Heat effects for free-radical polymerization in glass ampoule reactors

S. Zhu and A. E. Hamielec*
Institute for Polymer Production Technology, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7
(Received 9 March 1990; accepted 29 September 1990)

Herein is reported an experimental study to evaluate the level of temperature control during bulk free-radical polymerization of methyl methacrylate/ethylene glycol dimethacrylate in ampoule reactors of various sizes at various temperatures, initiator levels and for two heat transfer fluids (water and silicone oil). This monomer system was chosen because of the pronounced autoacceleration in polymerization rate that it experiences. Five ampoule diameters (3, 4, 5, 7 and 10 mm outside diameter, Pyrex glass), four temperatures (60, 70, 80 and 90°C) and five initiator levels (0.1, 0.3, 0.5, 1.0 and 2.5 wt% 2,2′-azobisisobutyronitrile) were investigated. Polymerization conditions and reactor size under which near-isothermal polymerizations during autoacceleration may be followed using glass ampoule reactors are presented.

(Keywords: glass ampoule reactor; free-radical polymerization; heat effect; temperature control; autoacceleration; Trommsdorff/gel effect; crosslinking polymerization; methyl methacrylate; ethylene glycol dimethacrylate)

INTRODUCTION

In free-radical polymerizations, the molecular processes involved in bimolecular termination of polymer radicals generally consist of three definable steps: two radicals migrate together via translational diffusion; the radical centres reorient by segmental diffusion; they overcome the chemical activation barrier and react. The activation energy for the bimolecular termination is usually small. The termination reaction is therefore likely to be diffusion-controlled. The latter is a strong function of monomer conversion to polymer. As the polymer concentration increases, the polymer chains become overlapped and entangled. This causes a significant reduction in termination rate. In turns, the radical concentration increases[1] and so does the conversion rate. This autoacceleration, often referred to as the Trommsdorff or 'gel' effect, has been widely studied for over four decades[2]. Many kinetic models have been proposed to give quantitative descriptions for the autoacceleration phenomenon based on polymer diffusion theories such as free-volume theory and reptation scaling law (see Mita and Horie[3] for a review of these models).

A model monomer system for these studies has been methyl methacrylate (MMA). The autoacceleration for this system is so pronounced that the conversion rate during autoacceleration can be one to two orders of magnitude higher than the initial rate in pure monomer. The polymerization of MMA is highly exothermic (polymerization heat: 55.5 kJ mol^{-1} at 74.5°C[4]). If the heat generated during autoacceleration cannot be removed at a sufficient rate, the temperature of the reacting mass will rise significantly. Kinetic data under non-isothermal conditions are difficult to interpret unless the temperature–time relationship is known.

To approach isothermal polymerization for measurements of kinetic data, Balke and Hamielec[5] developed a specialized glass ampoule technique. Using this technique, they made extensive measurements of monomer conversion and molecular weight development to high conversions for the bulk polymerization of MMA at 50, 70 and 90°C and with 0.3, 0.4 and 0.5 wt% 2,2′-azobisisobutyronitrile (AIBN) as initiator. These data have often been used in kinetic model evaluations.

Recently, Armitage *et al.*[6] suggested that a significant temperature rise may occur with the glass ampoule reactors. In reply to this suggestion, Balke[7] pointed out that Armitage *et al.*[6] used ampoule reactors with too low surface/volume ratios and this biased their conclusions about temperature rise.

In this work, direct measurements of the temperature rise during the bulk polymerization of MMA in ampoules of various surface/volume ratios were made. Measurements have also been made for the copolymerization of methyl methacrylate/ethylene glycol dimethacrylate (MMA/EGDMA), for which kinetic data measured in ampoule reactors have been published[1,8]. Because of gelation, autoacceleration and heat generation rates are greater in magnitude than for MMA homopolymerization. In addition, a few adiabatic polymerizations of MMA/EGDMA were done to provide an upper limit on rate of temperature rise and its magnitude.

