Bulk polymerization of methyl methacrylate: Part I: some kinetic and modelling considerations for isothermal reactions

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Kinetic studies of the bulk polymerization of methyl methacrylate have been carried out by differential scanning calorimetry (d.s.c.) and also by monitoring, gel permeation chromatography (g.p.c.). The residual monomer content in polymerizations was carried out in small thin-walled glass ampoules. Discrepancies have been found between the data acquired by the two experimental methods. These can be resolved by consideration of the measured temperature rise of the polymerizations (which can be up to 80 K above the bath temperature for a 5 g sample) carried out in the ampoules. Comparisons between the kinetic data obtained in these experiments with published data show that many of the reported kinetic constants for this polymerization are probably inaccurate because they were acquired under experimental conditions which may not have been isothermal. The implications of using inaccurate kinetic constants for the computer simulation of the high-conversion polymerization of methyl methacrylate are considered.

(Keywords: methyl methacrylate; polymerization kinetics; differential scanning calorimetry (d.s.c.); gel permeation chromatography (g.p.c.); differential temperature; modelling)

INTRODUCTION

The free radically initiated polymerization of methyl methacrylate (MMA) has been the subject of many research programmes and the kinetics of isothermal polymerization is the particular focus of a substantial proportion of published work[1-20]. Interest in the polymerization of MMA stems primarily from the commercial importance of poly(methyl methacrylate) (PMMA) and, from a more fundamental viewpoint, the fact that such a marked auto-acceleration effect is observed in the bulk polymerization of this monomer[1-3]. A quantitative understanding of the auto-acceleration behaviour in MMA polymerization is significant for the design and control of large-scale production methods for PMMA in conventional polymerization reactors and for reactive processing methods such as sheet-casting. The heat generated during the polymerization, particularly during the auto-acceleration period of the reaction, must be effectively dissipated, because the thermal history of the polymerization has considerable influence on the molecular weight and molecular weight distribution, and hence the observed thermal, mechanical and processing properties of the polymer.

In order to gain a good quantitative understanding of the polymerization it is essential to acquire reliable kinetic data for the bulk polymerization taken to high conversions. This data may then be used for the computer modelling and simulation of the polymerization process for the appropriate physical conditions used during polymer production. Modelling and simulation exercises demand not only good kinetic data but also a precise knowledge of other physical parameters such as heat transfer coefficients, diffusion coefficients and thermodynamic data. It is unfortunate that many of the parameters needed are not readily available or there is a lack of consistency amongst published data, i.e. there is poor agreement for published rate constants in the case of MMA polymerization even when these have been determined independently using identical methods[21]. Furthermore, there are many different views as to the way in which the isothermal polymerization chemistry can be described by deterministic or other modelling techniques[22-31].

The work reported here on the isothermal polymerization of MMA has been carried out as part of a more extensive programme on the reactive processing of MMA and MMA-related materials. The reactive processing studies have aimed at the very rapid bulk polymerization of monomers and other polymer precursors under conditions which make reactions non-isothermal[32]. Kinetic measurements under isothermal conditions have been made as part of the quantitative evaluation of the non-isothermal reactions which will be reported more fully elsewhere[33]. Here discussion will be limited to observations made and the kinetic results obtained for low conversion polymerization of MMA, i.e. conversions well before the onset of auto-acceleration where conventional free radical kinetics[34] are assumed to apply (equations 1, 2).

$$R = k[M][I]^{1/2} \qquad (1)$$

$$k = k_p(2fk_d/k_t)^{1/2} \qquad (2)$$

In these equations, R is the rate of polymerization; $[M]$ is monomer concentration; $[I]$ is the initiator

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concentration and k is the overall rate constant which is a function of k_p, the propagation rate constant; f, the initiator efficiency; k_d, the initiator decay rate constant and k_t, the termination rate constant.

Differential scanning calorimetry (d.s.c.) is a convenient and precise technique for directly measuring the rate of heat generation and has been used here to obtain isothermal kinetic data. Further kinetic studies were carried out using gel permeation chromatography (g.p.c.) to monitor residual monomer concentration for polymerizations carried out in small, thin-walled glass ampoules.

EXPERIMENTAL

Purification of materials

The initiator, 2,2′-azo-bis-isobutyronitrile (AIBN) (Akzo Chemie Ltd) was recrystallized twice from methanol. Methyl methacrylate (Koch Light Labs Ltd) containing 15 ppm hydroquinone was washed with 10% (w/v) aqueous sodium hydroxide solution and then twice with distilled water. After being dried over anhydrous sodium sulphate, the monomer was distilled at reduced pressure (1 mm Hg) and stored at 258 K. The monomer was degassed immediately prior to polymerization.

Differential scanning calorimetry (d.s.c.)

The bulk isothermal polymerization of MMA was investigated using a differential scanning calorimeter (Perkin Elmer Model DSC-2C). Data acquisition and reduction were carried out using an on-line data station (Perkin Elmer Model 3600 with TADS software). Indium was used as the calibrant for enthalpy and temperature measurements.

