[54,55]. Calculations using statistical[56] or kinetic[57,58] theories predict, however, monomodal weight–chain length distributions, which are fundamentally equivalent to the elution curve in the g.p.c. Calculated results for the sol phase near the gel point give flat curves extending across the molecular weight (elution volume) axis toward infinity. However, as shown in *Figure 11*, the actual behaviour is completely different. It is known that the molecules are separated in the g.p.c. columns according to their hydrodynamic volume. Thus, the molecules with the same molecular weight but different hydrodynamic volumes, i.e., those with shape polydispersity, are eluted at different times. Since the mean field theories only consider the molecular weight polydispersity, the difference between theory and experiment can be attributed to the shape polydispersity of the molecules present during the polymerization. One may expect that the large shape polydispersity due to the increasing extent of cyclization at high EGDM contents results in the observed strongly bimodal curves. Thus, the single peaks that appear at low conversion correspond to the microgels while their aggregates appear as a second peak in the small elution volumes side of the microgel peak.

CONCLUSIONS

Approximately 30% of the pendant vinyl groups are consumed by cyclization reactions during the pregel regime of the photoinitiated copolymerization of MMA and EGDM in toluene solutions. The fraction of units in cycles is independent of the EGDM concentration. However, since increasing EGDM concentration also increases the number of divinyl monomer units on the polymer molecules, the higher the EGDM content, the higher the number of cycles on polymer chains, and therefore the more compact are the 'primary particles' formed. Due to the cyclization reactions, the accessibility of the radical centres and pendant vinyl groups for other polymer molecules is strongly reduced. As a result, both termination and crosslinking reactions are controlled by the segmental diffusion of the polymer radicals. Variations in the polymerization rate and the molecular weights of the primary molecules with the EGDM concentration reflect the decrease of the diffusion-controlled termination rate constants with increasing crosslinker concentration. Since cyclization is a first-order reaction, the termination rate constant

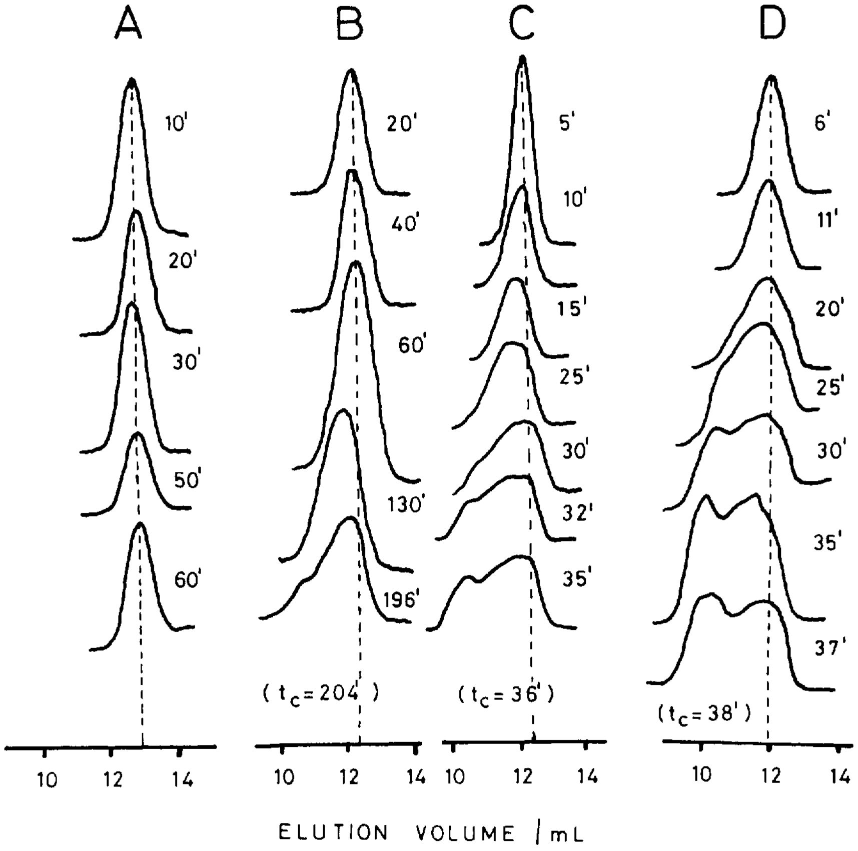


Figure 11 G.p.c. chromatograms of the pregel polymers isolated at different reaction times in MMA–EGDM copolymerization. The initiator was benzoin. EGDM concentration = 0 (A), 1 (B), 6 (C) and 9 mol% (D)

of zero conversion polymer radicals also depends on the crosslinker content of the monomer mixture.

