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Free-radical crosslinking copolymerization: effect of cyclization on diffusion-controlled termination at low conversion

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The pregelation period of free-radical methyl methacrylate/ethylene glycol dimethacrylate (MMA/EGDM) and acrylamide/*N,N'*-methylenebisacrylamide (AAm/BAAm) copolymerization systems was studied by means of the dilatometric technique. The amount of cyclization in MMA/EGDM copolymers was estimated using proton nuclear magnetic resonance and analytical titration methods. The results suggest that, in MMA/EGDM copolymerization and at a monomer concentration of $220\,\mathrm{g\,l^{-1}}$, nearly half of the pendent double bonds are consumed by cyclization. It was found that the average termination rate constant of macroradicals at zero conversion, k_{t0}, is dependent on the crosslinker concentration. k_{t0} increases first but then decreases continuously as the amount of crosslinker increases. Moreover, termination rate constants become less sensitive to conversion in the presence of small amounts of crosslinker. All of these phenomena can be explained in terms of cyclization, as it decreases the size of macroradical coils by producing intramolecular links.

(Keywords: cyclization; crosslinking; termination rate)

INTRODUCTION

Properties of polymer networks are known to depend on their structure, and the latter is closely related to the network formation process. Polymer networks are generally prepared by free-radical crosslinking copolymerization of monovinyl and divinyl monomers in a suitable solvent. Previous studies have shown that the mechanism of network formation in free-radical crosslinking copolymerization differs appreciably from the prediction of the network formation theories[1–19]. The difference between the actual and predicted behaviour of free-radical crosslinking copolymerization has mainly been attributed to cyclization and to diffusion control, which are not properly accounted for in network formation theories.

Cyclization is a characteristic feature of free-radical crosslinking copolymerization, especially at zero conversion, at which it strongly influences the polymer structure[11,20–24]. In the treatment of cyclization, it may be convenient to divide these reactions into two types[11], namely cyclization[2] (primary cyclization) and multiple crosslinking[25] (secondary cyclization[23]). With cyclization the cycle is formed when the macroradical attacks the pendent double bonds in the same chain, while with multiple crosslinking it is formed if the radical attacks double bonds pendent on other chains already chemically connected with the growing macroradical. The cyclization, multiple crosslinking and crosslinking reactions are shown schematically in *Figure 1*. Kinetic and statistical models that include constants for cyclization or for chain flexibility are only an approximation to the real situation because cyclization 'constants' are dependent on conversion[11,23]. On the other hand, very little is known about diffusion control in free-radical crosslinking copolymerization[6,15–17]. One may expect that, because of cyclization and crosslinking, the reactions of pendent vinyl groups and the radical end inside a polymer coil become diffusion controlled right down to zero conversion.

In the present study, we intend to elucidate the effect of cyclization reactions on the average termination rate constant of polymer radicals. This subject has not, to our knowledge, been studied previously. Two commonly used comonomer systems for network synthesis were selected for this purpose, namely methyl methacrylate/ethylene glycol dimethacrylate (MMA/EGDM) and acrylamide/*N,N'*-methylenebisacrylamide (AAm/BBAm) systems. The pregel regime of the crosslinking copolymerization reactions was studied by means of the dilatometric technique. Polymerization solvents, toluene and water for MMA/EGDM and AAm/BAAm systems respectively, were used at a high concentration to ensure that strong cyclization occurs during the reaction. The crosslinkers EGDM and BAAm were used in small amounts to provide a long pregel period. The amount of cyclization in MMA/EGDM copolymers was estimated using proton nuclear magnetic resonance, ^{1}H n.m.r. and analytical titration methods.

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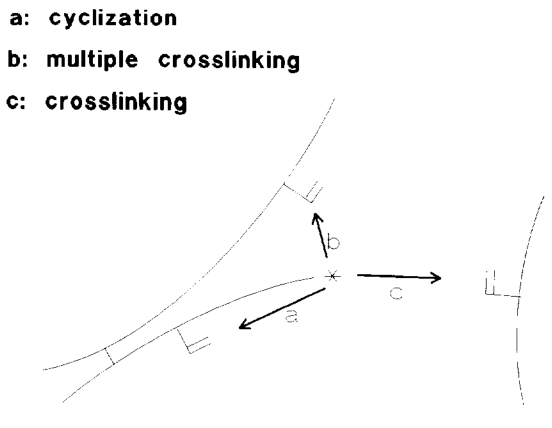

Figure 1 Schematic drawing of the processes of (a) cyclization, (b) multiple crosslinking and (c) crosslinking in free-radical crosslinking copolymerization

EXPERIMENTAL

Materials

Commercially available methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDM), acrylamide (AAm) and *N,N'*-methylenebisacrylamide (BAAm) monomers and the initiators 2,2'-azobisisobutyronitrile (AIBN) and potassium peroxodisulfate ($K_2S_2O_8$) were purified by usual methods. The polymerization solvents toluene (Merck p.a.) and water were twice distilled before use. Sodium hydrogen carbonate ($NaHCO_3$) and sodium thiosulfate ($Na_2S_2O_3$) (both analytical grades) were used without further purification.