Reaction mixtures were prepared by weighing the initiator and monomer. Samples of these solutions were weighed (2–10 mg) into d.s.c. sample pans and sealed. All kinetic data were obtained by heating the reaction mixtures from a temperature of 300 K to the desired polymerization temperature at a rate of 40 K min^{-1}. The enthalpies of polymerization were calculated by integrating the area between the d.s.c. thermograms and the baseline established by extrapolation from the trace produced after complete (equilibrium) polymerization. The residual monomer content was determined by heating the sample from 323 K to 453 K at a rate of 10 K min^{-1}. This technique minimizes any error which might occur due to depolymerization, which for MMA is only significant above 483 K (ref. 35). Typically, initial heat generation rates were of the order of 1.0 mJ s^{-1}.

Thermograms were obtained under the following conditions:

(1) Bulk MMA initiated with 0.073 mol dm^{-3} AIBN at the following temperatures: 338, 343, 353, 358, 363 and 368 K.

(2) Bulk MMA polymerized at 353 K in the presence of different amounts of AIBN.

All the data cited subsequently are taken from the average of at least two or more experiments. The use of small sample masses (<10 mg) ensured that the reacting sample was at a uniform temperature during an experiment. Computer data acquisition and reduction made it possible to observe, with greater precision, deviations from ideal kinetic behaviour, i.e. the inhibition due to residual traces of oxygen and the point of departure from first order kinetics (the onset of auto-acceleration).

Ampoule polymerizations

Polymerizations were followed by using g.p.c. to measure residual monomer concentrations to high conversion. A solution of AIBN in MMA (0.057 mol dm^{-3}) was dispensed (1 g or 5 g, surface to volume ratio 3.74 and 3.01 cm^{-1}, respectively) into twelve clean dry glass ampoules which were degassed by freeze–thaw cycles under vacuum before being finally sealed. The ampoules were placed in a constant temperature bath at 343 K and mechanically shaken.

Ampoules were removed at 5 min intervals and placed in liquid nitrogen to quench polymerization. Ampoules were opened and chloroform containing a small amount of hydroquinone (approximately 1% w/v) was added to produce a 1% solution based on the original charge of monomer.

A chromatograph (Perkin Elmer plc) fitted with 50 A 5 μ and 100 A, 10 μ PL gel columns (Polymer Laboratories Ltd) was used for residual monomer measurements with chloroform as the solvent at a flow rate of 1 ml min^{-1}. An i.r. detector (Du Pont Instruments) set at 5.75 μm was used to detect the polymer carbonyl group and a u.v./visible spectrophotometric detector (Perkin-Elmer LC-95) set at 250 nm for residual monomer. A fixed volume (200 μl) of 1% (w/v) solution was used for each analysis. The chromatograms were acquired by computer (Perkin Elmer Data Station, Model 3600 and CIT-2 software). The residual monomer content and sample conversion were obtained by measurement of the chromatographic peak areas. Monomer solutions of known concentrations were used for calibration purposes. G.p.c. has the advantage that it not only allows accurate determination of monomer content, but also gives the molecular weight distributions and averages for the reaction products. Whilst this additional information is not used here, it is extremely valuable in investigating the polymerization to high conversion[22,23,25,27,31,36].

Temperature measurement in ampoule polymerizations

The temperature change during polymerization was recorded by using a thermocouple (Type K, NiCr/NiAl) positioned at the centre of the reaction mixture. To achieve reproducible experimental results, the thermocouple was inserted into a thin-walled glass probe in the ampoule. The probe was filled with silicone oil in order to improve thermal contact. Two such vessels were used, one for reference, the other as the polymerization cell. The thermocouples were connected so as to give the differential temperature and the output logged on a chart recorder. A schematic diagram of the apparatus is shown in *Figure 1*.

Degassed monomer (1 g or 5 g) containing 0.057 mol dm^{-3} initiator was weighed into the polymerization cell. The reference cell was filled with a similar quantity of inhibited monomer. Both cells were sealed under reduced pressure and allowed to stand in the dark until thermally equilibrated at ambient temperature. The cells were then lowered into a thermostatted tank at 343 K and the differential temperature recorded with time. Results are presented in *Table 1* and are the average of two experiments.

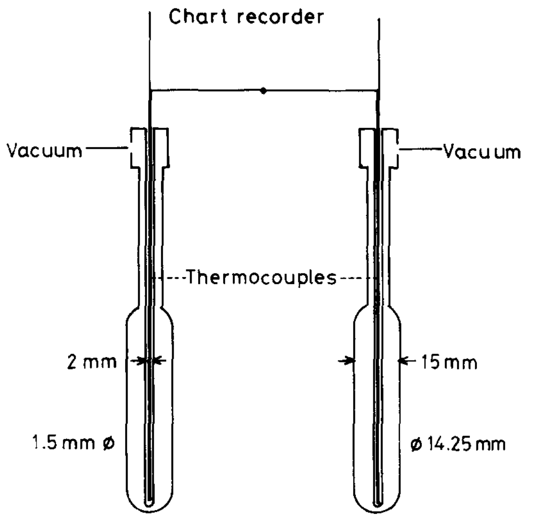

Figure 1 Schematic representation of the apparatus used for polymerization studies in glass ampoules where thermocouples were used to monitor reaction mixture temperatures. ϕ refers to internal diameters