EXPERIMENTAL

MMA (Fisher Scientific) and EGDMA (Aldrich Chemicals) were purified as follows. First they were washed with 10 wt% aqueous potassium hydroxide to remove inhibitor, washed with deionized water to neutralize the solution, dried successively with anhydrous sodium sulphate and 4 Å molecular sieves, and then distilled under reduced pressure. The middle fraction was collected (30°C for MMA and 75–80°C for EGDMA).

---

* To whom correspondence should be addressed

0032-3861/91/163021-05

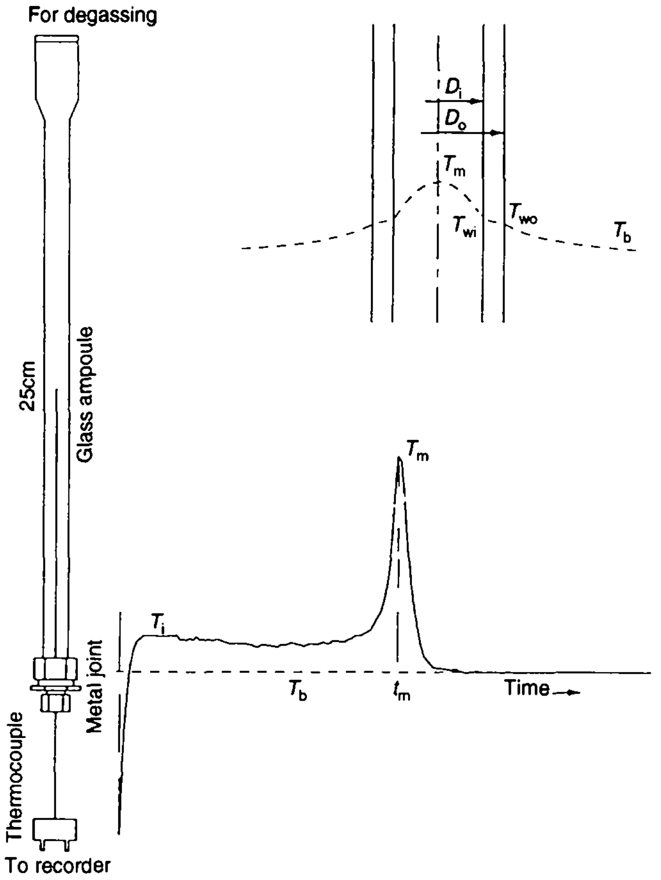

Figure 1 Schematic representation of the apparatus used for temperature measurement during polymerization. Left: glass ampoule reactor with thermocouple. Top right: temperature across ampoule. Bottom right: temperature profile measured during polymerization

AIBN (Eastman Kodak) was recrystallized three times from absolute methanol.

The ampoule reactor and associated equipment used for temperature measurement during polymerization is shown in *Figure 1* (left). Pyrex glass ampoules of 3, 4, 5, 7 and 10 mm outside diameter (the inside diameters are 1.8, 2.4, 3.4, 5.0 and 8.0 mm, respectively) were used. The samples were degassed using three freeze–thaw cycles with liquid nitrogen and a reduced pressure of $\sim 10^{-4}$ mmHg. Before the ampoules were sealed, they were filled with N_2 to reduce gas bubbles produced during reaction. The thermocouple (the diameter is 1 mm) was connected to an automatic recorder. The ampoule reactor containing monomer and initiator was then immersed into a heat transfer fluid. The temperature of the heat transfer fluid was controlled by a temperature regulator (Haake, Fisher Scientific) to ± 0.1°C. Two types of heat transfer fluid were used: silicone oil (Dow Corning 200 Fluid, 100 cSt) and tap water. Four bath temperatures were used: 60, 70, 80 and 90°C. The temperature at the centre of the ampoule reactor (see *Figure 1*, top right) was recorded continuously during polymerization. The recording system of a DIERS VSP reactor was used. An example of these temperature profiles is shown in *Figure 1* (bottom right).

To confirm that conduction losses along the thermocouple were negligible and that temperatures close to centreline were being measured, the position of the thermocouple was changed to several positions along the ampoule reactor length. No significant differences were found except when the thermocouple was located at the very ends of the ampoule reactor. In addition, much effort was made to centre the thermocouple in the reactor. For the data reported herein, three runs were done for each reaction condition. Good reproducibility was achieved when the outside diameter of the ampoule reactor used was not less than 4 mm.