Polymerization procedure

MMA–EGDM copolymerizations were carried out in toluene at 60±0.1°C with AIBN as the initiator. AAm–BAAm copolymerizations were carried out in water at 40±0.1°C with $K_2S_2O_8/NaS_2O_3$ redox initiator system in the presence of $NaHCO_3$ buffer. The conversion of monomers up to the onset of macrogelation was followed by dilatometry. The dilatometers 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 meniscus was read with a millimetric paper to 0.2 mm. The polymerization technique used was described in detail elsewhere[26]. The reproducibility of the kinetic data was checked by repeating the experiments. The deviation in the initial slopes of time *versus* conversion data between two runs was always less than 3%. The polymer samples for pendent vinyl group measurements were obtained by a gravimetric technique as described previously[27].

Different series of experiments were carried out. In each series, monomer and initiator concentrations were held constant while the crosslinker concentration was varied from 0 to 0.04. The crosslinker concentrations are expressed as the mole fraction of the vinyl groups in the initial monomer mixture contributed by the crosslinker, ρ_0. The number-average chain length of zero-conversion polymer radicals $\bar{X}_1^{\cdot *}$ was estimated using the equation[28]:

$$\bar{X}_1^{\cdot *} = a[M]_0[I]_0^{-0.5} \tag{1}$$

where $[M]_0$ and $[I]_0$ are the initial concentrations of the monomers and the initiator, respectively, and a is a constant which includes initiation, propagation and termination rate constants, i.e. $a = k_p/(2fk_tk_d)^{0.5}$. The value of a for the MMA/EGDM system at 60°C was estimated as $4 \times 10^1\,(\mathrm{l\,mol^{-1}})^{0.5}$.

In *Figures 2A, B* and *C*, some of the fractional conversion x *versus* time data are given for different crosslinker concentrations, ρ_0. The initial polymerization

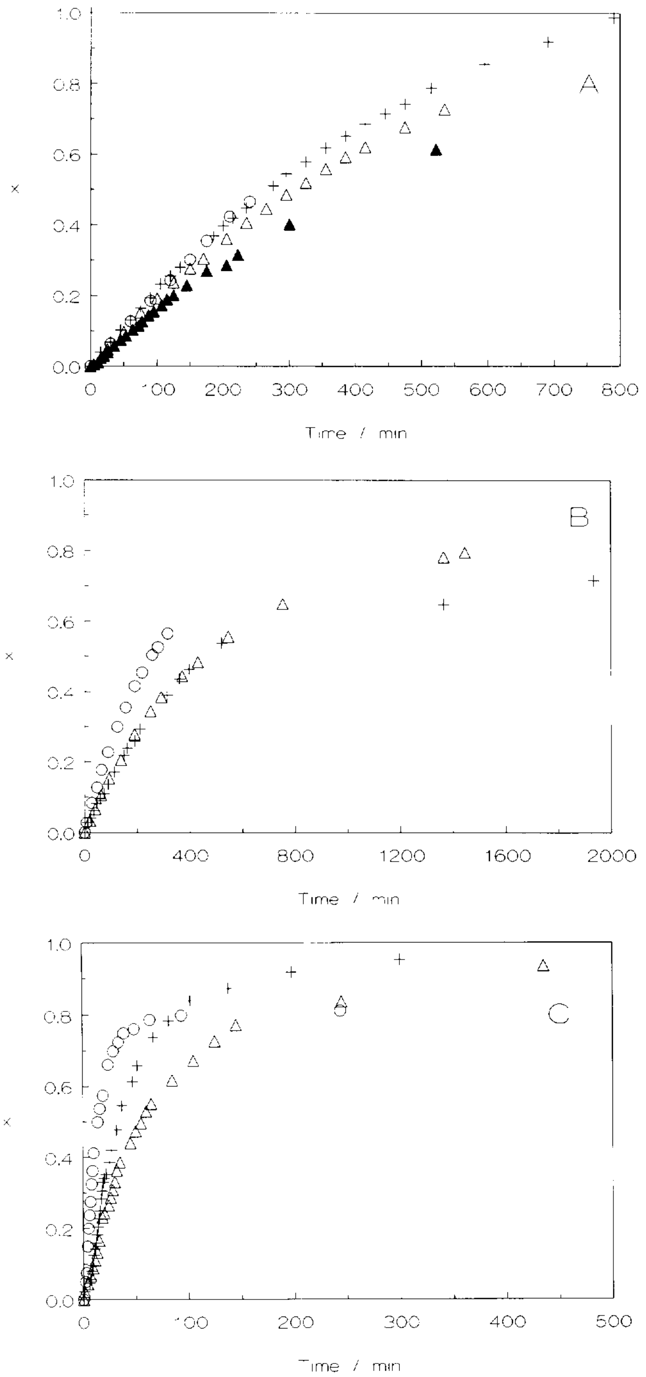

Figure 2 Variation of the conversion *versus* time histories in free-radical crosslinking copolymerization with the crosslinker concentration. (A) MMA/EGDM system: initial monomer concentration $(c) = 230\,\mathrm{g\,l^{-1}}$; $\bar{X}_1^{\cdot *} = 1 \times 10^3$; $10^2 \times \rho_0 = 0$ (+), 0.01 (▲), 0.15 (△), 1.5 (○). (B) MMA/EGDM system: $c = 100\,\mathrm{g\,l^{-1}}$; $\bar{X}_1^{\cdot *} = 4 \times 10^2$; $10^2 \times \rho_0 = 0$ (+), 3.4 (△), 7.6 (○). (C) AAm/BAAm system: $c = 35\,\mathrm{g\,l^{-1}}$; $[K_2S_2O_8] = [Na_2S_2O_3] = [NaHCO_3] = 1 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$; $10^2 \times \rho_0 = 0$ (+); 4×10^{-3} (△); 3.85 (○)