Table 1 Summary of data obtained from ampoule polymerization at 343 K

Mass (g)	1.0	5.0
Conversion	0.919	0.938
$10^3 \times k$ ($\mathrm{mol^{-1/2}\,dm^{3/2}\,s^{-1}}$)	0.70	0.85
Temperature difference after 300 s (K)	2.0	4.0
Peak temperature difference (K)	58.8	81.3
Time to peak temperature (s)	2436	2076

RESULTS

D.s.c. experiments

A typical thermogram obtained for the bulk polymerization of MMA at 343 K is shown in *Figure 2*. Polymerization proceeds via three distinct phases. In the first phase the rate of polymerization decreases as described by the conventional free radical kinetics of equations (1) and (2). In the second phase an acceleration in the rate of polymerization[1] takes place after approximately 20% conversion of monomer, at which point the diffusion controlled macro-radical termination reaction rate constant falls due to the increasing viscosity of the polymerizing medium. The exact point at which auto-acceleration starts is not readily defined and previous work has led to the suggestions that auto-acceleration may start as early as the commencement of polymerization[26] or at as late as 30% monomer conversion[37]. In the third phase, the reaction rate falls rapidly to very low values. This decrease in rate is caused by a combination of monomer depletion and diffusion control of the propagation reaction resulting from the formation of an essentially glassy reaction medium. Irrespective of the reaction conditions, none of the reactions went to 100% conversion. All polymerizations showed a short induction period before the onset of polymerization (A–B in *Figure 2*). The induction period was found to be greater for smaller sample masses (*Figure 3*) and to decrease with increasing polymerization temperature. The induction period appears to be caused by oxygen inhibition of the polymerization. For small sample masses, a relatively greater volume of oxygen is encapsulated in the sealed sample pan than is the case for large sample masses. Consequently, a longer induction period is observed in the case of the former.

Figures 4–9 show the results of the kinetic measurements at both fixed temperature and at constant initiator concentration. The kinetic constants derived from these data are summarized in *Tables 1* and *2*.

The final monomer conversion was calculated as a fraction given by the ratio of the observed enthalpy of isothermal polymerization to that of the sum of the observed enthalpies for isothermal polymerization and that obtained from the subsequent dynamic polymerization where the reaction temperature was raised by approximately 100 K. The initial kinetic rate constant, k', during the first phase of polymerization was calculated from the d.s.c. thermogram using equation (3) (ref. 38).

$$\ln[A/(A-a)]=k't \qquad (3)$$

where A is the sum of the enthalpies of the isothermal and dynamic experiments, a the isothermal enthalpy up to time, t and $k'=k[I]_0^{1/2}$.

The polymerization enthalpies show no systematic variation with temperature. This is in contrast to the

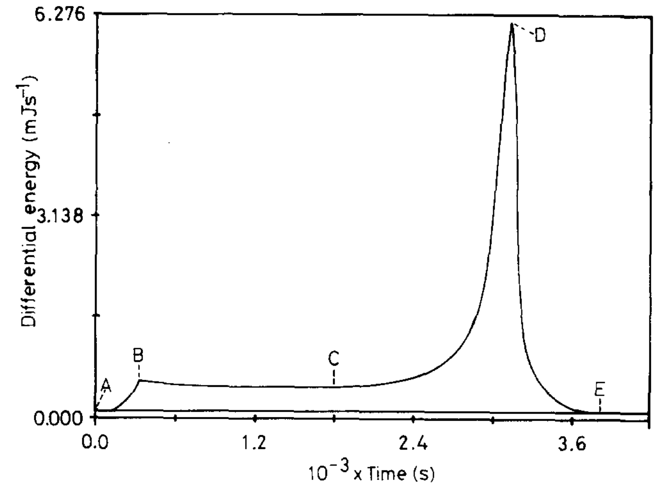

Figure 2 A typical isothermal thermogram (343 K, [AIBN] = 0.073 $\mathrm{mol\,dm^{-3}}$, monomer = 7.1 mg) obtained by d.s.c. indicating: induction period A–B; period when conventional free radical polymerization kinetic behaviour is observed, B–C; onset of auto-acceleration, C, maximum reaction rate D, equilibrium polymerization due to formation of a polymer glass, D–E, baseline A–E

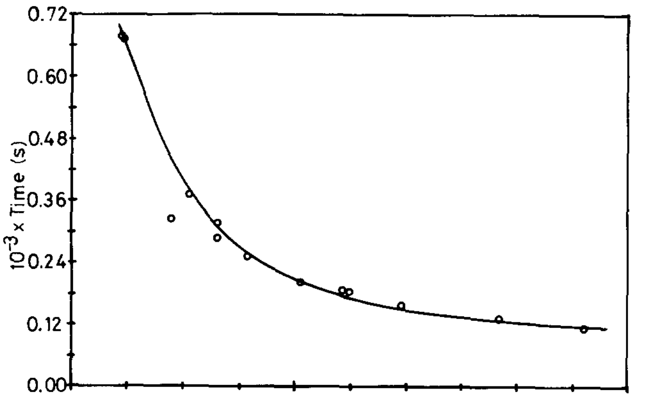

Figure 3 Variation of the induction period with the mass of monomer used for kinetic studies by differential scanning calorimetry with constant temperature and initiator concentration (363 K, [AIBN] = 0.065 $\mathrm{mol\,dm^{-3}}$)

