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# A critical evaluation of reaction calorimetry for the study of emulsion polymerization systems: thermodynamic and kinetic aspects

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## Abstract

Protocols were examined for the measurement of rates and enthalpies of polymerization ($\Delta H_p$) using reaction calorimetry. $\Delta H_p$ was determined to be 70.2 kJ mol$^{-1}$ for a series of seeded styrene emulsion polymerizations under typical emulsion conditions, in good agreement with literature values. However, there was a significant deviation from this value for small-particle systems, which is ascribed to surface effects, i.e. environmental effects on $\Delta H_p$. Careful comparison between rate data obtained by calorimetry and by dilatometry leads to recommended procedures for obtaining reliable and accurate rate data using the former technique.

*Keywords:* Emulsion polymerization; Enthalpy of polymerization; Styrene

## 1. Introduction

Two of the most precise techniques used experimentally in the study of emulsion polymerization kinetics are dilatometry and reaction calorimetry. Reaction calorimetry, used frequently in both academia and industry, can be employed in many circumstances where dilatometry cannot, for example, obtaining accurate rate data while one or more components are being fed into the system (semi-batch conditions). There are still questions as to the necessary protocols to enable accurate kinetic data to be acquired using calorimetry in emulsion polymerizations. Methods for utilizing a reaction calorimeter with the polymerization of styrene have been reported for monitoring emulsion polymerization kinetics [1–8], nucleation effects [9–11], control of molecular weight [12] and other novel processes [13–15]. Urretabizkaia et al. [16] and de Buruaga et al. [17, 18] have also discussed online control of emulsion copolymerizations by calorimetry. In all of these reports, the calorimetric determination of conversion was verified by sampling from the reaction and analysis by gravimetry or gas chromatography.

This work aims to extend the verification of the reaction calorimetric technique by a detailed comparison of reaction rates measured by both this technique and dilatometry. The motivation is to provide an independent check of protocols for obtaining rate data calorimetrically, with a resolution that is as high as possible. This is particularly useful for extracting reliable rate coefficients from appropriate rate data where such rate data are combined with sufficiently accurate knowledge of associated parameters (such as particle number).

A major potential application of these protocols is in mechanistic understanding. Extensive mechanistic knowledge has been obtained for emulsion polymerizations in systems involving thermal initiators, from dilatometric measurements of both the steady state and the time dependence of the polymerization rate, including use of $\gamma$-radiolysis initiation following removal from the radiation source ('relaxation' data) [19–21]. Equivalent knowledge cannot be obtained using dilatometry for systems with redox initiation, because this is perforce a semi-batch process; however, such experiments are possible using accurate rate data from reaction calorimetry. The aim of this paper is to

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determine the necessary experimental protocols for this purpose.

## 2. Polymerization enthalpy and rate

To utilize calorimetric data for the analysis of chemical kinetics, an accurate value for the enthalpy of the reaction must be known. The enthalpy of polymerization, $\Delta H_p$, in conjunction with the volume of latex (discrete plus continuous phases) provides the conversion factor from heat flux due to reaction, $Q_r$, into rate. This approach is applicable to conventional free radical emulsion homopolymerization reactions, due to the validity of the assumption that the vast majority (by number) of reactions that occur are between a monomer unit and a long polymer chain. That is, all polymerization reactions beyond the first few propagation steps are essentially equivalent due to the degree of polymerization of the reactive chain being sufficiently high. Significant chain length dependencies of reaction enthalpy are expected to be significant only in the first few propagation steps. Furthermore, all other reactions in the system, such as initiation, aqueous propagation, transfer and bimolecular termination, are not considered following similar reasoning (it is noted that this treatment may need correction for 'controlled' radical polymerizations where degrees of polymerization may be much lower).

Given the assumption that the heat transfer coefficient is sufficiently well known, the rate of reaction can only be as accurate as the chosen value for $\Delta H_p$. (The analysis of per-particle kinetics in addition requires the average number of radicals per particle, in turn requiring that the particle number be accurately known.) This might depend upon chemical environment, conversion and temperature, amongst other factors, and so ideally should be determined in a system as close as possible to that being studied. Variations in polymerization enthalpies have been reported in the literature for systems with differences in the phase of the reaction, temperature and environment. For the emulsion polymerization of styrene, reported values for $\Delta H_p$ range from 68.5 to 73.0 kJ mol$^{-1}$ [22].

