Kinetics of the free-radical copolymerization of methyl methacrylate/ethylene glycol dimethacrylate: 1. Experimental investigation

W.-H. Li, A. E. Hamielec* and C. M. Crowe
Institute for Polymer Production Technology, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7
(Received 19 July 1988; accepted 21 October 1988)

An experimental investigation was made of the kinetics of the bulk free-radical copolymerization of methyl methacrylate (MMA) and the divinyl monomer ethylene glycol dimethacrylate (EGDMA) initiated with AIBN at 70°C for levels of EGDMA of 0–25 wt% and chain transfer agent (CBr_4) levels of 0–1 wt%. The conversion of monomers to sol and crosslinked gel was measured by gravimetry using Soxhlet extraction. This provided measurements of monomer conversion at the gelation point as a function of EGDMA and CBr_4 levels and the weights of sol and gel as a function of time and monomer conversion. The experimental data are interpreted in terms of the pseudo-kinetic rate constant method in Part 2 of this series.

(Keywords: methyl methacrylate; ethylene glycol dimethacrylate; free-radical copolymerization kinetics; chain transfer; crosslinking)

INTRODUCTION

Significant interest has recently developed in the synthesis of crosslinked networks with controlled structure. This has been motivated in part by the phenomenal success achieved by superabsorbent polymers in the manufacture of babies' nappies. It is felt that a deeper understanding of the kinetics of synthesis of crosslinked gels and the microscopic processes which are responsible for gel structure development would permit the development of a whole range of useful polymer products.

There are few comprehensive investigations of the kinetics of copolymerization of vinyl/divinyl monomer systems in the literature and fewer attempts to model the kinetics of polymerization.

Some aspects of the copolymerization of methyl methacrylate (MMA) with ethylene glycol dimethacrylate (EGDMA) have been investigated since 1945[1–9]. Some authors estimated the efficiency of crosslinking[2,5] or determined the glass transition temperatures of the copolymers[3]. Only a few[6,7] reported experimental results on the kinetics of synthesis. Haydon *et al.*[6] estimated the propagation and termination rate constants, k_p and k_t, at different conversions for various levels of EGDMA. Horie *et al.*[7] reported a secondary gel effect due to the formation of microgels. Measurements of the gelation point have been done mainly by observing the fluidity of the reacting mixture[1,9] or by extrapolation of bulk viscosity measurements[4,8]. However, the results depend strongly on the technique. Investigations of vinyl/divinyl network formation by estimating cyclization and reactivity of pendant vinyl groups have been reported by Whitney *et al.*[8] and very recently by Landin and Macosko[9].

There have been no comprehensive experimental studies of free-radical copolymerization of vinyl/divinyl monomer systems, especially for the gelation and gel/sol fractions. The objective of this study was to provide comprehensive kinetic data for the MMA/EGDMA comonomer pair, covering a wide range of monomer conversion and levels of divinyl monomer and chain transfer agent (CBr_4). Another objective, which is reported in Part 2 of this series[10], was to evaluate the effectiveness of the pseudo-kinetic rate constant method for the modelling of the copolymerization up to the point of gelation.

EXPERIMENTAL

Materials

The monomer, methyl methacrylate (MMA) (Reagent Grade, Fisher Scientific Co.), was washed with 10% aqueous potassium hydroxide to remove inhibitor, followed by several washings with deionized water. After drying successively with anhydrous sodium sulphate and 4 Å (40 nm) molecular sieves, it was distilled under reduced pressure. The middle fraction was collected ($n_D^{20} = 1.4142$).

The crosslinker, ethylene glycol dimethacrylate (EGDMA) (Aldrich Chemical Co.), was washed similarly and then distilled under reduced pressure (≈0.9 mmHg; ≈120 Pa). The fraction boiling at about 77°C was collected ($n_D^{20} = 1.4541$). The initiator, 2,2′-azobis (2-methyl-propionitrile) (AIBN) (Eastman Kodak Co.), was recrystallized three times from absolute methanol, followed by drying in a vacuum oven at room temperature. The chain transfer agent (CTA), carbon tetrabromide (BDH Chemicals Ltd), was recrystallized

---

* To whom correspondence should be addressed

0032-3861/89/081513-05$03.00

from absolute ethanol, followed by drying in a vacuum oven at room temperature.