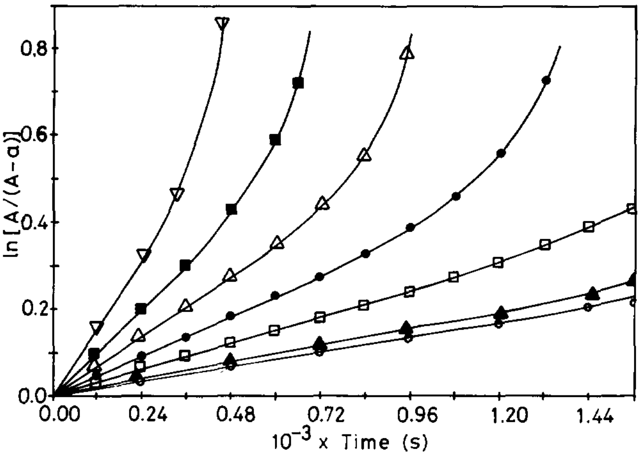

Figure 4 Typical first order plots (obtained from the initial rates of polymerization as observed by d.s.c.) obtained at 353 K. ○, [AIBN] = 0.0071 mol dm^{-3}; ▲, [AIBN] = 0.0167 mol dm^{-3}; □, [AIBN] = 0.0262 mol dm^{-3}; ●, [AIBN] = 0.0384 mol dm^{-3}; △, [AIBN] = 0.0505 mol dm^{-3}; ■, [AIBN] = 0.073 mol dm^{-3}; ▽, [AIBN] = 0.0865 mol dm^{-3}

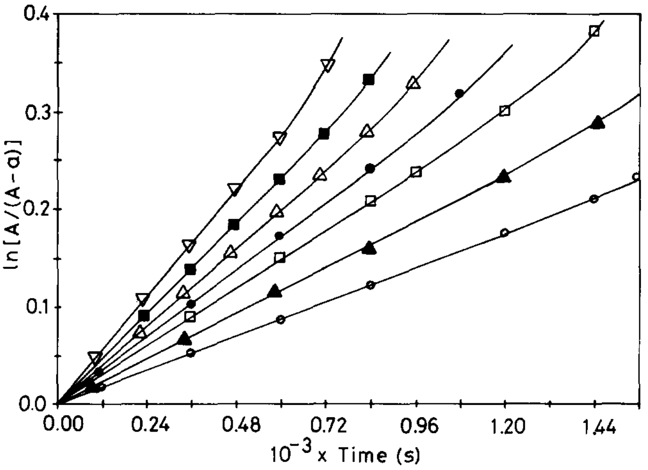

Figure 5 First order plots obtained from the initial rate of polymerization as observed by d.s.c. with [AIBN] = 0.073 mol dm^{-3} at various temperatures. ○ = 338 K; ▲ = 343 K; □ = 348 K; ● = 353 K; △ = 358 K; ■ = 363 K; ▽ = 368 K

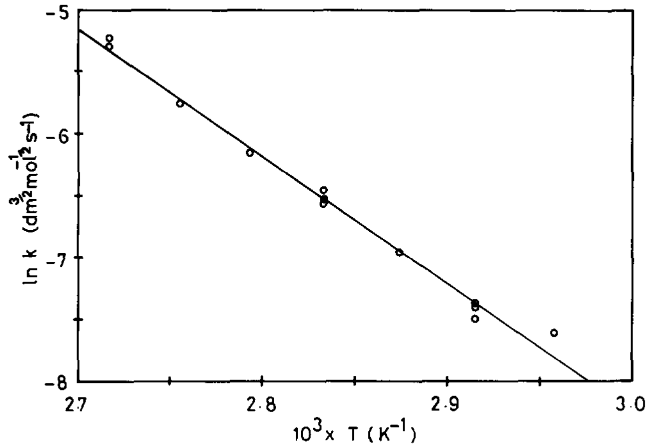

Figure 6 Arrhenius plot of k obtained by d.s.c.

results of Malavasic[38], who found that enthalpies increased with polymerization temperature and suggested that this trend resulted from the differences in the heat capacities of monomer and polymer, which can be readily seen in the d.s.c. experiments. The value of the enthalpy of polymerization is important in determining the

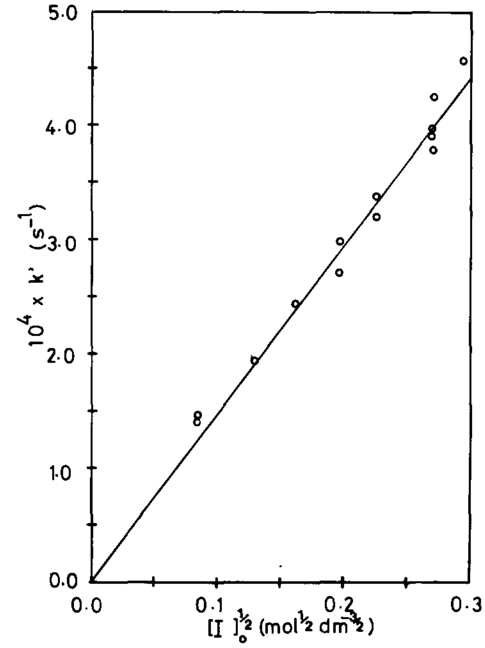

Figure 7 Plot of initial polymerization rate constant, k', against $[AIBN]_0^{1/2}$ at 353 K