rates were estimated from the lines drawn through the data points for $x < 0.10$ by using a least-squares fit. In *Figures 3A* and *B*, the initial rate of polymerization $(dx/dt)_0$ is plotted as a function of the crosslinker concentration, ρ_0, for MMA/EGDM and AAm/BAAm systems, respectively.

Pendent vinyl groups

Measurement of the number of pendent vinyls on MMA/EGDM copolymers was first attempted by proton nuclear magnetic resonance, ^1H n.m.r., as in the work of Landin and Macosko[23]. N.m.r. spectra were obtained with a Bruker 200 MHz spectrometer. The sample preparation method and measurement conditions were identical to those described by Landin and Macosko[23] (one-pulse sequence with a 45° pulse, 2 s delay time, and 2.05 s acquisition time; approximately 100 acquisitions were obtained per spectrum; quadrature detection was used and the spectral window was 4000 Hz). A typical n.m.r. spectrum of the region from 4 to 6.5 ppm is shown in *Figure 4*. The pendent vinyl conversion p_p, i.e. the fraction of EGDM units with both vinyl groups reacted, was measured from a comparison of the pendent methylene peaks at 5.65 and 6.2 ppm with the ethylene glycol peaks at 4.2 to 4.4 ppm. Pendent conversion was calculated as:

$$p_p = 1 - \frac{A_{CH_2=}/2}{A_{OCH_2}/4} \tag{2}$$

where $A_{CH_2=}$ and A_{OCH_2} are the areas under the peaks. Note that $p_p = 0$ corresponds to linear polymers in which all EGDM units bear pendent vinyl groups.

Measurement of pendent conversion in the MMA/EGDM system was also carried out by bromometry using pyridine sulfate dibromide (PSDB) reagent in glacial acetic acid solution. From various titration methods, bromination with PSDB in the presence of mercury acetate catalyst is reported to be capable of very accurate results[29]. The method is based on the reaction of pendent vinyl groups with bromine produced *in situ* from the PSDB reagent and back-titration of the excess bromine. For the calculation of pendent conversion, the reactivities of monomeric vinyls were assumed to be equal[8,23].

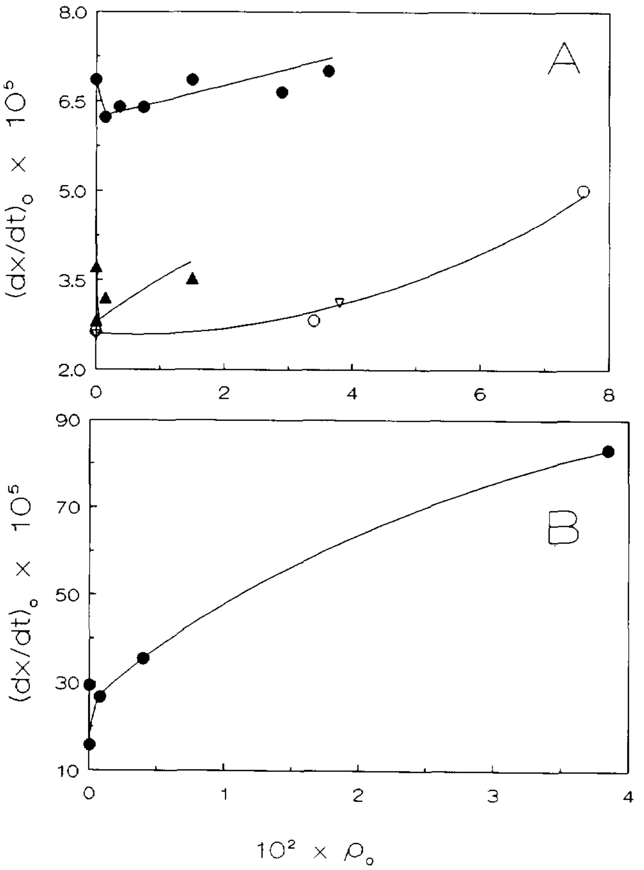

Figure 3 Variation of the initial rate of polymerization $(dx/dt)_0$ with the crosslinker concentration. (A) MMA/EGDM system: $\bar{X}_1^* = 4 \times 10^2$; $c = 230\ \mathrm{g\,l^{-1}}$ (●), $100\ \mathrm{g\,l^{-1}}$ (○), $90\ \mathrm{g\,l^{-1}}$ (▽); $\bar{X}_1^* = 1 \times 10^3$; $c = 230\ \mathrm{g\,l^{-1}}$ (▲). (B) AAm/BAAm system: $c = 35\ \mathrm{g\,l^{-1}}$; $[K_2S_2O_8] = [Na_2S_2O_3] = [NaHCO_3] = 1 \times 10^{-3}\ \mathrm{mol\,l^{-1}}$