In order to satisfy the goal of exploring reliable procedures for obtaining accurate rates from reaction calorimetry, a series of experiments were performed whereby polystyrene seed latexes of different sizes were swelled with monomer to saturation and polymerized using persulfate as initiator. The heat evolved during the reaction could then be checked from the conversion, as determined externally by gravimetry, to deduce a value for the overall enthalpy of reaction using:

$$\Delta H_p = \frac{\int Q_r \mathrm{d}t}{n_M} \tag{1}$$

Here $n_M$ is the number of moles of monomer polymerized. Any possible artifacts caused by the measurement of polymerization in the glassy region (for styrene, this corresponds to a weight fraction $w_p \gtrsim 0.85$ for a reaction temperature of 50 °C) need to be avoided, since the enthalpy of polymerization could change significantly due to the large environmental changes that occur upon the glass transition being achieved. Each reaction was, therefore, terminated using a shot of inhibitor before such a conversion was attained.

The calorimeter measures the temperatures of the reaction mass and of the surrounding jacket oil to determine the heat either evolved or absorbed in the reacting system. The equation governing heat flow $Q$ through the reactor wall is:

$$Q = UA(T_r - T_a) \tag{2}$$

where $U$ is the heat transfer coefficient, $A$ the heat exchange area, $T_r$ the reaction mass temperature and $T_a$ the adjusted jacket temperature. It is apparent from Eq. (2) that there are three key aspects to this measurement: (a) the net heat flow (b) the calibration constant ($UA$) and (c) the measurement of a meaningful reaction and jacket temperature.

$UA$ is determined in a standard manner by measuring the response of the calorimeter to a known heat input. It should be noted that a key aspect of the calorimetric technique is that there may be a delay in the response of the system, of the order of a few minutes, to any change in the evolving heat (depending on the size of the heat flow), limiting the dynamic resolution of the instrument.

Another key aspect of such calorimetric measurements is that the reaction heat flow is measured relative to a baseline. This is the heat flow through the reactor wall for the same system in the absence of reaction, and incorporates the heat associated with other aspects of the system, such as specific heat and agitation energy. The baseline may drift due to changes in the system and variations in the heat transfer coefficient. This implies that significant error may arise if the incorrect choice of baseline form is made, particularly if there is a large shift in baseline over the course of the reaction. The baseline may be chosen to be, for example, proportional to conversion or a linear interpolation (i.e. proportional to time) between the beginning and end of the reaction phase. For accurate calorimetry, we believe it is useful to report the raw heat-flow data, including baseline, to evaluate the quality of results. A dramatic shift of the baseline during a run makes the data collected susceptible to significant error if the choice of baseline form is not physical. The standard choice, of baseline proportionality to conversion, has been assumed in this work and, in all cases, efforts were made to ensure the shifts in baseline level were small enough that this choice should not lead to erroneous conclusions.

Dilatometry, measuring polymerization rate from the change in reaction volume, provides a useful comparison to the data collected by calorimetry. The experimental conditions are quite different between the techniques: typically the reaction volume in a dilatometric experiment will be 30–50 ml and the agitation provided by a magnetic ‘flea’, compared to calorimetric experiments with larger reaction volumes (typically 500 ml to 5 l) and better shear.

Even given an accurate value of $\Delta H_p$, it is necessary to check the reliability of calorimetry for obtaining rate data in emulsion polymerizations systems, i.e. reliable dynamic response on the timescales required for monitoring polymerization rate. For this reason, measurements were performed on the steady-state rate of a seeded styrene emulsion polymerization initiated by persulfate. Rates were determined using both calorimetry and dilatometry, with experimental conditions such as particle number, monomer concentration and initiator concentration maintained as constant as possible between the two procedures.

The results from both experimental techniques are also compared against those deduced from well established models [19] for the rates in these seeded systems. Comparison between experiment and theory was not the principle motivation of this work but is informative nevertheless.

## 3. Experimental

Because the objective of this study is to establish conditions for obtaining reliable rate data from calorimetry, experimental procedures are described in considerable detail.