The conversion of monomer data shown in *Figure 2* were determined by gravimetry. The polymer products were precipitated with absolute methanol.

For the copolymerizations of MMA/EGDMA with 0.5 wt% AIBN and 0, 0.5, 1.0, 5.0, 15.0 and 25.0 wt% EGDMA at oil bath temperature 70°C, the conversion–time data are available[8]. The temperature profiles measured here were under these same reaction conditions.

For the adiabatic copolymerizations of MMA/EGDMA in the Diers VSP reactor, the monomer/initiator solutions were bubbled with N_2 for more than 30 min at ice temperature. The atmosphere inside the reactor was evacuated and the cell was flushed with N_2 three times prior to injecting the monomer solution. After injection, the cell was heated rapidly to the set initial temperature, 60°C. The temperatures inside the cell were recorded continuously. The experiment was terminated when the rate of temperature rise approached zero.

RESULTS AND DISCUSSION

Figure 3 reports the temperature profiles measured in this work for the bulk polymerization of MMA as a function of ampoule size and bath type. At low conversions, the temperature control is good. The temperature differences ($T_i - T_b$) are 0.2, 0.3, 0.5, 0.8 and 2.3°C for the five ampoule diameters used (3, 4, 5, 7 and 10 mm o.d.) when the water bath temperature is set to 70°C. At the bath temperature of 90°C, they are 0.8, 1.1 and 2.1°C for 3, 4 and 5 mm o.d. These values can be a little higher when an oil bath is used (see *Figure 3*).

Surface/volume ratios of the ampoules used in this work are 3.70, 2.78, 1.73, 1.12 and 0.63 mm^{-1} (corresponding to 3, 4, 5, 7 and 10 mm o.d.). A plot of the values of $T_i - T_b$ *versus* the surface/volume ratios of the ampoule reactors used does not give a straight line. The plot of $T_i - T_b$ *versus* the square of inside diameter does, however (slope 3.457°C cm^{-2} for water at 70°C).

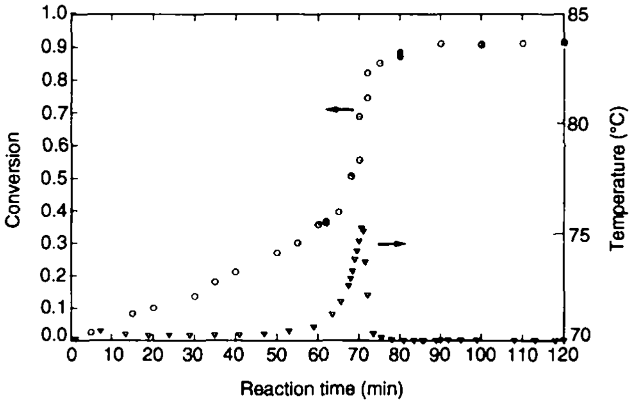

Figure 2 Monomer conversion (circles) and temperature (triangles) *versus* reaction time for the bulk polymerization of MMA with 0.3 wt% AIBN in a silicone oil bath at 70°C. Ampoule diameter: 5 mm o.d.