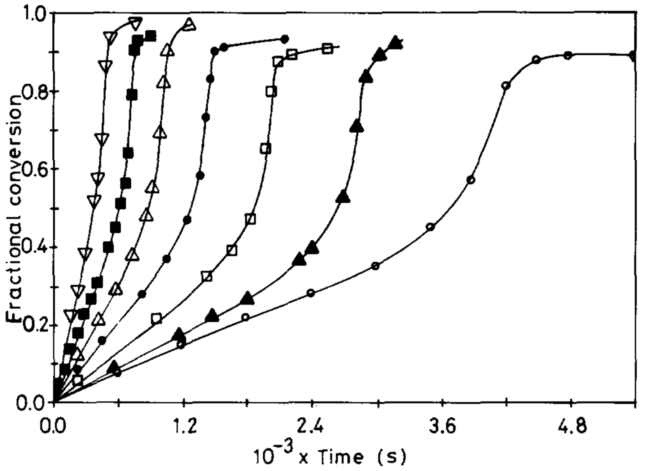

Figure 8 Plots of conversion with time as determined by d.s.c. at constant temperature (353 K) and different initiator concentrations. ○, [AIBN] = 0.0071 mol dm^{-3}; ▲, [AIBN] = 0.0167 mol dm^{-3}; □, [AIBN] = 0.0262 mol dm^{-3}; ●, [AIBN] = 0.0384 mol dm^{-3}; △, [AIBN] = 0.0505 mol dm^{-3}; ■, [AIBN] = 0.073 mol dm^{-3}; ▽, [AIBN] = 0.085 mol dm^{-3};

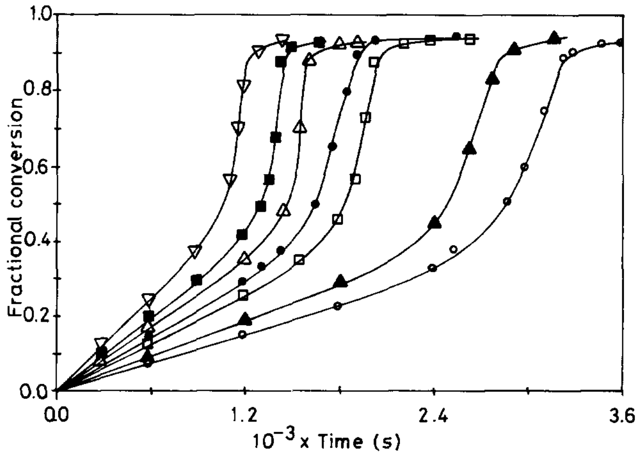

Figure 9 Plots of monomer conversion with time as determined from d.s.c. measurements at various temperatures. ○ = 338 K; ▲ = 343 K; □ = 348 K; ● = 353 K; △ = 358 K; ■ = 363 K; ▽ = 368 K

Table 2 D.s.c. results for MMA polymerizations at various temperatures, $[AIBN]_0 = 0.073$ (mol dm^{-3})

Temperature (K)	ΔH polymerization (kJ mol^{-1})	Fractional conversion	$10^3 \times k$*
338	−59.5	0.89	0.50
343	−53.5	0.91	0.60
348	−56.2	0.91	0.95
353	−54.0	0.93	1.48
358	−53.9	0.95	2.13
363	−56.6	0.94	3.15
368	−55.3	0.98	5.17

* Values of k, in mol$^{-1/2}$ dm$^{3/2}$ s^{-1}, are the mean values from all experiments at that temperature

Table 3 D.s.c. results for MMA polymerizations at various initiator concentrations at 353 K

$10^2 \times [AIBN]_0$ (mol dm^{-3})	ΔH polymerization (kJ mol^{-1})	Fractional conversion	$10^3 \times k$*
0.71	−53.7	0.93	1.71
1.67	−55.6	0.94	1.51
2.62	−51.9	0.94	1.51
3.84	−55.5	0.94	1.46
5.05	−55.1	0.93	1.47
7.30	−54.0	0.93	1.48
8.65	−52.0	0.92	1.56
average	−54.0 ± 1.42		

* Values of k, in mol$^{-1/2}$ dm$^{3/2}$ s^{-1}, are mean values from all experiments at that initiator concentration