Procedure

Monomer solutions were prepared shortly before use by weighing the required amounts of MMA, EGDMA, AIBN and CTA. Each of the pyrex ampoules (o.d. 5 mm) was filled with ≈2 g of monomer solution. After degassing by four successive freeze–thaw cycles using liquid nitrogen and a reduced pressure of 10^{-4} mmHg (10^{-2} Pa) the ampoules were torch sealed. The polymerization was initiated by immersing the ampoules in an oil bath maintained at a constant temperature, 70±0.1°C, and the reaction was quenched by thrusting the ampoules into liquid nitrogen.

The ampoule was then broken and the reactant mixture, together with pieces of glass if not separated well, was put into a covered flask with acetone and hydroquinone. After being shaken on the shaker for at least 24 h, most of the sol was dissolved out into the solution. The swollen gel, if present, was concentrated using a centrifuge and the concentrated gel suspension was then extracted by acetone in a Soxhlet extractor with a coarse grade glass thimble for about 1 d. The sol-free gel was dried at 120°C in a vacuum (<3 mmHg) for at least 7 d to constant weight. The sol polymer was precipitated from solution using a 20-fold excess of methanol and then dried at 50°C in a vacuum oven (<3 mmHg) for 2 d.

Conversion to gel, sol and the total polymer were determined by gravimetry.

For the runs done to measure the reactivity ratios, the final monomer concentrations were measured using gas chromatography with *p*-xylene as the internal standard (HP-5890A gas chromatograph equipped with an OV351 column, 6 ft (1.8 m) in length and $\frac{1}{8}$ inch (3 mm) in diameter).

RESULTS AND DISCUSSION

Reactivity ratios

MMA/EGDMA was polymerized at 25, 50 and 75 wt% EGDMA. The Meyer–Lowry equation was used with the error-in-variables method (EVM)[11] to estimate reactivity ratios at 70°C and the values found are $r_1=0.67\pm0.07$ and $r_2=1.49\pm0.21$. Monomer 1 (M_1) is MMA and monomer 2 (M_2) is EGDMA. *Figure 1* shows a plot of the Meyer–Lowry equation with the measured data.

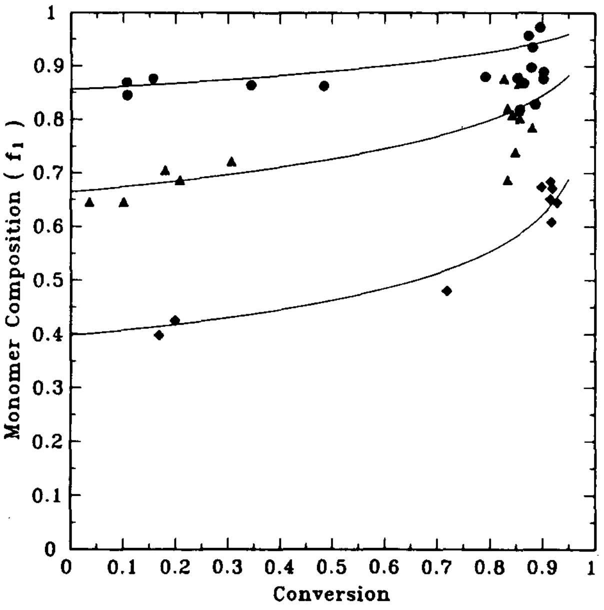

Figure 1 Meyer–Lowry equation, with reactivity ratios $r_1=0.67$ and $r_2=1.49$, and measured data at 70°C, 0.3 wt% AIBN and initial MMA mole fractions of $f_{10}=0.856$ (●), 0.664 (▲) and 0.398 (◆) for MMA/EGDMA comonomer pair