### *3.1. Seed latex preparation*

Seed latexes were prepared using the following reagents: styrene (Synthetic Resins), sodium dodecyl sulfate (SDS, Sigma-Aldrich), Aerosol MA-80 (sodium bis(1,3-dimethylbutyl) sulfosuccinate, Cytec), sodium hydrogencarbonate (Sigma-Aldrich), sodium persulfate (NaPS, Fluka) and potassium persulfate (KPS, Sigma-Aldrich). These reagents were used as supplied, with the exception of styrene monomer, which was purified prior to reaction by passage through a column of basic alumina to remove inhibitor. Deionized (DI) water was obtained from a Milli-Q ultrafiltration system.

Two seed preparations were employed. The first was designed to produce a latex with a small average particle diameter and the second is that found in the work of Hawkett et al. [23], producing a size for which extensive rate data are available [23]. In the first seed preparation, 250 g of styrene, 5 g of SDS and 0.5 g of $NaHCO_3$ were added to 733 g of de-ionized water. The pre-emulsion was added to a Mettler-Toledo RC1 reaction calorimeter using a Mettler HP-60 reactor with anchor stirrer. The reaction temperature was 90 °C and agitation speed was 300 rpm. When these conditions were reached, 2.5 g of NaPS (dissolved in 10 g DI water) was added shot-wise to initiate polymerization.

In the second preparation, 300 g styrene, 10.5 g AMA-80 and 1.0 g $NaHCO_3$ were added to 600 g DI water. The preparation was also performed in the HP-60 reactor with an anchor stirrer at a reaction temperature of 90 °C and agitation speed of 300 rpm. This preparation was initiated by the shot-wise addition of 1.0 g KPS dissolved in 30 g DI water.

The first seed preparation was performed three times producing particles with average diameters of 55.0, 58.0 and 60.3 nm as measured by photon correlation spectroscopy (PCS average values, obtained with a Brookhaven instrument comprising a BI-200SM Version 2 goniometer with 633 nm, 35 mW HeNe laser, BI-APD avalanche photodiode detector, and PC1 B1-9000AT EN correlator). The first latex was used in the following enthalpy experiments and the latter two used in the two rate comparison experiments (all three are referred to as the ‘55 nm’ latex preparation throughout the following). The second preparation produced a latex with an average particle diameter of 130 nm as determined by both PCS and transmission electron microscopy.

### *3.2. Enthalpy of polymerization*

The seed latexes used for the determination of polymerization enthalpy were diluted with DI water and swollen with sufficient monomer to ensure interval 2 conditions (polymerization in the presence of emulsion droplets and the absence of secondary nucleation) prior to addition to the reactor. For the 55 nm seed latex, 100 g of seed latex was diluted with 900 g of DI water, and 50 g of styrene was then added. The initiator solution consisted of 0.513 g NaPS dissolved in 5.0 g DI water and the inhibitor shot consisted of 0.270 g 4-methoxy phenol (MEHQ) dissolved in 10 g DI water. In the case of the 130 nm seed latex, 200 g of latex was diluted with 600 g DI water before swelling with styrene for two runs (100 g styrene in the first and a reduced amount of 60 g in the second) and two runs performed using 100 g of seed latex and 50 g styrene. The initiator shot consisted of 1.18 g NaPS dissolved in 10 g DI water and the inhibitor shot consisted of 0.700 g MEHQ in 20 g DI water.

A HP-60 reactor was used with an anchor stirrer and the reaction temperature was 50 °C. The reaction phase consisted of the shot-wise addition of initiator followed by a period of steady-state polymerization rate, terminated by the addition of MEHQ inhibitor. Gravimetric sampling prior to reaction and after reaction had ceased and was used to determine the conversion of monomer throughout the reaction phase. Using Eq. (1), this conversion is related to the integrated reaction heat flow to determine $\Delta H_p$.

The calibration of the reactor requires a value for the conversion at the end of the reaction. This was determined by gravimetry, with duplicate measurements in each case. For the 130 nm sample, in the first two reactions the final gravimetric sample was taken after the final calibration and for the second two runs this sample was taken after inhibitor addition. For the 55 nm latex a variation was made with samples taken from the reactor at the end of the calibration phase as well as at the same time as inhibitor addition. These 55 nm samples taken at the addition of inhibitor were immediately frozen with liquid nitrogen before thawing and the volatiles were removed in a vacuum oven held at room temperature. This same freezing and drying procedure was also applied to the final sample taken after calibration in this series.