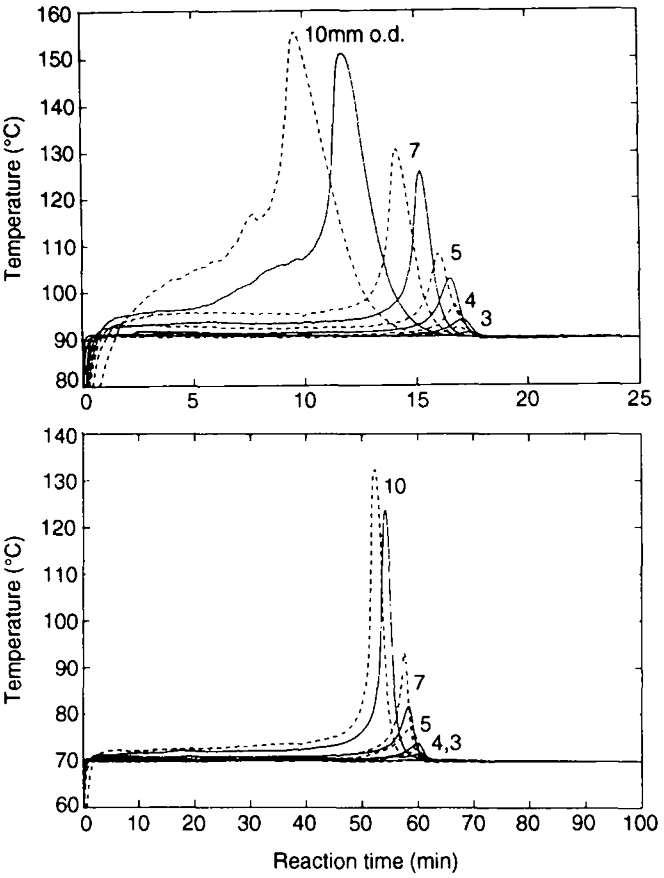

Figure 3 Temperature profiles for the bulk polymerization of MMA with 0.5 wt% AIBN. Reaction conditions: ampoule diameters are 3, 4, 5, 7 and 10 mm o.d. (as indicated); heat transfer fluids are water (full curves) and silicone oil (broken curves); bath temperatures are 90°C (top) and 70°C (bottom)

This may indicate that heat transfer inside the ampoule plays an important role.

The present experimental results, which include conditions used by Balke and Hamielec[5] (the bulk polymerization of MMA, with 0.3–0.5 wt% AIBN, at water bath temperature 50, 70 and 90°C, ampoule diameters 3–5 mm o.d.), permit one to conclude that the temperature difference ($T_i - T_b$) for low conversions of monomer is not over 0.5°C for 50 and 70°C, and is 1–2°C for 90°C. The higher $T_i - T_b$ values found by Armitage *et al.*[6] (2°C for 1 g reacting mass and 4°C for 5 g reacting mass) are due to the low surface/volume ratios of the ampoules (0.374–0.301 mm^{-1}) and the high initiator concentration ($\sim$1 wt% AIBN) used.

At high conversions where autoacceleration occurs, $T_m - T_b$ depends strongly on both the ampoule size and the heat transfer fluid type used. This can be clearly seen in *Figure 3*. The maximum temperature difference ($T_m - T_b$) for these temperature profiles for the five sizes of ampoule used are listed below:

water bath 70°C	0.4, 1.5, 3.2, 12.0 and 54.0°C
oil bath 70°C	0.6, 1.8, 7.4, 23.0 and 62.0°C
water bath 90°C	1.3, 4.0, 12.7, 36.0 and 61.0°C
oil bath 90°C	2.2, 7.1, 18.0, 41.0 and 65.0°C

The influence of initiator concentration on the temperature profile is shown in *Figure 4*. The higher the initiator concentration, the higher the conversion rate and, in turn, the poorer the temperature control. The influence of bath temperature on the temperature profile is shown in *Figure 5*. There is a better temperature control at lower reaction temperatures because the conversion and heat generation rates are lower.

Indeed, isothermal conditions for a strong exothermic polymerization with pronounced autoacceleration as found with MMA are only approximated. In practice, the use of ampoule reactors with high surface/volume ratios is recommended.

Non-isothermal kinetic data at low conversions can be readily interpreted by using Arrhenius equations for the rate constants. During autoacceleration, the temperature dependence of reaction rates, such as bimolecular termination of polymer radicals, that are diffusion-controlled is not generally known. The termination rate constant is a function of radical chain lengths, and a particular difficulty among many others is that the reversibility of polymer chain entanglements with temperature increase is not certain. Readers may refer to Mita and Horie[3] for a review of the recent theoretical modelling work on diffusion-controlled termination.