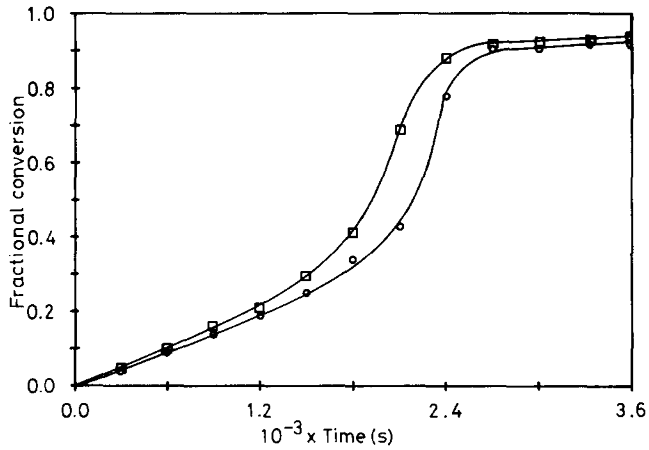

Figure 10 Plots of monomer conversion with time for reactions carried out in glass ampoules with different monomer masses. ○ = 1 g MMA; □ = 5 g MMA

temperature at which the maximum theoretical conversion of monomer to polymer occurs[39].

Because all polymerizations were carried out at temperatures below that of the glass transition of pure PMMA, conversions of less than 100% were expected and, indeed, observed. Horie and Kambe[14] have explained that the formation of a glassy polymer–monomer mixture before the completion of polymerization leads to a retardation of reaction rate. In addition, when the polymerization temperature approaches the glass transition temperature of the polymer, the limiting conversion increases. The experimental results reported here are in agreement with these theoretical predictions.

No systematic variation of limiting conversion with initiator concentration can be seen. This is in contrast to Wunderlich and Stickler[40] who noted that the limiting conversion increases with increasing initiator concentration.

Ampoule polymerizations

The conversion profiles obtained for different polymerization masses (1 g and 5 g) are shown in *Figure 10*. Comparison of the conversion profiles indicates that the larger the polymerization mass the greater the rate of polymerization. The rate constant for the initial period of the polymerization reaction was calculated from the kinetic data illustrated in *Figure 11* and these are summarized in *Table 1*.

The data presented in *Figure 11* illustrate that by extrapolating to zero conversion, there is an apparent time delay before polymerization commences. During this period, the ampoule and contents are equilibrating to the tank temperature and the rate of polymerization is increasing to that at the equilibrium temperature. The 1 g sample of initiated monomer achieves thermal equilibration in approximately 25 s while the larger sample requires approximately 80 s to do the same. This is a consequence of the greater thermal capacity of the larger mass combined with the lower surface/volume ratio of the system.

The variation of temperature with time for different initial polymerization masses is shown in *Figure 12*. It is clear that reaction mixtures in the ampoule experiments

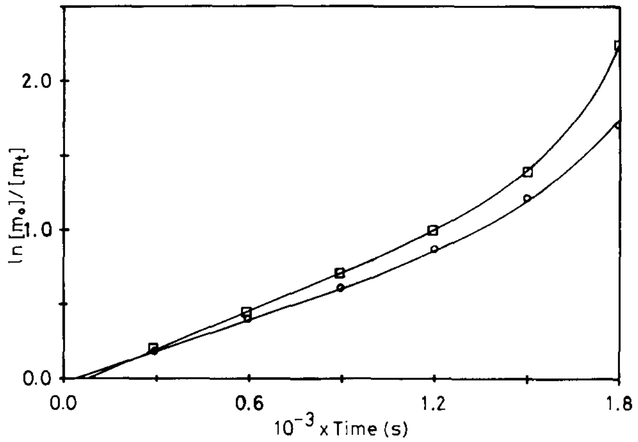

Figure 11 First-order plots for ampoule experiments with different masses of monomer. ○ = 1 g MMA; □ = 5 g MMA

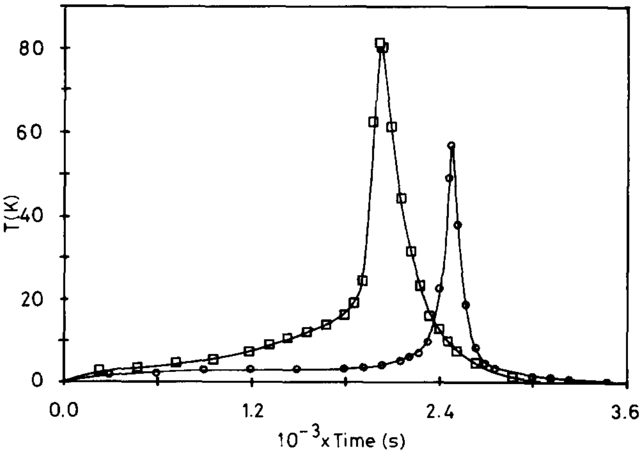

Figure 12 Differential temperature measurements in typical ampoule experiments with different masses of monomer. ○ = 1 g; □ = 5 g

do not stay at constant temperature. At no time during the polymerization is the temperature in the reaction vessel equal to that of the inert standard. There is a short but significant period during which the temperature of the polymerization vessel increases by only 2–4 K above that of the reference cell until the onset of the auto-acceleration effect when the temperature rise is very large. The maximum temperature differences recorded were 58.8 K and 81.3 K for the 1 g and 5 g samples, respectively. When the temperature of the polymerization cell decreased to that of the glass transition temperature of the reacting mass and the polymerization stopped, the rate at which the temperature difference decreases below the glass transition of the polymer is first order with time, i.e. Newton's Law of cooling applies.