For assessing the quality of calorimetric data, it is desirable that all heat flows exhibit a steady state or only slowly changing rate (i.e. no gel effect or other phenomena that may indicate the polymerization matrix has changed significantly), and that there are no rapid shifts in the baseline. Furthermore it is desirable that, after the shot of inhibitor was added, the reaction returns to a temperature difference as close as possible to that observed prior to the initiation step. This was again to ensure that the reaction is successfully terminated and that there were no baseline artifacts.

### 3.3. Rate of polymerization

The 55 nm seed latex was used for the comparison of calorimetric and dilatometric rate measurements. As in the previous experiments, the seed latex was diluted with DI water before swelling with sufficient monomer to ensure the reaction commenced in interval 2 conditions. Replicates of this preparation were performed for the two comparison studies presented here. For the first comparison the calorimeter and dilatometer samples were prepared separately and for the second comparison the same swollen latex was used for both experimental techniques. The reagents and amounts are given in Table 1.

The two calorimetric experiments were performed using the standard calibration method outlined previously. Initiator was added shot-wise to commence reaction during the reaction phase. For the second comparison the reaction was terminated by a shot of inhibitor (as in the enthalpy experiments).

## 4. Results and discussion

### 4.1. Enthalpy of polymerization of styrene

The heat flow data acquired from the calorimetric experiments meets the criteria we have outlined for an acceptable experiment. Steady-state rates of polymerization were observed, as is expected by commencing polymerization in interval 2, and addition of inhibitor appeared to quench the production of radicals in the aqueous phase and to stop the polymerization, i.e. the heat flow appeared to return to the level observed prior to reaction. The baselines for all experiments also exhibited good stability and no large shifts were observed, so standard baselines (proportional to conversion) should be acceptable. Further, the exotherms were sufficiently large to ensure accurate measurement (i.e. $T_r - T_a$ sufficiently large, in these cases above 1–2 °C) and $UA$ values ($\sim 550\ \mathrm{W\ m^{-2}\ K^{-1}}$) were in the range recommended by the manufacturer for accurately using the HP60 reactor.

The final conversions, evolved heats and enthalpy values determined across three replicate runs using the 130 and 55 nm seed latex are presented in Table 2. The values of $\Delta H_p$ obtained were $70.2 \pm 2.7\ \mathrm{kJ\ mol^{-1}}$ for the 130 nm latex, and $57.9 \pm 7.5\ \mathrm{kJ\ mol^{-1}}$ for the 55 nm latex. The value for the larger latex is consistent with that reported in the literature, while that for the smaller one is well below literature values, and the difference appears to be statistically significant. Attention is, therefore, turned to possible experimental artifacts causing this difference.

Fig. 1 shows the raw heat-flow data, (a), and the baseline subtracted reaction heat flow data, (b), for a representative example; this indicates that the shift of baseline was minimal and that the choice of a baseline proportional to conversion is acceptable for this series of experiments. While the raw heat-flow data ($Q$) shows a slight increase with time, once the baselines correction has been made,

Table 1
Conditions for kinetic comparison studies; all runs at 50 °C

| Conditions | Comparison 1 | | Comparison 2 | |
|---|---|---|---|---|
| | RC1 | Dilatometer | RC1 | Dilatometer |
| Seed latex (g) | 160 | 9.93 | 75 | – |
| Final dilution $H_2O$ (g) | 950 | 50.15 | 800 | – |
| Styrene (g) | 48.12 | | 37.5 | – |
| Initial swollen latex charge (g) | – | – | 734 | 38.0 |
| NaPS (g) | $8.24 \times 10^{-1}$ g in 32.3 g $H_2O$ | $3.17 \times 10^{-2}$ g in 5.00 g $H_2O$ | $5.13 \times 10^{-1}$ g in 5.10 g $H_2O$ | $2.65 \times 10^{-1}$ g in 1.00 g $H_2O$ |
| [NaPS] (M) | $3.32 \times 10^{-3}$ | $3.17 \times 10^{-3}$ | $2.97 \times 10^{-3}$ | $3.14 \times 10^{-3}$ |
| Agitation | 200 rpm anchor stirrer | Magnetic flea | 200 rpm anchor stirrer | Magnetic flea |
| Final $N_p$ ($l^{-1}$) | $4.12 \times 10^{17}$ | $3.70 \times 10^{17}$ | $2.01 \times 10^{17}$ | $2.08 \times 10^{17}$ |