Because of the sensitive dependence of the gel point on the average reactivity of pendant vinyl groups represented by $\bar{r}_{32}$, the set of equations (1)–(6) of the kinetic model are convenient for determining the value of $\bar{r}_{32}$ once the cyclization parameters have been found by using equation (2). Calculations indicate a 1–2 orders of magnitude decrease in the average reactivity of pendant vinyls for intermolecular reactions compared with monomeric vinyl. In accord with our previous results[14], this drastic decrease in pendant reactivity is mainly responsible for the delay in the gel point. Thus, the discrepancy between the observed and calculated gel points, reported in the literature already as early as 1945[59], is mainly due to the reduced reactivity of pendant vinyl groups.

Contrary to the gelation theories, the size distribution curves of the pregel polymers change from monomodal to bimodal distributions as polymerization proceeds. The position and shape of the large elution volume peak corresponding to polymers with small hydrodynamic volumes remain essentially unchanged during the reactions, while a second peak corresponding to small elution volumes appears as the polymerization time approaches the gelation time. This finding confirms the coagulation-type gelation mechanism of compact primary particles and indicates the shape polydispersity of the pregel polymers. It must be noted that by modifying the termination and crosslinking reaction rate constants to include their dependence on the structure of the reacting molecules, one may incorporate the size and structure dependent kinetics into the mean field model calculations.

The experimental data obtained in the present study were studied within the framework of a kinetic model. The model takes into account all the kinetic features of the copolymerization reactions. It is to be noted that as the mean-field theories neglect excluded volume effects and concentration fluctuations, which should play an important role in the vicinity of the gel point, these kinetic equations may be used up to the critical region.

REFERENCES

1 Kloosterboer, J. G. *Adv. Polym. Sci.* 1988, **84**, 1
2 Kloosterboer, J. G. and Lijten, G. F. C. M. in 'Cross-Linked Polymers. Chemistry, Properties, and Applications' (Eds R. A. Dickie, S. S. Labana and R. S. Bauer), ACS Symp. Ser. 367, 1988, Ch. 28
3 Decker, C. *Acta Polym.* 1994, **45**, 333
4 Okay, O. *Angew. Makromol. Chem.* 1987, **153**, 125
5 Wilson, T. W. *J. Appl. Polym. Sci.* 1990, **40**, 1195
6 Kloosterboer, J. G., van de Hei, G. M. M. and Boots, H. M. J. *Polym. Commun.* 1984, **25**, 354
7 Decker, C. and Moussa, K. *J. Polym. Sci., Polym. Chem. Ed.* 1987, **25**, 739
8 Zhu, S., Tian, Y., Hamielec, A. E. and Eaton, D. R. *Polymer* 1990, **31**, 154
9 Allen, P. E. M., Bennett, D. J., Hagias, S., Hounslow, A. M., Ross, G. S., Simon, G. P., Williams, D. R. G. and Williams, E. H. *Eur. Polym. J.* 1989, **25**, 785
10 Funke, W. *Chimia* 1968, **22**, 111
11 Storey, B. T. *J. Polym. Sci.* 1965, **A3**, 265
12 Kast, H. and Funke, W. *Makromol. Chem.* 1979, **180**, 1335
13 Flory, P. J. *J. Am. Chem. Soc.* 1941, **63**, 3083
14 Okay, O., Kurz, M., Lutz, K. and Funke, W. *Macromolecules* 1995, **28**, 2728
15 Pappas, S. P. 'U.v. Curing in Science and Technology', Technology Marketing Corp., Norwalk, CT, 1978, p. 13