However, the effect of non-isothermal conditions on the initiator concentration throughout the whole course of polymerization can be readily calculated. Neglecting volume contraction, for non-isothermal conditions:

$$\frac{d[I]}{dt} = -K_d[I]$$

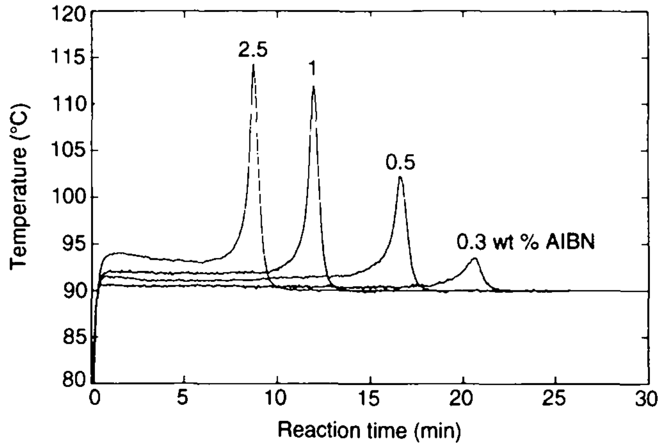

Figure 4 Temperature profiles for the bulk polymerization of MMA with different AIBN levels of 0.3, 0.5, 1.0 and 2.5 wt% (as indicated). Ampoule diameter: 5 mm o.d.; water bath temperature: 90°C

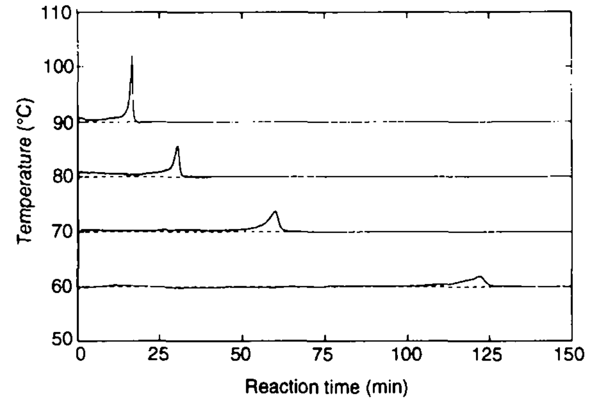

Figure 5 Temperature profiles for the bulk polymerization of MMA at 0.5 wt% AIBN at different water bath temperatures of 60, 70, 80 and 90°C. Ampoule diameter: 5 mm o.d.

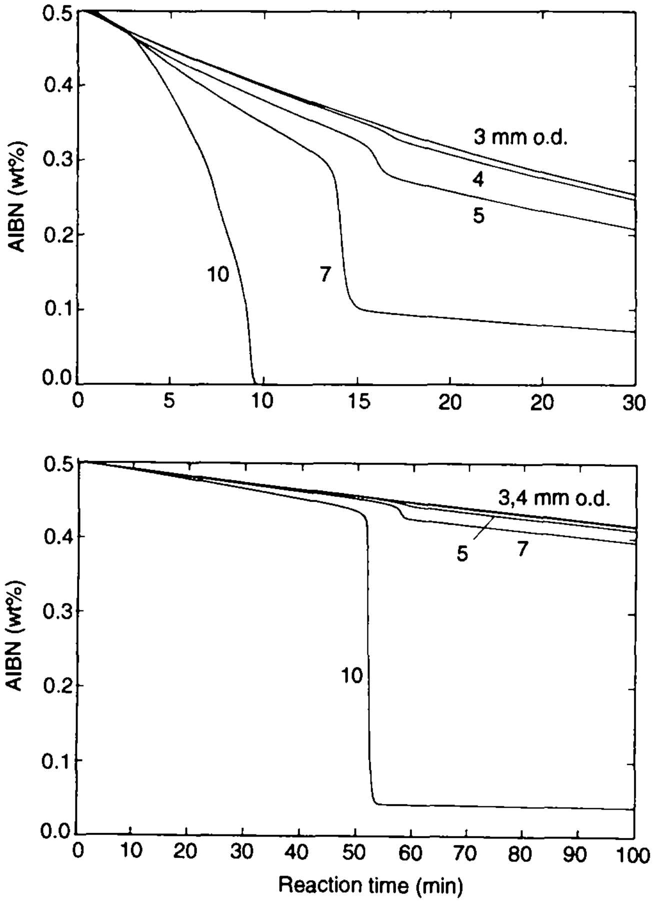

Figure 6 Changes in the initiator concentrations. Reaction conditions are the same as for *Figure 3*