Table 2
Gravimetric and calorimetric results for determination of polymerization enthalpy of styrene in two different sized particles

| Conversion (%) | Total heat (kJ) | $\Delta H_p$ (kJ mol$^{-1}$) |
|---|---|---|
| Replicate runs—latex with 130 nm unswollen diameter | | |
| 44.79 | 27.58 | 66.46 |
| 47.69[a] | 20.93 | 72.06 |
| 9.44[b] | 2.86 | 70.02 |
| 18.55[b] | 6.54 | 72.34 |
| Replicate runs—latex with 55 nm unswollen diameter | | |
| 27.1 | 7.16 | 54.9 |
| 22.6[b] | 7.16 | 65.7 |
| 28.3 | 7.26 | 53.4 |
| 22.9[b] | 7.26 | 65.9 |
| 36.3 | 8.25 | 46.8 |
| 28.2[b] | 8.25 | 60.4 |

[a] Sample with reduced monomer concentration.

[b] Sample taken immediately after inhibitor addition, and thus with improved matching between conversion and heat-flow data during the reaction phase.

there is a good steady state observed in $Q_r$, which gives the baseline-corrected rate. The final conversions were all between 35 and 48% and no gel effects were observed.

It is noted that in some cases following the addition of initiator, the total heat flow, $Q$, does not return to the exact value it exhibited before the addition. This is not uncommon; addition processes slightly disturb the system and the observed background heat flow. As this is during the inhibition period, it can be included in the baseline for the calculation of $Q_r$, since it does not play a significant role in overall reaction rates. The choice of baseline start, prior to or immediately after initiator addition, makes little difference to the integrated heat evolution or the instantaneous rate later during the steady state. Complementary to Fig. 1(b), Fig. 2 shows the reaction heat flow data, $Q_r$, for the second replicate pair of 130-nm unswollen diameter polymerizations. These data were used solely in the determination of reaction enthalpy.