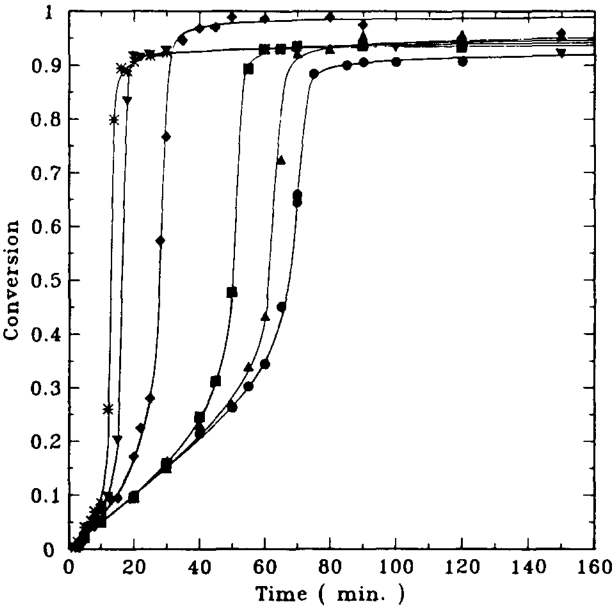

Figure 2 Conversion–time histories for the polymerization of MMA/EGDMA at 70°C, 0.3 wt% AIBN, 0% CTA and various levels of EGDMA (wt%): ●, 0; ▲, 0.3; ■, 1.0; ◆, 5.0; ▼, 15.0; ✱, 25.0

Conversion–time histories, rate constants and gelation points

Figure 2 shows the effect of EGDMA level on conversion–time history (70°C, 0.3 wt% AIBN and 0% CBr_4). The conversion of monomer at which there is an autoacceleration in conversion rate decreases with increase in divinyl monomer level. The maximum conversion rate appears to increase with increase in divinyl monomer level. The sudden decrease in conversion rate at high conversions is probably due to a combination of diffusion-controlled propagation and a significant increase in initiator radical recombination in the 'cage' as the monomer/polymer mixture approaches a glass state. We have no obvious explanation for the strange variation of limiting conversion with EGDMA level.

Figure 3 shows the effect of CTA level on conversion rates. The pronounced decrease in conversion rate with increase in CTA level is probably due to the conversion of gel radical centres to mobile CTA radicals with a concomitant increase in bimolecular termination of radicals and the associated reduction in polymerization rate. In addition, the presence of CTA delays gelation.

Figure 4 shows the variation of the product $k_p[R^\cdot]$ with conversion for various levels of EGDMA. The fundamental rate equation

$$\frac{dX}{dt}=k_p[R^\cdot](1-X) \qquad (1)$$

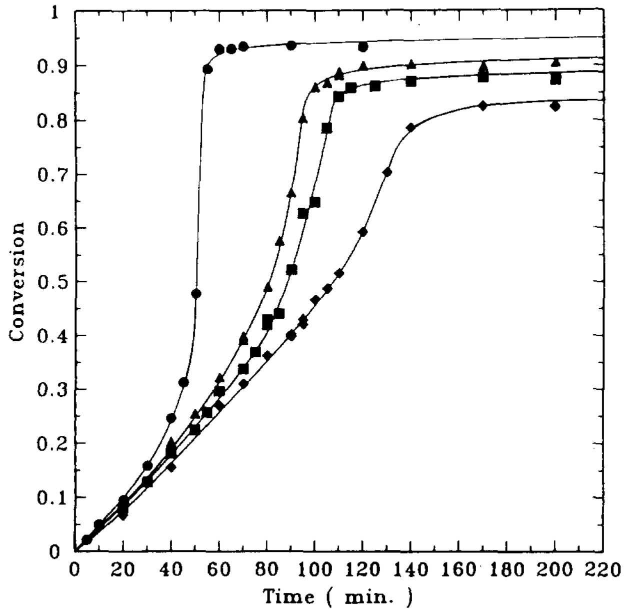

Figure 3 Conversion–time histories for the polymerization of MMA/EGDMA at 70°C, 0.3 wt% AIBN, 1.0 wt% EGDMA and various levels of CBr_4 (wt%): ●, 0; ▲, 1.0; ■, 2.0; ◆, 4.0