where $K_d = 6.32 \times 10^{16} \exp(-15\,440/T\ \mathrm{K})$ (min^{-1}) for AIBN[9]. Under isothermal conditions the initiator concentration [I] falls exponentially. *Figure 6* shows the initiator concentration changes using the temperature data from *Figure 3*. It is found that AIBN is almost completely consumed in the large ampoules.

Indirect evidence that has been used to define the isothermal conditions inside ampoule reactors is the agreement of conversion *versus* time from ampoule reactors with different sizes[7]. *Figure 7* shows the time (t_m; see *Figure 1*, bottom right) required to reach the maximum temperature *versus* ampoule size. Clearly the polymerizations using larger ampoules reach t_m sooner. However, these times depend mainly on the temperature control at low conversions. They do not clearly reflect the level of temperature control achieved during autoacceleration (the reaction time period during autoacceleration is relatively small).

Another point worth mentioning here is that the rate of temperature rise at the very beginning of polymerization is also a strong function of ampoule size. As shown in *Figure 8*, the time for the ampoule with 3 mm o.d. to achieve thermal equilibration is 0.5 min, while it is ~2 min for 10 mm o.d.

Recently, free-radical polymerization rates with crosslinking have been measured in ampoule reactors[8]. Because of the nature of gelation, one can expect that heat generation rates during autoacceleration are even greater than with pure MMA. Li *et al.*[8] carried out extensive measurements of conversion *versus* time data for the bulk copolymerization of MMA/EGDMA at 70°C with 0.3 wt% AIBN using 5 mm o.d. ampoule reactors in an oil bath. In this investigation, temperature profiles under the same reaction conditions were measured. As shown in *Figure 9*, the temperature control at high EGDMA levels is relatively poor during autoacceleration. The maximum temperature rises during autoacceleration are 5°C for pure MMA, but 18°C with 25 wt% EGDMA (with EGDMA levels higher than 25 wt%, the $T_m - T_b$ values are lower). However, $T_i - T_b$ before gelation are less than 0.5°C. The use of smaller ampoules with water as the heat transfer fluid should permit substantially better temperature control. The data for pure MMA show that the values of $T_m - T_b$ using 3 mm o.d. ampoules are less than 20% of those for 5 mm o.d. Zhu *et al.*[1] measured radical concentrations for the copolymerization of MMA/EGDMA at 70°C with 0.3 wt% AIBN using 3 mm o.d. (1.8 mm i.d.) ampoules in an e.s.r. cavity (inside diameter of the cavity was 5 mm). The temperature was controlled by a gas bath with flow rates ~20 m s^{-1}. The measured $T_m - T_b$ are about 20% of those measured for 5 mm o.d. in the oil bath, i.e. 1°C with pure MMA and 4°C with 25 wt% EGDMA.

Finally, it is of interest to compare temperature profiles for adiabatic polymerizations with those found using ampoule reactors. We therefore carried out a few adiabatic measurements using the Diers VSP reactor, and these data are shown in *Figure 10*. The polymerizations stop when all of the AIBN initiator has