RESULTS AND DISCUSSION

Extent of cyclization

Landin and Macosko[23] attempted to measure the pendent double bonds in MMA/EGDM copolymers by the ^1H n.m.r. technique. They obtained linear pendent conversion *versus* monomer conversion relations in a series of experiments with varying amounts of EGDM (0.57–1.70 mol%) and monomer (25–100 vol% in toluene). Unfortunately, they reported only a few data points for each system studied and did not mention the reproducibility of their data. More recently, Dotson *et al.*[18] reported that ^1H n.m.r. measurements result in negative pendent conversion values for a series of highly branched MMA/EGDM copolymers. They explained these anomalies by the decreased mobility of protons in such highly intramolecularly crosslinked structures.

In the present work, we have also tried to measure the pendent vinyl group content of MMA/EGDM copolymers by ^1H n.m.r. For this purpose, a MMA/EGDM copolymerization was conducted in a 500 ml reactor and 22 samples were taken during the course of the reaction.

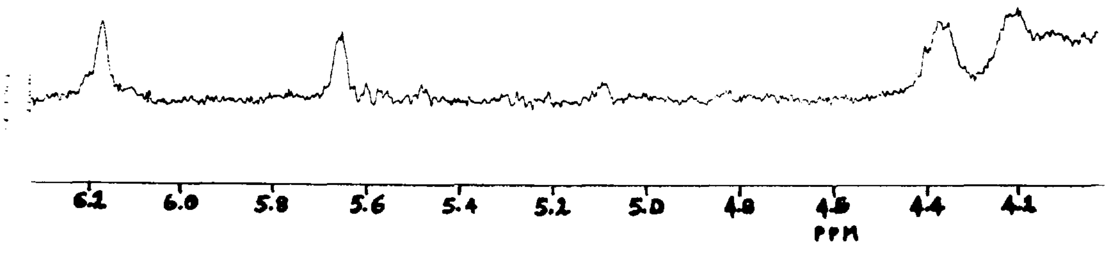

Figure 4 ^1H n.m.r. spectrum (4–6.5 ppm region) of a MMA/EGDM copolymer sample with $10^2 \times \rho_0 = 0.75$

The monomer concentration, c, was 220 g l^{-1} and the crosslinker concentration ρ_0 was 0.75×10^{-2}. No macrogelation was observed under the reaction conditions. The samples were analysed for fractional conversion x and for pendent conversion p_p. The results are given in *Figure 5A*. Large scatter in the pendent conversion data indicates that the ^{1}H n.m.r. technique is inadequate for such measurements. This is probably due to the low EGDM concentration and/or due to the broad ethylene glycol peaks of the EGDM unit. In order to characterize accurately the pendent double bonds, an analytical titration method using PSDB reagent was tried. Again, no reproducible data were obtained at low crosslinker contents. However, by increasing the EGDM concentration in the reaction mixture, the technique of bromination with PSDB proved satisfactory and has been used throughout. In *Figure 5B*, the results are shown for the crosslinker concentrations $\rho_0 = 0.126$ and 0.256. The critical monomer conversions at the gel point were 0.149 and 0.135, respectively. The solid lines in *Figure 5A* and *B* are drawn through the pendent conversion data points by using a least-squares fit. By extrapolating this line to zero conversion, we obtain a limiting value for pendent conversion of about 0.5, indicating that nearly half of the pendent double bonds are consumed by cyclization at zero monomer conversion; this value seems to be independent of the crosslinker content.