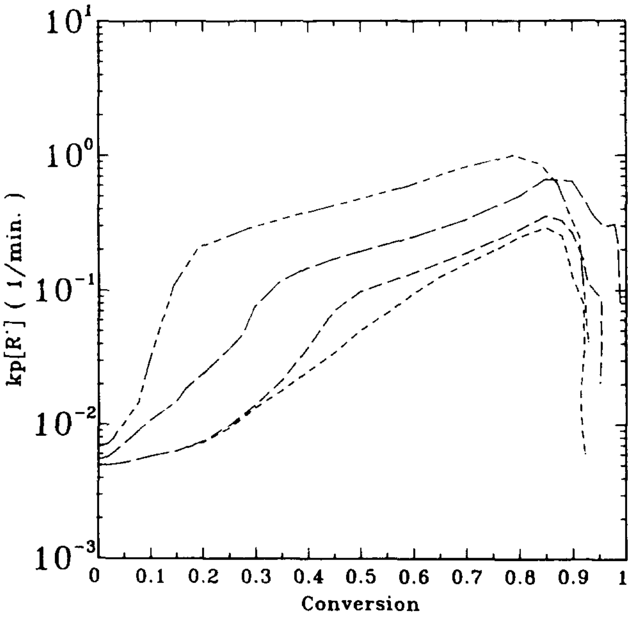

Figure 4 Variation of the product $k_p[\mathrm{R}^{\cdot}]$ with conversion for the polymerization of MMA/EGDMA at 70°C, 0.3 wt% AIBN, 0% CTA and various levels of EGDMA (wt%): -----, 0.1; ------, 0.3; ———, 5.0; ———, 25.0

where X is the conversion of monomer to polymer, t is time, k_p is the propagation rate constant, and $[\mathrm{R}^{\cdot}]$ is the total polymer radical concentration, can be used to fit experimental conversion–time data and establish the variation of the product $k_p[\mathrm{R}^{\cdot}]$ with conversion. For a binary copolymerization using the terminal model, k_p and $[\mathrm{R}^{\cdot}]$ are given by

$$k_p = k_{p11}\phi_1^{\cdot}f_1 + k_{p12}\phi_1^{\cdot}f_2 + k_{p21}\phi_2^{\cdot}f_1 + k_{p22}\phi_2^{\cdot}f_2 \quad (1a)$$

$$[\mathrm{R}^{\cdot}] = [\mathrm{R}_1^{\cdot}] + [\mathrm{R}_2^{\cdot}] = \text{total polymer radical concentration} \quad (1b)$$

where $\phi_1^{\cdot}$ is the number fraction of polymer radicals with the radical centre located on monomer 1, $\phi_2^{\cdot} = 1 - \phi_1^{\cdot}$, f_i is the mole fraction of M_i ($i = 1, 2$), and $\phi_1^{\cdot}$ is given by

$$\phi_1^{\cdot} = k_{p21}f_1/(k_{p21}f_1 + k_{p12}f_2) \quad (1c)$$

The ratio of k_{p22}/k_{p11} near zero conversion was estimated using homopolymerization of two monomers[12] and it was found that $k_{p22} = 2.04k_{p11}$. One might expect for MMA/EGDMA that k_{p22} would be twice k_{p11}.