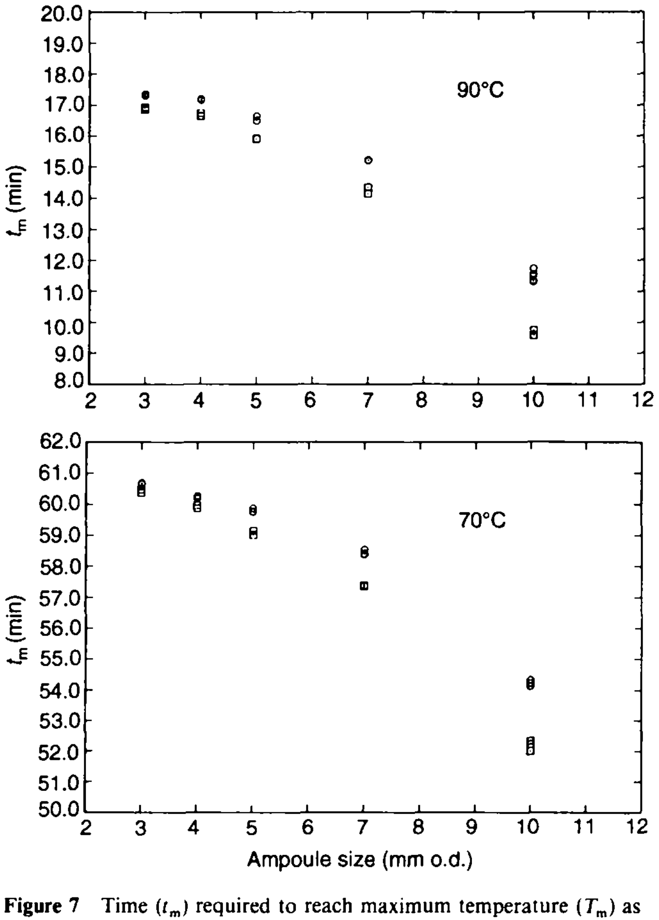

Figure 7 Time (t_m) required to reach maximum temperature (T_m) as a function of ampoule size for the bulk polymerization of MMA with 0.5 wt% AIBN. Bath fluid: water (circles) and silicone oil (squares); bath temperature 90°C (top) and 70°C (bottom)

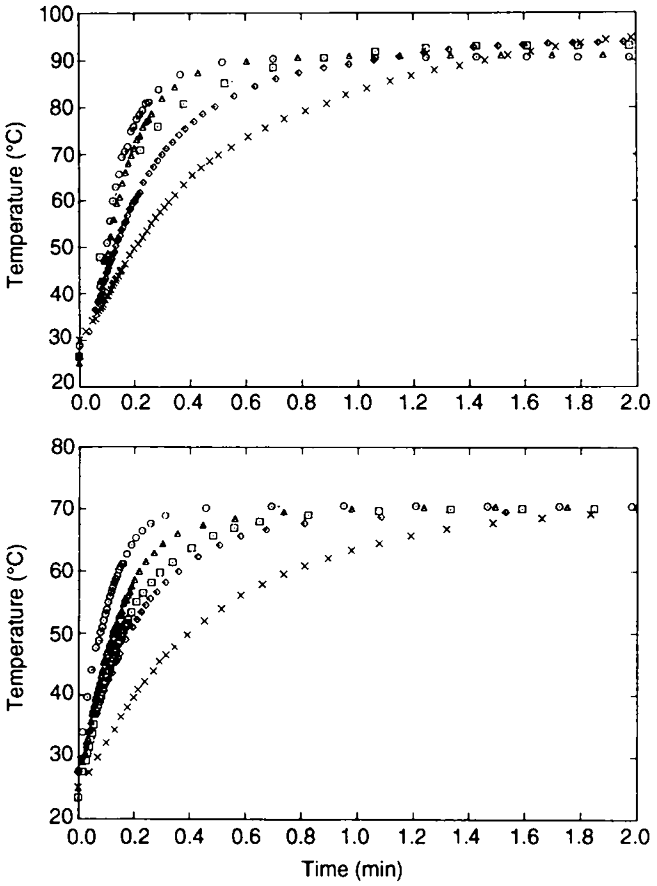

Figure 8 Heating effect: temperatures inside ampoule reactors begin to increase at the very beginning of bulk polymerization of MMA with 0.5 wt% AIBN, immediately when the ampoules are immersed in the silicone oil at 90°C (top) and 70°C (bottom). Ampoule diameters are 3, 4, 5, 7 and 10 mm o.d.

been consumed. The total temperature rise calculated by heat balance for complete monomer conversion should be ~250°C.