For the 55 nm seed latex, the final conversions, evolved

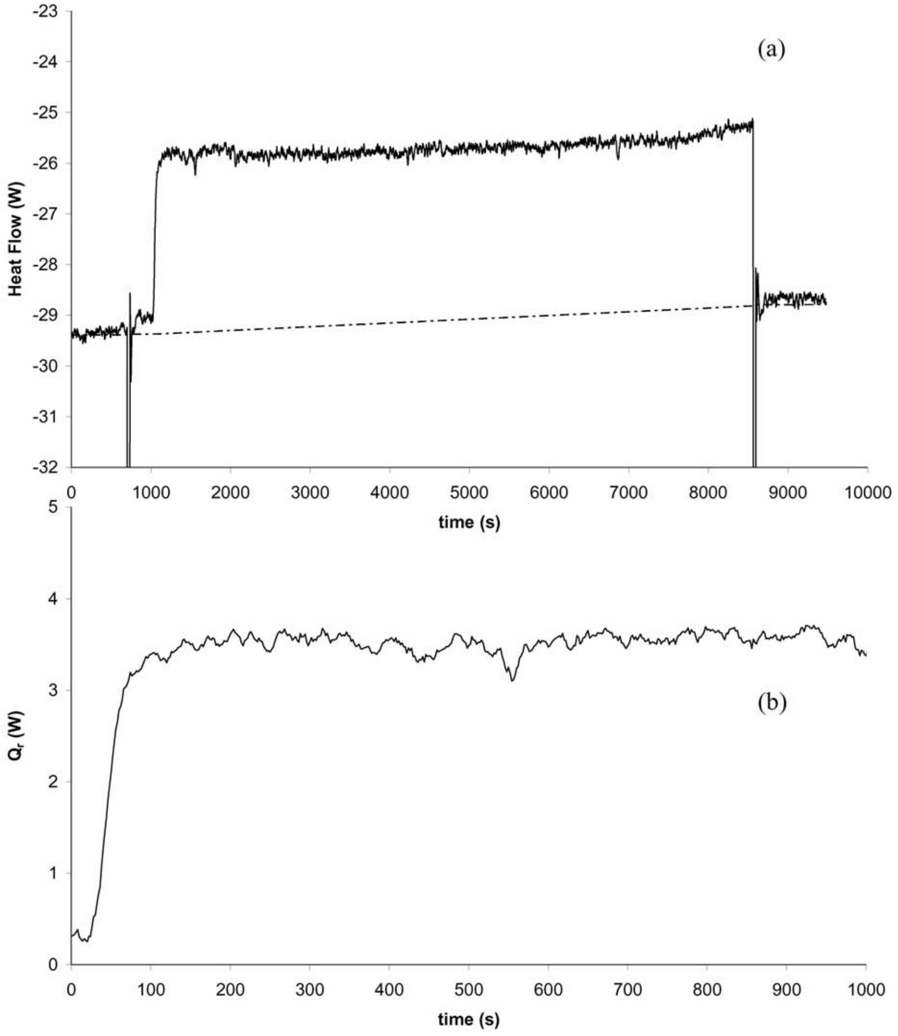

Fig. 1. (a) Raw heat flow data, $Q$, and (b) reaction heat flow data, $Q_r$ (baseline subtracted), for the seeded emulsion polymerization of styrene using 130-nm unswollen diameter seed latex.

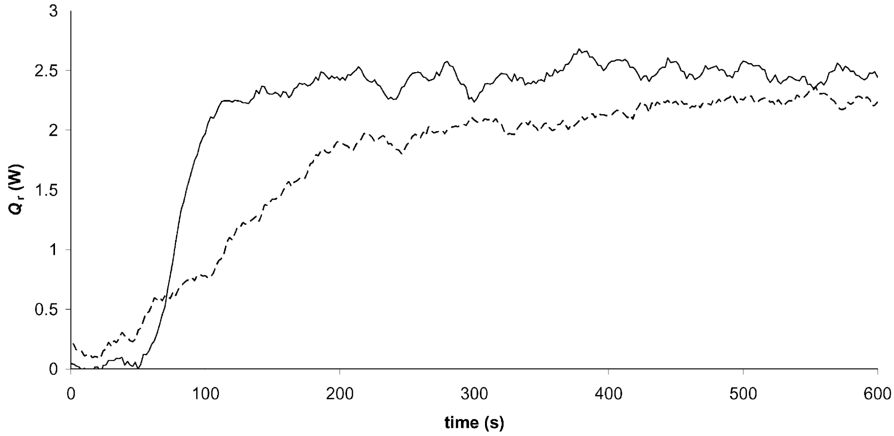

Fig. 2. Heat of reaction $Q_r$ (baseline subtracted data) for the first 1000s of the seeded styrene emulsion polymerizations of 130-nm unswollen diameter latex used for enthalpy determinations.

heats and enthalpy values determined across three replicate runs, for both sampling protocols, clearly indicate that there is no significant source of error due to a shifting baseline, with only a steady state being observed as expected. This series exhibited final conversions in the range of 20–30% and again there was no gel effect. However, the samples taken show that the conversion determined at the end of the reaction varied significantly from that determined at the end of the final calibration phase, resulting in apparent enthalpies of polymerization differing by 11–12 kJ mol$^{-1}$.

### 4.2. Discussion of apparent enthalpies of polymerization

As stated, the enthalpies of polymerization for the 130 and 55 nm latexes were significantly different, with the larger latex showing agreement with literature values. We now consider the possibility of artifacts in these measurements.

An unrealistic value for conversion can be obtained in experiments such as those performed in this work by ineffective quenching of the reaction upon addition of inhibitor. This may lead to polymerization continuing during the final stages of the calorimetric experiment and/or during the drying of sample for gravimetric study. Residual polymerization during drying seems implausible, as the ambient temperature should result in very low levels of thermal polymerization, in addition to the drying pans being exposed to air, which would cause radical quenching. There are other possibilities for errors in conversion values such as coagulation leading to incorrect solids contents; however, there was no visible coagulum or floc in the systems and it is reasonable to conclude that this would be at most a small effect.

The heat-flow data indicated that the reaction rate returned to a level very close to that before the addition of initiator, i.e. no significant polymerization. It is common with such calorimetric measurements to have drifts in baseline, as shown in Fig. 1. The absence of any significant drift in these systems, combined with the knowledge that the system should exhibit a steady state in rate (or possibly a slightly decreasing rate), implies that this baseline is not causing an erroneous enthalpy value. As the determination of reaction rate by reaction calorimetry is a relative measurement, however, a low and relatively constant background rate is difficult to detect. Therefore, a small amount of polymerization not inhibited by the MEHQ could yield a higher conversion at the end of the final calibration step than was actually present at the inhibition step. It is this effect that is postulated to lead to the different apparent values of $\Delta H_p$, depending on the sampling protocol.