An examination of *Figure 1* reveals that k_p should decrease modestly as the more reactive divinyl monomer is consumed. Therefore, up to about 80% conversion of monomer, the significant increase in $k_p[\mathrm{R}^{\cdot}]$ may be taken as due to the increase in total polymer radical concentration, $[\mathrm{R}^{\cdot}]$. At conversions above about 80%, the propagation reactions are likely to become diffusion-controlled and the initiator efficiency is likely to fall rapidly because of significant initiator radical recombination in the 'cage'. *Figure 5* has similar plots, but essentially shows the reduction in polymer radical concentration with increase in CTA level.

It is estimated that k_p changes by $<6\%$ over the conversion range 0–80%. Hence one may assume that k_p is constant and calculate the ratio $[\mathrm{R}^{\cdot}]/[\mathrm{R}^{\cdot}]_0$ at different conversion levels. Typical results are shown in *Figure 6* for two CTA levels. As expected, the CTA does not affect $[\mathrm{R}^{\cdot}]$ appreciably where bimolecular termination is chemically (or segmental-diffusion) controlled.

By application of the stationary-state hypothesis (SSH) for the total polymer radical concentration, one can show that

$$[\mathrm{R}^{\cdot}]/[\mathrm{R}^{\cdot}]_0 = (fk_{t0}/f_0\bar{k}_t)^{1/2} \quad (2)$$

Here, we have assumed that $[I] \approx [I]_0$ for AIBN, which has a relatively long half life at 70°C in these polymerizations. The variation of $(f_0\bar{k}_t/fk_{t0})$ with conversion is shown in *Figure 7*. The decrease of f with conversion over the conversion range 0–80% is expected to be modest and one therefore could consider that the fall in

$$\left(\frac{\bar{k}_t}{k_{t0}}\right)\left(\frac{f_0}{f}\right)$$

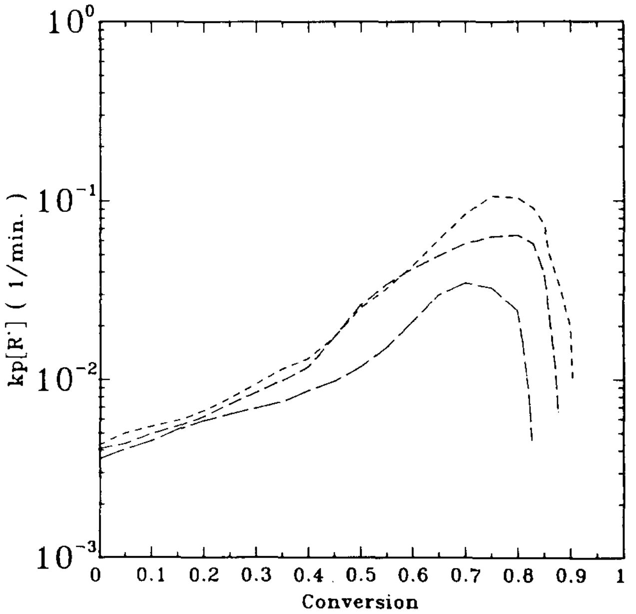

Figure 5 Variation of the product $k_p[\mathrm{R}^{\cdot}]$ with conversion for the polymerization of MMA/EGDMA at 70°C, 0.3 wt% AIBN, 1.0 wt% EGDMA and various levels of CBr_4 (wt%): -----, 1.0; ----, 2.0; ———, 4.0