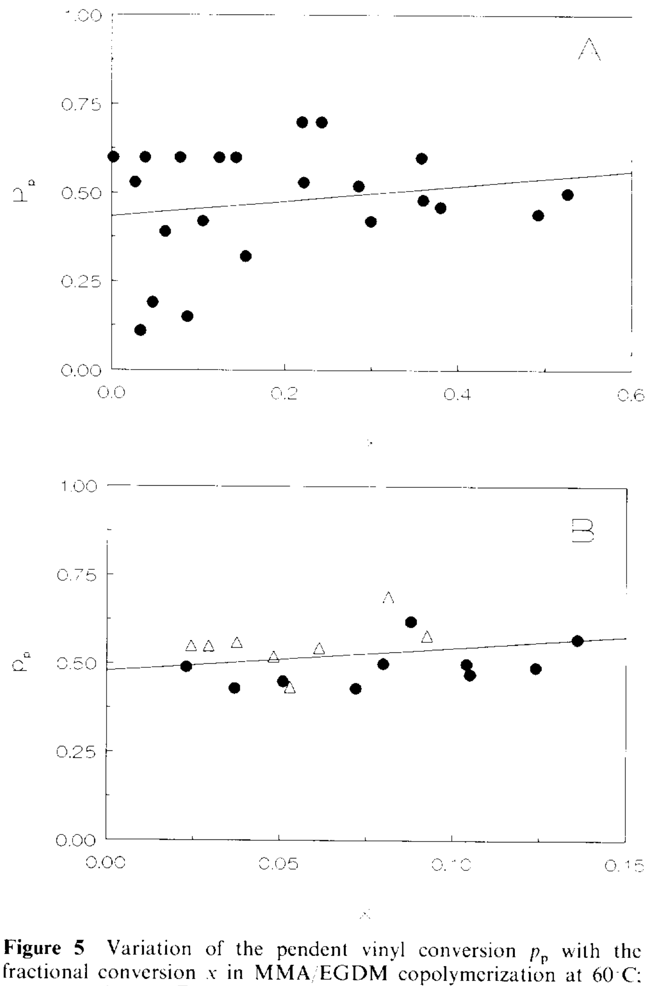

Figure 5 Variation of the pendent vinyl conversion p_p with the fractional conversion x in MMA/EGDM copolymerization at 60°C; $c = 220$ g l^{-1}. (A) $\bar{X}_1^* = 4 \times 10^2$; $\rho_0 = 0.75 \times 10^{-2}$. (B) $\bar{X}_1^* = 1 \times 10^3$; $\rho_0 = 0.126$ (△), 0.256 (●). Measurements of pendent vinyl conversion were carried out by ^{1}H n.m.r. (A) and by bromometry using PSDB reagent (B). Experimental data points are shown as symbols. The solid lines represent least-squares fit to pendent conversion data

Initial termination rate constant (k_{t0})

Invoking the steady-state approximation for radicals, the expression for the rate of polymerization in homogeneous, free-radical crosslinking copolymerization before the gel point is given by:

$$dx/dt = k_p[R^*](1-x) \tag{3}$$

$$[R^*] = (2fk_d[I]/k_t)^{0.5} \tag{3a}$$

where x is the fractional conversion, f is the initiator efficiency, k_d is the decomposition rate constant of the initiator, k_p and k_t are the pseudo-kinetic rate constants for propagation and termination, respectively[30] and the other symbols have their usual meanings. The expression for the initial rate of polymerization follows from equation (3) as:

$$(dx/dt)_0 = k_{p0}[R^*]_0 \tag{4}$$

$$[R^*]_0 = (2f_0k_{d0}[I]_0/k_{t0})^{0.5} \tag{4a}$$

where the subscript 0 holds for the initial values.

Since $\rho_0 \ll 1$ in the present study, it is reasonable to assume a constant k_{p0} in each series of experiments (constant initial concentrations of the total monomer and the initiator). Additionally, f_0 and k_{d0} should also remain constant in each series because of the fixed solvent concentration. Thus, from equation (4) and assuming that k_{t0} is constant, we would expect the initial rate to be independent of the amount of crosslinker. This will not hold here, however, since the initial rate $(dx/dt)_0$ has been seen to be a function of ρ_0 (*Figure 3*). At low crosslinker contents, the initial rates are slow compared with the linear polymerization. As the amount of crosslinker increases, an enhancement in the rate is observed in all series of experiments. Thus, the dependence of the initial rate on ρ_0 can be described by a curve with a minimum at a certain crosslinker concentration. The enhancement of the rate of polymerization with increasing ρ_0 has also been observed previously for moderate to high crosslinker concentrations[6,17,18,31,32]. However, reduced polymerization rates at low crosslinker contents are reported for the first time here. According to equation (4), the variation of the initial rates with ρ_0 must be due to the change in the initial termination rate constant of the polymer radicals, k_{t0}.

In order to extract k_{t0} from the initial rates, we define here 'relative initial termination rate constant', $k_{t0,\mathrm{ref}}$. It is the ratio of k_{t0} for the crosslinking polymerization to that for the linear polymerization at the same reaction condition. $k_{t0,\mathrm{rel}}$ can be calculated from equation (4) as:

$$k_{t0,\mathrm{rel}} = \frac{k_{t0}}{k_{t0,l}} = \left(\frac{(dx/dt)_{0,l}}{(dx/dt)_0}\right)^2 \tag{5}$$

where the subscript l denotes linear polymerization.

In *Figure 6A* and *B*, $k_{t0,\mathrm{rel}}$ *versus* ρ_0 data are given on a double logarithmic scale. The initial termination rate constant decreases continuously as the amount of crosslinker in the reaction mixture increases. At low crosslinker contents, the termination rate constant of macroradicals is higher than that of the macroradicals present in the linear system.