CONCLUSIONS

In conclusion, one may say that near-isothermal conversion–time data for free-radical polymerizations of MMA and MMA/EGDMA (both for initial rates and during autoacceleration) may be obtained with ampoule reactors of high surface/volume ratios when AIBN levels are not excessive and heat transfer coefficients in heat transfer fluids employed are adequate. One should note that autoacceleration rates for MMA are larger than for most other monomers and therefore the above conclusions should apply to those monomer systems as well.

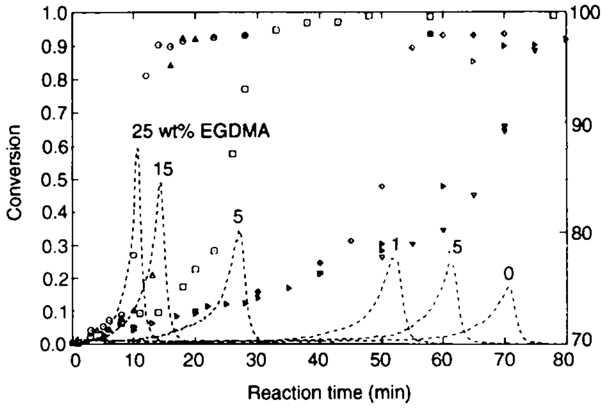

Figure 9 Conversion (points) and temperature (broken curves) *versus* reaction time of the copolymerization of MMA/EGDMA with 0.3 wt% AIBN. Ampoule size: 5 mm o.d.; bath type: silicone oil; bath temperature: 70°C; EGDMA levels: 0, 0.5, 1.0, 5.0, 15.0 and 25.0 wt% as indicated. The conversion data are taken from Li *et al.*[8]

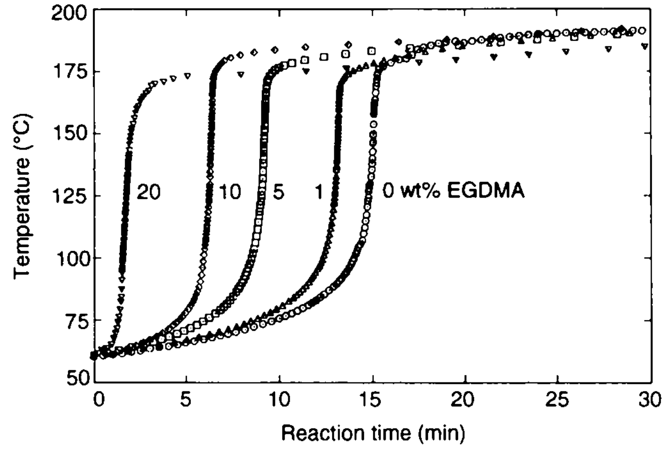

Figure 10 Temperature profiles for the adiabatic copolymerization of MMA/EGDMA with 0.5 wt% AIBN. EGDMA levels are 0.0, 1.0, 5.0, 10.0 and 20.0 wt% as indicated. Initial temperature: 60°C

ACKNOWLEDGEMENTS

Financial assistance from the Natural Sciences and Engineering Research Council of Canada, the Ontario Center for Materials Research and the McMaster Institute for Polymer Production Technology is appreciated.

REFERENCES

1 Zhu, S., Tian, Y., Hamielec, A. E. and Eaton, D. R. *Polymer* 1990, **31**, 155
2 Trommsdorff, E., Kohle, H. and Lagally, P. *Makromol. Chem.* 1948, **1**, 169
3 Mita, I. and Horie, K. *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.* 1987, **C27(1)**, 91
4 Ivin, K. J. 'Polymer Handbook', 2nd Edn (Eds J. Brandrup and E. H. Immergut), Wiley, New York, 1975
5 Balke, S. T. PhD Thesis, McMaster University, Hamilton, Ontario, 1972
6 Armitage, P. D., Hill, S., Johnson, A. F., Mykytiuk, J. and Turner, J. M. C. *Polymer* 1988, **29**, 2221
7 Balke, S. T. *Polym. Commun.* 1989, **30**, 304
8 Li, W. H., Hamielec, A. E. and Crowe, C. M. *Polymer* 1989, **30**, 1513
9 Tobolsky, A. V. and Baysal, B. *J. Polym. Sci.* 1953, **11**, 471