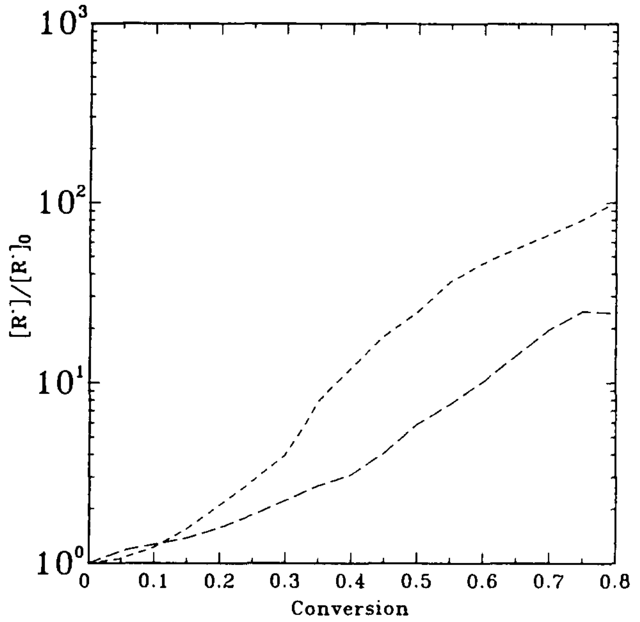

Figure 6 Change in total polymer radical concentration $[R^{\cdot}]$ with conversion for the polymerization of MMA/EGDMA at 70°C, 0.3 wt% AIBN, 1.0 wt% EGDMA and two levels of CBr_4 (wt%): ------, 0; ----, 1.0

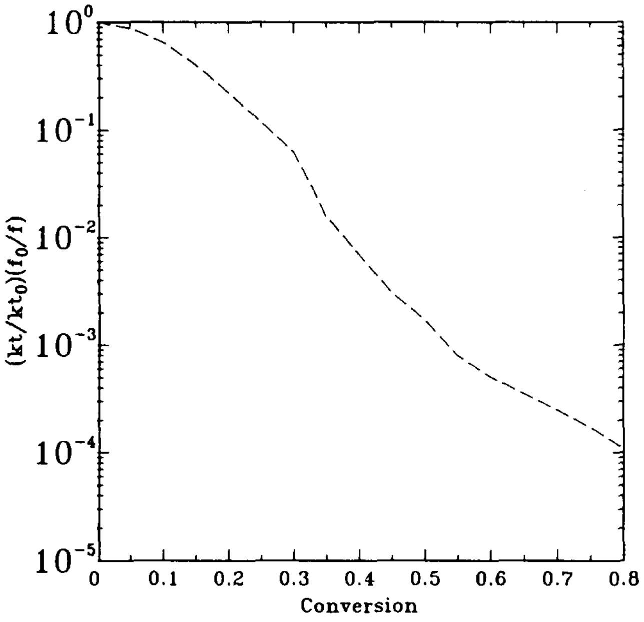

Figure 7 Variation of the number-average termination constant (k_t)/initiator efficiency (f) with conversion for the polymerization of MMA/EGDMA at 70°C, 0.3 wt% AIBN, 1.0 wt% EGDMA and 0 wt% CTA

with conversion is largely due to a decrease in $\bar{k}_t$, suggesting that the bimolecular termination of polymer radicals is diffusion-controlled.

The termination rate constant $\bar{k}_t$ may be considered to be the number average defined as

$$\bar{k}_t = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} k_t(i,j)\psi_i\psi_j$$

where $k_t(i,j)$ is the most general form of the termination rate constant which accounts for diffusion-controlled termination with chain length dependence. For convenience, the overbars will be dropped hereafter. ψ_i and ψ_j are number fractions of polymer radicals of chain length i and j.

Figure 8 shows typical conversion–time histories for sol and gel and the conversion at the point of gelation (X_c). The gel once formed grows very rapidly, consuming sol polymer molecules as well as monomer.

Figure 9 is a repeat of *Figure 8* but at a higher CTA level. The CTA clearly delays the onset of gelation and reduces the conversion rate of monomer and sol to gel.