DISCUSSION

Least squares treatment of the Arrhenius plot (*Figure 6*) of values of k obtained from d.s.c. experiments with constant initiator concentration showed that

$$k/\text{mol}^{-1/2}\,\text{dm}^{3/2}\,\text{s}^{-1} = \exp((22.4 \pm 0.8) - (10210 \pm 273)/T) \quad (4)$$

Comparison of the overall rate constants shown in *Tables 1* and *2* with the previously published values for the bulk polymerization of MMA at 343 K are shown in *Table 4* and reveal some significant differences.

Generally the overall rate constants obtained by d.s.c. are lower than those obtained by other methods. The results of Malavasic *et al.*[38,41] are anomalous because they appear to have been obtained by identical methods but the rate constants differ by a factor of almost two. No reference is made to this discrepancy by Malavasic[41]. The accuracy of the rate constant found by Horie and Kambe[14] is of questionable value because of the substantial monomer loss during polymerization which was due to the use of an unsealed sample plan. The value of 8.5×10^{-3} (mol$^{-1/2}$ dm$^{3/2}$ s^{-1}) obtained for the rate constant from the 5 g ampoule polymerization is supported by the similar value obtained using dilatometers containing 3–5 g of MMA, with a 2 mm bore capillary[37].

The rate of monomer conversion measured from the ampoule polymerizations at 343 K is between 21% and 40% greater than that observed by d.s.c. This discrepancy can be resolved by taking into consideration the temperature rise occurring during the ampoule polymerizations. The temperature increases measured during the initial period of the ampoule polymerizations amounted to between 2 and 4 K for the 1 g and 5 g cases, respectively. Substitution of the measured ampoule temperatures (instead of that of the reference cell) into equation (4) gave values for the initial rate constant of 7.4×10^{-3} and 8.8×10^{-3} (mol$^{-1/2}$ dm$^{3/2}$ s^{-1}) for 1 g and 5 g sample masses respectively. These values should be compared with the values of 7.0×10^{-3} and 8.5×10^{-3} (mol$^{-1/2}$ dm$^{3/2}$ s^{-1}) obtained from the ampoule polymerizations. Hence data presented here, obtained by d.s.c. and ampoule polymerizations is consistent to within 5% when the true ampoule temperature is taken into account.

Both dilatometry and gravimetry have been used by Balke and Hamielec[15] in an extensive study of the kinetics and molecular weight development in bulk MMA polymerizations. Although there have been other similar investigations, the work of Balke and Hamielec has been used as a source of kinetic and molecular weight parameters in a number of modelling and simulation exercises[23–26,28–31], and hence is of particular significance. These data have therefore been chosen for comparison with results presented here.

The value given for k at 343 K by Balke and Hamielec[15] is similar to that measured here for the polymerization of a 1 g sample of MMA, in which the initial polymerization temperature was 345 K, 2 K higher than the expected polymerization temperature. A possible explanation is that there was a similar temperature rise in the initial stages of the experiments Balke and Hamielec used to obtain k, i.e. the results were not obtained under truly isothermal conditions at the quoted temperature. Although the ampoules used had a large surface area to volume ratio in order to maximize heat transfer through the polymerizing mass to the isothermal environment, this does not guarantee isothermal conditions in the reaction vessel. Attempts which were made to directly measure the temperature within the reacting medium were unsuccessful due to interference of the thermocouple with material in the polymerization process. The fact that samples taken from polymerization mixtures in ampoules of differing surface to volume ratios had similar molecular weight distributions was given as supporting evidence that polymerizations were isothermal. This indirect evidence is of questionable value in view of the relatively insensitive nature of the g.p.c. data to conversion and temperature. A comprehensive analysis of the experimental method of Balke and Hamielec is not possible because complete details are not given in ref. 15.

It would appear self-evident that sample masses of less than 10 mg contained in metal d.s.c. sample pans are more likely to remain at constant temperature during polymerization than 1–5 g samples in glass ampoules immersed in a thermostatted tank because of the superior heat transfer characteristics of the former. It is instructive

Table 4 Experimental and literature values for the overall polymerization rate constant for MMA

$10^{-9} \times A$ factor (mol$^{-1/2}$ dm$^{3/2}$ s^{-1})	Activation energy (kJ mol^{-1})	$10^3 \times k$ (at 343 K) (mol$^{-1/2}$ dm$^{3/2}$ s^{-1})	Method and reference
0.00149	62.0	0.54	D.s.c. (ref. 14)
0.103	74.0	0.56	D.s.c. (ref. 38)
5.30	84.9	0.63	D.s.c. (calculated from equation (4) in this paper)
–	–	0.70	1 g ampoule (this paper)
3.01	82.7	0.78	dilatometry (ref. 15)
4.86	83.7	0.80	adiabatic calorimetry (ref. 9)
3.10	82.6	0.82	dilatometry (ref. 37)
–	–	0.85	5 g ampoule (this paper)
0.49	76.8	0.97	D.s.c. (ref. 41)

to compare the reaction rate obtained by d.s.c. when different reaction masses are used, all other reaction conditions remaining constant as in *Table 5*.