Since we are dealing here with zero-conversion polymer radicals (i.e. the polymer radicals in the absence of

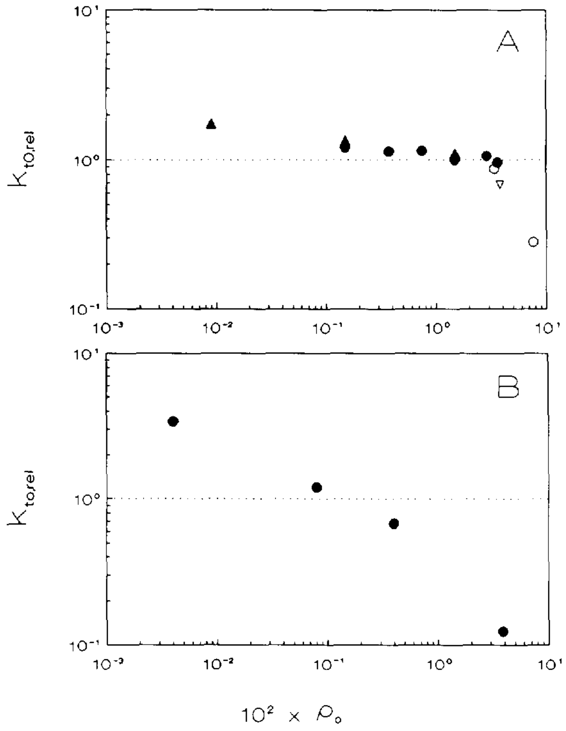

Figure 6 Variation of the relative termination rate constant at zero conversion, $k_{t0,rel}$, with the crosslinker concentration in free-radical MMA/EGDM (A) and AAm/BAAm copolymerizations (B). See legend to *Figure 3* for the reaction conditions. The horizontal dotted lines represent $k_{t0,rel}$ of linear polymerization

preformed polymers), the chain length and the chain length distribution of the polymer radicals must be the same in each series of experiments; hence, the deviation of $k_{t0,rel}$ from unity cannot be explained by the chain length dependence of the termination rate constant. Also, the low concentration of the crosslinker and its similar thermodynamic property to monovinyl monomer exclude a possible change of the viscosity and the solvating power of the medium, through which the polymer radicals must diffuse. Thus, the only remaining possibility is that the zero-conversion polymer radicals exhibit different structures depending on ρ_0, which affects their termination process.

At the beginning of the reaction, the individual polymer radicals dissolved in monomer–solvent mixture are isolated from each other; hence, the local concentration of pendent vinyls inside a macroradical coil is much higher than their overall concentration in the reaction system. Consequently, cyclization should happen predominantly in the early stage of the copolymerization leading to decreased coil size at the same molecular weight. Indeed, experimental data also show this trend[11,22]. In smaller coils, the segmental diffusion of the radical centre out of the coil to encounter another radical becomes easier, or in other words, the chain end will be found more easily by the other chain end[33,34] (*Figure 7*). Thus, the reduction in the macroradical coil size due to cyclization increases k_t at low crosslinker contents and thereby decreases the overall rate of polymerization. However, as ρ_0 further increases, the local concentration of pendent vinyls within a coil should increase. Thus, the polymer radicals would tend to form more cycles and exhibit more compact structures, as schematically illustrated in *Figure 7*. This results in a decreased mobility of segments and suppresses the diffusion-controlled termination due to steric reasons.

Variation of the termination rate constant (k_t) *with conversion*

Owing to the low monomer concentration used in the present study, we assume that f and k_p remain constant during the course of the copolymerization. Dividing equation (3) by equation (4) and solving for k_t/k_{t0} gives:

$$\frac{k_t}{k_{t0}} = \left[\frac{(\mathrm{d}x/\mathrm{d}t)/(1-x)}{(\mathrm{d}x/\mathrm{d}t)_0}\right]^{-2} \exp(-k_d t) \qquad (6)$$

where k_t/k_{t0} represents the ratio of the termination rate constant of macroradicals at conversion x to that at $x=0$. Using a numerical fit of the experimental time–conversion data, the variation of the average termination rate constant with conversion can be calculated from equation (6). Here, we have assumed $k_d=0$ (constant initiator concentration) and $0.85 \times 10^{-5}\,\mathrm{s}^{-1}$ for AAm/BAAm and MMA/EGDM systems, respectively[35]. The results are shown in *Figures 8A–D*. In linear MMA or AAm polymerizations (curves 0), the termination rate constant decreases slightly with increasing conversion, indicating that the rate of the termination process is governed by segmental diffusion. The steeper decrease of k_t in MMA polymerization at $x > 0.80$ can be interpreted as the result of a change from segmental diffusion to translational diffusion, being the rate-controlling process[36]. The figures also show that, at low crosslinker contents, the conversion dependence of k_t in crosslinking polymerization is weaker than that in linear polymerization, in accord with our explanations in the previous section. In fact, at very small crosslinker contents or at a high degree of dilution, k_t seems to increase with increasing conversion. However, as the amount of crosslinker increases, the decrease in k_t with conversion becomes more dominant due to the increase in the degree of branching, which leads to the formation of larger macroradical coils.