Figure 10 shows the dependence of the conversion at the gelation point (X_c) on the concentration of EGDMA at two CBr_4 levels and finally *Figure 11* shows the dependence of X_c upon the concentration of CBr_4. It is

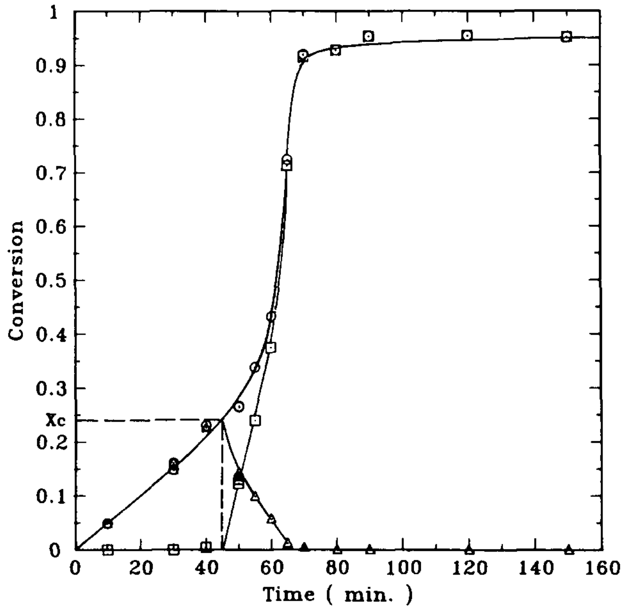

Figure 8 Conversion–time histories for the conversion of monomer to sol and gel (△, sol; □, gel; ○, total) for the polymerization of MMA/EGDMA at 70°C, 0.3 wt% AIBN, 0.3 wt% EGDMA and 0 wt% CTA, showing the onset of gelation (X_c)

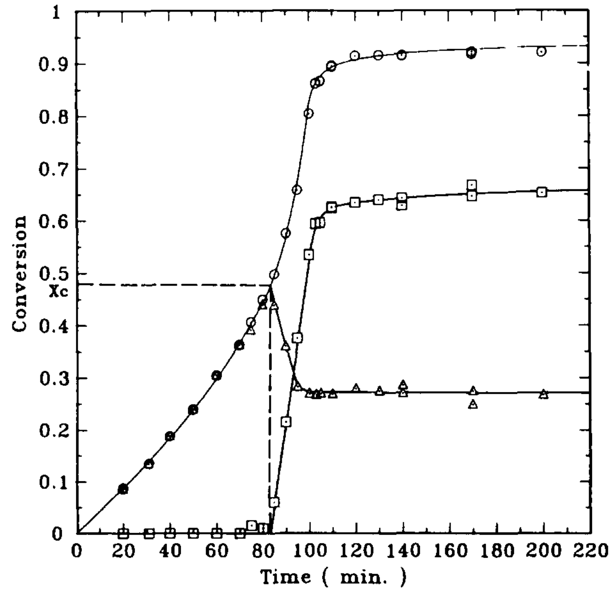

Figure 9 Conversion–time histories for the conversion of monomer to sol and gel (△, sol; □, gel; ○, total) for the polymerization of MMA/EGDMA at 70°C, 0.3 wt% AIBN, 0.3 wt% EGDMA and 1.0 wt% CBr_4, showing a delay in the onset of gelation (X_c) and the freezing in of monomer, sol and gel at high conversions