A complete profile of $T_r$ for an experiment with the 55 nm seed latex is given in Fig. 3, showing the length of time during the final calibration over which such low levels of polymerization could continue largely undetected. During the reaction phase (compared to the calibration phase), the uncertainty in heat flow does not exceed 0.2 W, based on the fluctuations observed in a particular run where the reaction heat flow is ~4 W. During the calibration phase, however, this uncertainty is compounded by the calibrating temperature ramp and heat pulses. In addition, there can be a slow but significant polymerization (see below) during the calibration phase which can lead to significant although small conversion, which in turn can lead to an uncertainty is determining $\Delta H_p$ from samples taken after the calibration phase.

Sampled data of this small particle system, therefore, appears to support the presence of such residual polymerization, at least for that seed latex. The gravimetric data consistently shows a shift to higher conversion across this series when sampling was performed after the calibration phase. However, it appears that the experiments with the larger (130 nm) seed latex did not suffer from significant amounts of uninhibited polymerization.

The slow but significant polymerization which is noticeable during the calibration phase can lead to artifacts in measuring $\Delta H_p$ if one measures the conversion

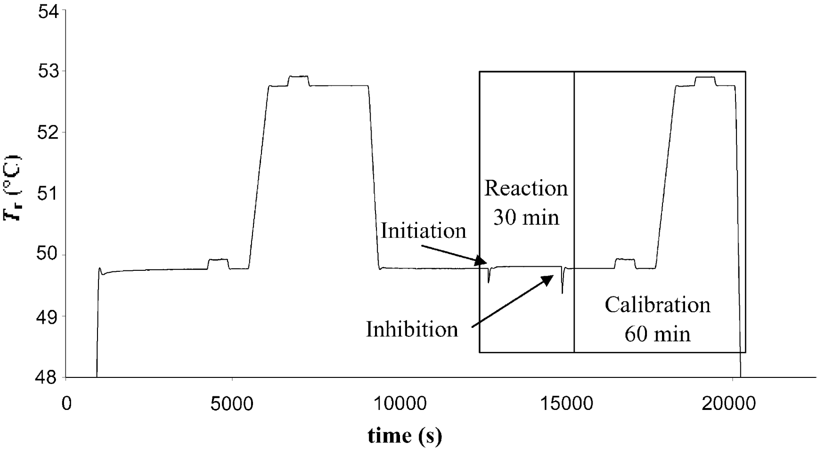

Fig. 3. Complete profile of reaction mass temperature for a 55-nm latex run for enthalpy determination, showing initial calibration, reaction phase (including initiator addition and inhibitor addition) and final calibration phase.

gravimetrically after the calibration phase but takes the heat flow to be that during the reaction phase. One possible origin of this residual polymerization is ‘spontaneous’ polymerization, which is a well-known effect in emulsion polymerization whose origin is uncertain [20,23–30]. A further possible source of some ‘spontaneous’ polymerization that could be considered is the impulse of energy from the calibration heater. The RC1/HP60 reactor used in this study utilized a 20 W calibration heater that is a potential source of some additional radical production. An increase in the reactor temperature of the order of a degree is typically observed but higher amount of local heating close to the probe cannot be ruled out as another source of enhanced initiation.

This “spontaneous polymerization” during the calibration phase is of note for establishing protocols for experiments requiring the measurement of a parameter, such as final conversion, determined at the apparent end of a reaction. This phenomenon occurred in our system despite rigorous quenching procedures (addition of a large excess of inhibitor) being followed in the calibration phase. The origin of the polymerization occurring during the calibration phase, although of intrinsic interest, has no bearing on the aims of the present paper.

It is strongly recommended that the quenching protocol used here be employed if accurate rate data are desired, or in general a sampling protocol that does not require waiting for the final calibration period to conclude before acquiring the sample. Specifically, the measurement of conversion, as required for calibration or other reason, should be measured at the end of reaction, i.e. at the end of the reaction phase and not after the calibration period.

### 4.3. Solvent/surface effects on enthalpy of polymerization

If background polymerization accounts for the reduced enthalpy values determined in the 55 nm latex experiments, then the sampled values indicate a small but statistically significant reduction in enthalpy with the smaller seed. This enthalpy difference is significantly greater than the uncertainties due to heat flow discussed above, provided that the sampling for gravimetric measurements is performed at the end of the reaction phase (because uncertainties are significantly increased during the subsequent calibration phase, as discussed above). A possible explanation for this is environmental effects on $\Delta H_p$. The enthalpy associated with a reaction is a function of both the reacting species and their environment. The enthalpy values presented in the literature [22] were measured for pure polymer/monomer mixtures, with the exception of the polymerization in methylene chloride solution; this last-named enthalpy appears to be somewhat outside the other values, being 5.5 kJ mol$^{-1}$ below the average enthalpy of the other experiments and the literature.