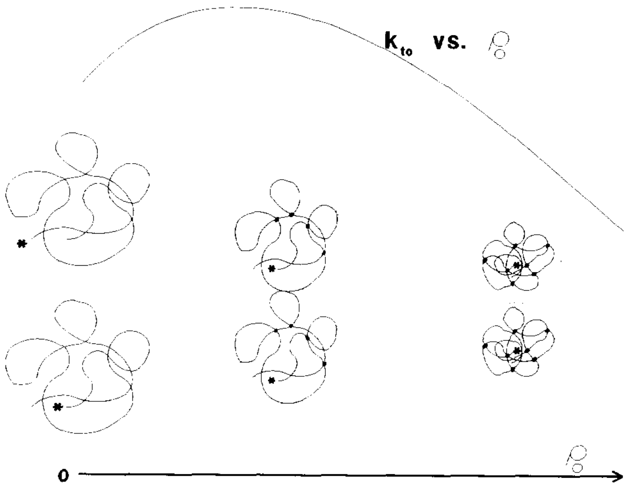

Figure 7 Schematic representation of the structural changes of macroradical coils with increasing concentration of crosslinker. The curve represents the resulting variation of the initial termination rate constant

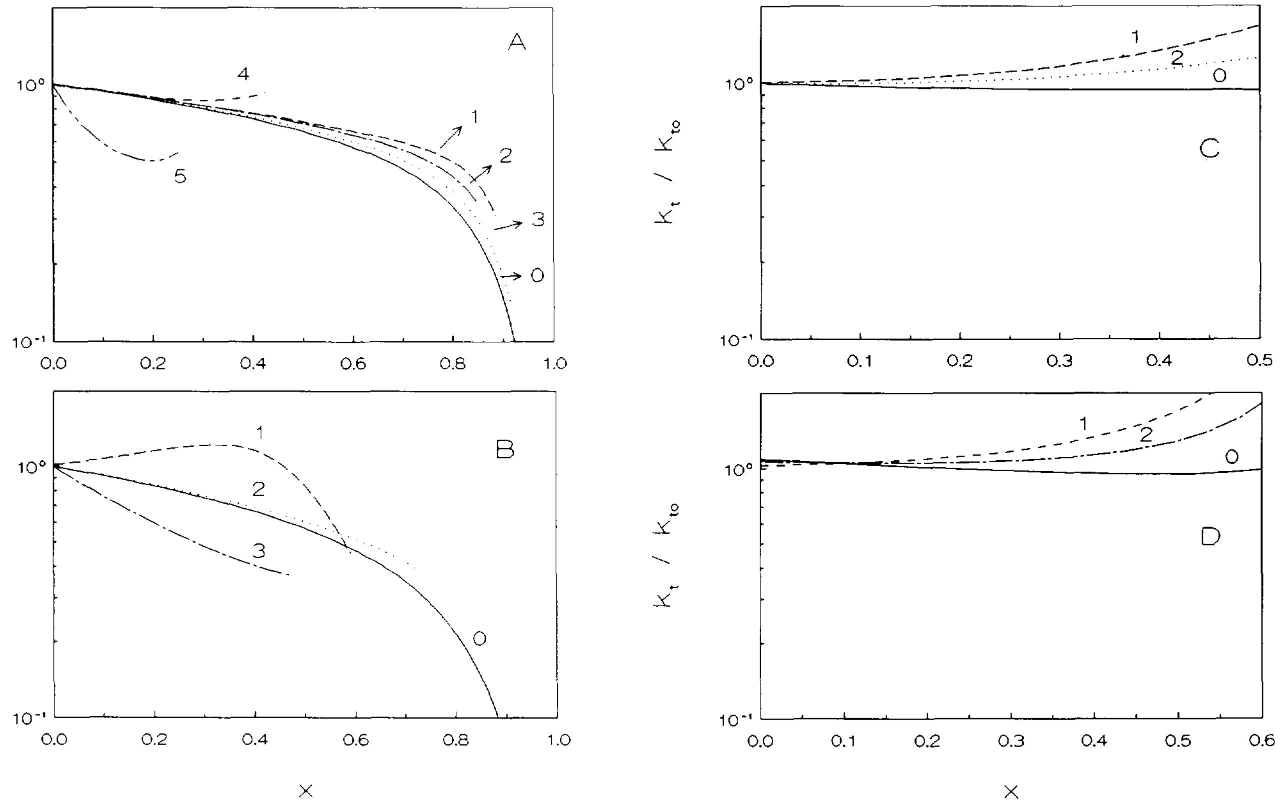

Figure 8 Variation of the relative termination rate constant k_t/k_{t0} with conversion x. (A) MMA/EGDM system, $c=230\,\mathrm{g\,l^{-1}}$, $\bar{X}_1^{\cdot *}=4\times10^2$, $10^2\times\rho_0=0$ (0); 0.15 (1); 0.375 (2); 0.75 (3); 1.50 (4); 3.6 (5). (B) MMA/EGDM system, $c=100\,\mathrm{g\,l^{-1}}$, $\bar{X}_1^{\cdot *}=1\times10^3$, $10^2\times\rho_0=0$ (0); 0.01 (1); 0.15 (2); 1.5 (3). (C) MMA/EGDM system, $c=100\,\mathrm{g\,l^{-1}}$, $\bar{X}_1^{\cdot *}=4\times10^2$, $10^2\times\rho_0=0$ (0); 3.4 (1); 7.6 (2). (D) AAm/BAAm system, $c=35\,\mathrm{g\,l^{-1}}$, $[K_2S_2O_8]=[Na_2S_2O_3]=[NaHCO_3]=1\times10^{-3}\,\mathrm{mol\,l^{-1}}$, $10^2\times\rho_0=0$ (0); 4×10^{-3} (1); 3.85 (2)