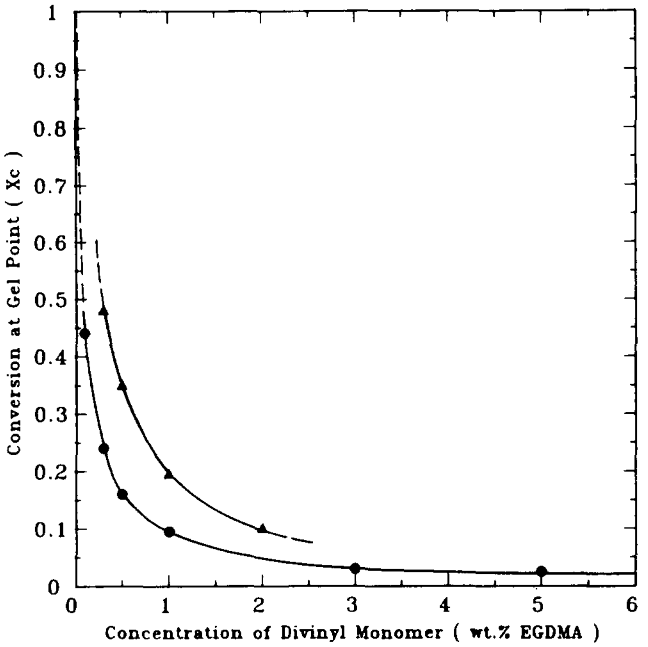

Figure 10 Conversion at the gelation point (X_c) and its dependence on levels of EGDMA and CBr_4 for the polymerization of MMA/EGDMA at 70°C and 0.3 wt% AIBN: ●, 0 wt% CBr_4; ▲, 1.0 wt% CBr_4

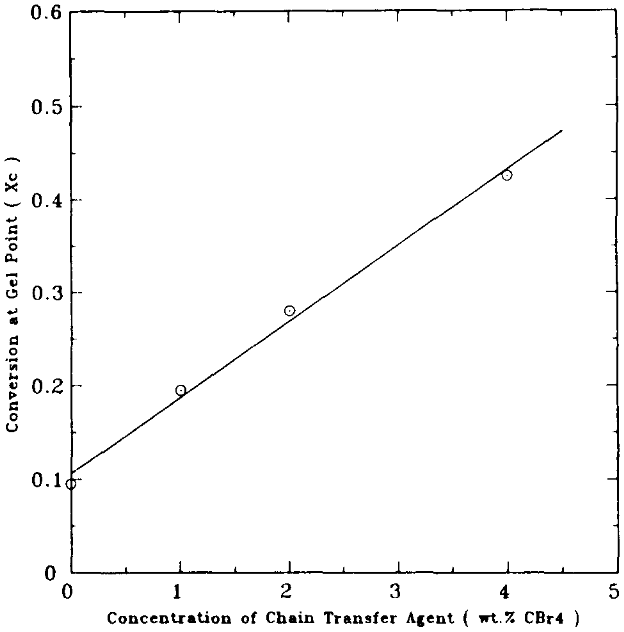

Figure 11 Dependence of conversion at gelation (X_c) on CBr_4 concentration for the polymerization of MMA/EGDMA at 70°C, 0.3 wt% AIBN and 1.0 wt% EGDMA

clear that a CTA may be used to delay the onset of gel formation.

Detailed experimental data may be obtained in tabular form by writing to one of the authors (A.E.H.)[12].

SUMMARY

A comprehensive set of experimental data on the kinetics of polymerization of MMA/EGDMA has been reported. These data should provide an opportunity to evaluate gelation theories such as the pseudo-kinetic rate constant method, which has been used to interpret these data in Part 2 of this series.

ACKNOWLEDGEMENTS

We acknowledge general financial support provided by the Natural Sciences and Engineering Research Council of Canada, and by the Ontario Centre for Materials Research.

REFERENCES

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

2 Loshaek, S. and Fox, T. G. *J. Am. Chem. Soc.* 1953, **75**, 3544

3 Loshaek, S. *J. Polym. Sci.* 1955, **15**, 391

4 Gordon, M. and Roe, R.-J. *J. Polym. Sci.* 1956, **21**, 27, 39, 57, 75

5 Shultz, A. R. *J. Am. Chem. Soc.* 1958, **80**, 1854

6 Hayden, P. and Melville, S. H. *J. Polym. Sci.* 1960, **43**, 215

7 Horie, K., Otagawa, A., Muraoka, M. and Mita, I. *J. Polym. Sci., Polym. Chem. Edn.* 1975, **13**, 445

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

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

10 Li, W.-H., Hamielec, A. E. and Crowe, C. M. *Polymer* 1989, **30**, 1518

11 Box, M. J. *Technometrics* 1970, **12**, 219

12 Li, W.-H., Hamielec, A. E. and Crowe, C. M. Unpublished results, McMaster University, Canada, 1988