The d.s.c. findings are consistent over a considerable sample weight range. The slight differences in the initial rate which are observed can be accounted for by the shorter inhibition period noticed in the polymerizations involving the larger reaction masses. This in turn leads to a lower monomer consumption in the side reactions involved during the inhibition period and hence has a small effect on the observed rate constant and the characteristic features of the d.s.c. thermogram.

When estimating the relative values of dilatometry and d.s.c. as techniques for following low conversion polymerization, it is necessary to examine potential sources of error in the experimental method and also carefully question any assumptions made during data processing. In dilatometry, conversion is measured by observing the movement of liquid level in a narrow bore tube. The technique is sensitive to changes in the bore regularity, temperature and the viscosity of the reaction medium. A linear relationship between conversion and volume contraction is the main assumption made in converting the experimental observations into kinetic constants. The d.s.c. technique uses very small samples and therefore relies on accurate weight measurements for enthalpy determinations. The absolute temperature and heat output measurements rely on precise calibration with known standards and on the accuracy of measurement of the differential heat input between the reference and sample cells. Any effects due to change in machine performance over the polymerization period would be obvious since the extrapolated baseline would not meet the initial heat output rate as seen in *Figure 2*. Accuracy in the measurement of sample heat output rate is determined by errors in measurement of power in the cell heaters, by discretization errors introduced by digital sampling and by thermal and electronic noise. The overall contribution of noise can be seen by measuring the heat output under steady-state conditions, such as at the end of polymerization. The peak to peak noise at the end of polymerization is typically 5×10^{-4} (mJ s^{-1}) at 343 K.

Good heat transfer is the essential criterion for maintaining isothermal polymerization conditions. It is particularly important to be able to remove the heat generated during auto-acceleration, when the rate of heat output from the polymerization increases approximately ten-fold. At this point even small increases in temperature can lead to thermal runaway[31] with subsequent dead-end polymerization, monomer evaporation and depolymerization. The problems encountered in seeking very fast polymerization rates of acrylic monomers in reactive processing, e.g. reaction injection moulding (RIM) will be discussed elsewhere[42].

The differences in kinetic constants summarized in *Table 4* have important implications. The consequences of using inaccurate kinetic data in the modelling of polymerization phenomena can be highlighted by considering a typical deterministic model of the type reported by Hamielec *et al.*[15]. This model can fit data obtained under isothermal conditions but cannot deal with heat transfer and temperature changes which might occur in high conversion reactions although it can, in principle, be used to simulate non-isothermal conditions if the temperature–time variation during polymerization is known. There is good reason to assume that the kinetic data used with this model was not obtained under isothermal conditions even though the conversion time data used with this model were not obtained under isothermal conditions even though the conversion time data are very similar to those expected for true isothermal data will be used it cannot be used to simulate non-isothermal polymerization behaviour.

Table 5 Variation of d.s.c. observations with sample mass

	Expt. 1	Expt. 2	Expt. 3
Sample mass (mg)	3.81	6.41	9.08
Initial rate (mJ g^{-1} s^{-1})	0.46	0.46	0.50
Peak position (s)	756.6	750.0	750.6
Peak rate (mJ g^{-1} s^{-1})	3.52	3.52	3.64

Numerical integration routines for partial differential equations of the type resulting from a mathematical analysis of heat transfer problems associated with the non-isothermal polymerization MMA cannot accommodate the complex models needed to describe the auto-acceleration effect, and finite element techniques are excessively time consuming. Recently it has been shown that finite difference methods can be employed to deal with heat transfer in one dimension for MMA polymerization to produce kinetic and molecular weight data over the complete conversion range[33].

In addition, it is found that when the measured temperature profiles (*Figure 12*) are used as a forcing function in order to simulate the initiator decomposition rates under non-isothermal conditions, a very rapid loss of initiator is predicted during the exotherm resulting from auto-acceleration as can be seen in *Figure 13*. This observation is particularly significant because of the dependence of the instantaneous polymerization rate and polymer molecular weight on the initiator concentration.

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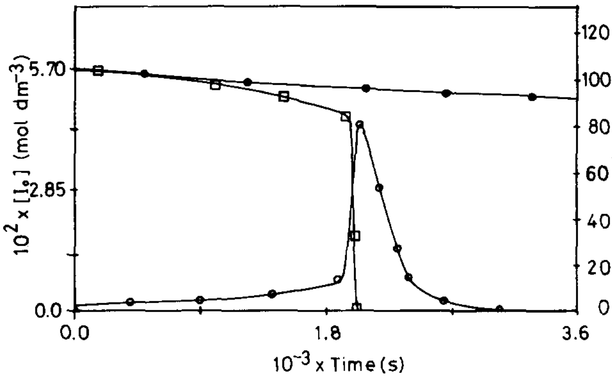

Figure 13 Simulated initiator decomposition behaviour under □, non-isothermal conditions typical of those observed during the auto-acceleration period for MMA polymerizations in the ampoule experiments reported here; ●, isothermal conditions (343 K); ○, simulated differential temperature profile

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