16 Ledwith, A., Russel, J. P. and Sutcliffe, L. H. *J. Chem. Soc., Perkin Trans.* 1972, **II**, 1925

17 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953

18 Stockmayer, W. H. *J. Chem. Phys.* 1943, **11**, 45

19 Stockmayer, W. H. *J. Chem. Phys.* 1944, **12**, 125

20 Gordon, M. *Proc. R. Soc. Lond., Ser. A* 1962, **268**, 240

21 Macosko, C. W. and Miller, D. R. *Macromolecules* 1976, **9**, 199

22 Miller, D. R. and Macosko, C. W. *Macromolecules* 1976, **9**, 206

23 Dotson, N. A. *Macromolecules* 1992, **25**, 308

24 Aso, C. *J. Polym. Sci.* 1959, **39**, 475

25 Dusek, K. in 'Developments in Polymerization—3' (Ed. R. N. Haward), Applied Science, London, 1982, p. 143

26 Fukuda, T., Ma, Y.-D. and Inagaki, H. *Macromolecules* 1985, **18**, 17

27 Mikos, A. G., Takoudis, C. G. and Peppas, N. A. *Macromolecules* 1986, **19**, 2174

28 Landin, D. T. and Macosko, C. W. *Macromolecules* 1988, **21**, 846

29 Tobita, H. and Hamielec, A. E. *Makromol. Chem. Macromol. Symp.* 1988, **20/21**, 501

30 Tobita, H. and Hamielec, A. E. *Macromolecules* 1989, **22** 3098

31 Tobita, H. and Hamielec, A. E. *Makromol. Chem. Macromol. Symp.* 1990, **35/36**, 193

32 Okay, O. *Polymer* 1994, **35**, 796

33 Okay, O. *Polymer* 1994, **35**, 2613

34 Okay, O. *Macromol. Theory Simul.* 1994, **3**, 417

35 Broadbent, S. R. and Hammersley, J. M. *Proc. Camb. Philos. Soc.* 1957, **53**, 629

36 Stauffer, D., Coniglio, A. and Adam, M. *Adv. Polym. Sci.* 1982, **44**, 103

37 Bansil, R., Herrmann, H. J. and Stauffer, D. *Macromolecules* 1984, **17**, 998

38 Holt, T. and Simpson, W. *Proc. R. Soc. Lond.* 1956, **A238**, 154

39 Skeist, I. *J. Am. Chem. Soc.* 1946, **68**, 1781

40 Odian, G. 'Principles of Polymerization', McGraw-Hill, NY, 1981, Ch. 6

41 Anseth, K. S., Wang, C. M. and Bowman, C. N. *Macromolecules* 1994, **27**, 650

42 Anseth, K. S., Kline, L. M., Walker, T. A., Anderson, K. J. and Bowman, C. N. *Macromolecules* 1995, **28**, 2491

43 Okay, O, Naghash, H. J. and Capek, I. *Polymer* 1995, **36**, 2413

44 Okay, O. and Naghash, H. J. *Polym. Bull.* 1994, **33**, 665

45 Capek, I. and Funke, W. *Makromol. Chem.* 1990, **191**, 2549

46 Luskin, L. S. in 'Encyclopedia of Industrial Chemical Analysis' (Eds F. D. Snell and C. L. Hilton), Vol. 4, John Wiley, New York, 1967, p. 190

47 Whitney, R.. S. and Burchard, W. *Makromol. Chem.* 1980, **181**, 869

48 Dietliker, K. 'Chemistry and Technology of U.v. to EB Formulation for Coatings, Inks and Paints', SITA Technology Ltd, London, 1991, p. 118

49 Pappas, S. P. and Chattopadhyay, A. K. *J. Polym. Sci., Polym. Lett. Ed.* 1975, **13**, 483

50 Anseth, K. and Bowman, C. N. *Chem. Eng. Sci.* 1994, **49**, 2207

51 Okay, O., Naghash, H. J. and Pekcan, O. *Macromol. Theory Simul.* 1995, **4**, 967

52 Schah, A. C., Holdaway, I., Parsons, I. W. and Haward, R. N. *Polymer* 1978, **19**, 1067

53 Galina, H. and Rupicz, K. *Polym. Bull.* 1980, **3**, 473

54 Soper, B., Haward, R. N. and White, E. F. T. *J. Polym. Sci. A-1* 1972, **10**, 2545

55 Shindo, Y., Sugimura, T., Horie, K. and Mita, I. *Eur. Polym. J.* 1986, **22**, 859

56 Flory, P. J. *J. Am. Chem. Soc.* 1941, **63**, 3091

57 Tobita, H. *Macromol. Theory Simul.* 1993, **2**, 761

58 Arzamendi, G. and Asua, J. M. *Macromolecules* 1995, **28**, 7479

59 Walling, C. *J. Am. Chem. Soc.* 1945, **67**, 441