CONCLUSIONS

The pregelation period of free-radical MMA/EGDM and AAm/BAAm copolymerization reactions was studied. Copolymerizations were carried out in dilute solutions to ensure that strong cyclization occurs during the reactions. Indeed, it was found that in solution MMA/EGDM copolymerization, nearly half of the pendent double bonds are consumed by cyclization at zero conversion. The following conclusions were drawn from the kinetic data:

1. The average termination rate constant of macroradicals at zero-conversion, k_{t0}, first increases but then decreases continuously with increasing concentration of crosslinker in the reaction mixture (ρ_0).
2. The variation of k_{t0} with ρ_0 is not universal and depends on the type of comonomer system.
3. The termination rate constant of macroradicals becomes less sensitive to conversion in the presence of a small amount of crosslinker. An increase in k_t with conversion is even observed in several reaction systems.

All of these phenomena can be explained in terms of cyclization. Cyclization has two opposite effects on the termination rate of macroradicals. First, it decreases the coil size of macroradicals and thereby increases k_t. Thus, this effect seems to be similar to the effect of decreasing solvating power of the polymerization solvent, which shrinks the macroradical coils and enhances the rate of diffusion-controlled termination[37]. Second, it produces crosslinks inside the macroradical coil, which decrease the mobility of segments and therefore decrease k_t. The combination of these two opposite effects determines the average termination rate of macroradicals controlled by segmental diffusion.

REFERENCES

1 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953, Ch. 9
2 Walling, C. *J. Am. Chem. Soc.* 1945, **67**, 441
3 Funke, W. *J. Polym. Sci.* (*C*) 1967, **16**, 1497
4 Funke, W. *Chimia* 1968, **22**, 111
5 Malinsky, J., Klaban, J. and Dusek, K. *J. Macromol. Sci.-Chem* (*A*) 1971, **5**, 1071
6 Horie, K., Otagawa, A., Muraoka, M. and Mita, I. *J. Polym Sci., Polym. Chem. Edn* 1975, **13**, 445
7 Kast, H. and Funke, W. *Makromol. Chem.* 1980, **180**, 1335
8 Whitney, R. S. and Burchard, W. *Makromol. Chem.* 1980, **181**, 869
9 Galina, H., Dusek, K., Tuzar, Z., Bohdanecky, M. and Stokr, J. *Eur. Polym. J.* 1980, **16**, 1043
10 Dusek, K., Galina, H. and Mikes, *J. Polym. Bull.* (*Berlin*) 1980, 3, 19
11 Dusek, K. in 'Developments in Polymerization – 3', (Ed. R. N. Haward), Applied Science, London, 1982, p. 143
12 Hild, G. and Okasha, R. *Makromol. Chem.* 1985, **186**, 93, 389
13 Hild, G., Okasha, R. and Rempp, P. *Makromol. Chem.* 1985, **186**, 407
14 Kloosterboer, J. G., Lijten, G. F. C. M. and Greidanus, F. J. A. M. *Polym. Commun.* 1986, **27**, 268
15 Li, W., Hamielec, A. E. and Crowe, C. M. *Polymer* 1989, **30**, 1513, 1518
16 Zhu, S., Tian, Y., Hamielec, A. E. and Eaton, D. R. *Polymer* 1990, **31**, 154

17 Tobita, H. and Hamielec, A. E. *Polymer* 1990, **31**, 1546

18 Dotson, N. A., Diekmann, T., Macosko, C. W. and Tirrel, M. *Macromolecules* 1992, **25**, 4490

19 Zhu, S. and Hamielec, A. E. *Makromol. Chem., Macromol. Symp.* 1992, **63**, 135

20 Dusek, K. and Spevacek, J. *Polymer* 1980, **21**, 750

21 Galina, H. and Rupicz, K. *Polym. Bull. (Berlin)* 1980, **3**, 473

22 Batzilla, T. and Funke, W. *Makromol. Chem. Rapid Commun.* 1987, **8**, 261

23 Landin, D. T. and Macosko, C. W. *Macromolecules* 1988, **21**, 849

24 Funke, W., Bauer, H., Joos, B., Kaczun, J., Kleiner, B. and Okay, O. *Polym. Int.* 1993, **30**, 519

25 Holt, T. and Simpson, W. *Proc. R. Soc. (London)* 1956, **A238**, 154

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

27 Okay, O. *Makromol. Chem.* 1988, **189**, 2201

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

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

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

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

32 Shah, A. C., Parsons, I. W. and Haward, R. N. *Polymer* 1980, **21**, 825

33 Mahabadi, H. K. and O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Edn.* 1977, **15**, 283

34 O'Driscoll, K. F. *Pure Appl. Chem.* 1981, **53**, 617

35 Odian, G. 'Principles of Polymerization', McGraw-Hill, New York, 1981, Ch. 6

36 Dionisio, J., Mahabadi, H. K., O'Driscoll, K. F., Abuin, E. and Lissi, E. A. *J. Polym. Sci., Polym. Chem. Edn.* 1979, **17**, 1891

37 Mahabadi, H. K. *Makromol. Chem., Macromol. Symp.* 1987, **10/11**, 127