It is plausible that polymerization in very small particles (55 nm in the present case) may exhibit what are essentially polar solvent effects, i.e. the polymerization matrix has a different polarity due to the close proximity of water, perhaps due to significant reaction occurring in the interfacial region between ‘pure’ aqueous phase and ‘pure’ particle interior. Some additional polarity may also be postulated to arise from water and surfactant dissolved or imbibed into the particle, but such effect may not exhibit a similar trend with the ratio of surface area to volume.

If changing particle surface area to volume ratios has an effect upon reaction enthalpy in the emulsion polymerization of styrene, then it follows that some insight should be gained by examining the hydration enthalpy of reactants and products. If one considers the addition of a monomer unit to a growing radical chain, then the difference in hydration enthalpy of an unsaturated styrene monomer group to that of a saturated monomeric group within the polymer chain should correspond to the change in polymerization enthalpy by moving from a polymer/monomer mix to that of water.

The enthalpy of hydration is related to the mole fraction, $x$, of a solute (under saturated conditions) by:

$$\frac{d(\ln x)}{d(1/T)} = -\frac{\Delta H_{\mathrm{hyd}}}{R} \quad (3)$$

Data have been reported for the solubility of styrene and ethyl benzene in the literature for a range of temperatures [31–33]; these have been reproduced in Fig. 4. The slopes of these two data sets for a linear region around 50 °C yields enthalpy of hydration values for styrene and ethyl benzene of 12.4 and 16.7 kJ mol$^{-1}$, respectively. This is an enthalpy difference of 4.3 kJ mol$^{-1}$, or 6%.

It is plausible that the difference between these hydration enthalpies is similar to the change in polymerization enthalpy from inside a polymer particle to the hydrated surface region in the small (55 nm unswollen diameter) particles. However, it should be noted that the amount of polymer at the particle surface by no means comprises the majority of the polymer/monomer and so the hydration value is a upper bound to such an effect.

### 4.4. Rate of polymerization of styrene

The first 1000s of polymerization rate data from calorimetry and dilatometry for the duplicate runs are presented in Fig. 5. These polymerization rates $R_p$ can be converted to the average number of radicals per particle, $\bar{n}$, using:

$$R_p = k_p C_p \bar{n} \frac{N_p}{N_A} \quad (4)$$

where $k_p$ is the propagation rate coefficient, $C_p$ is the monomer concentration inside the particles, $N_p$ the particle number density, and $N_A$ is the Avogadro constant. The value of $k_p$ for this system was taken as $2.4\times10^2$ M$^{-1}$ s$^{-1}$ [34], and $C_p$ as 5.5 M [23]. The resulting values of $\bar{n}$ are shown in Table 3. The data for the two runs show only small differences between the rates measured by calorimetry and dilatometry: 7 and 4%. This close agreement supports the validity of the procedures adopted here.

Table 3
Values of $\bar{n}$ from dilatometry and calorimetry

| | RC1 | Dilatometer | Theory |
|---|---|---|---|
| $\bar{n}$ comparison 1 | 0.13 | 0.15 | 0.11 |
| $\bar{n}$ comparison 2 | 0.20 | 0.20 | 0.12 |

Although consistency between experimental techniques has been the principle goal of this work, it is of interest to compare these experimental values with the theoretically expected values of $\bar{n}$. The 55 nm latex was chosen for this purpose because it is sufficiently small that it is expected [35] to obey ‘zero-one’ kinetics [19], when intra-particle termination is not rate-determining. Standard models for entry and exit [19,36,37] require a knowledge of the following rate parameters: $k_p$ (it is assumed here that this has the same value in particle and water phases), $k_d$ (the initiator dissociation rate coefficient), $z$ (the critical degree of polymerization for entry), $k_p^1$ (the propagation rate coefficient of a monomeric radical inside the particle), $k_{t,aq}$ (the rate coefficient for termination of oligomeric radicals in the water phase), $C_W^{sat}$ (the water solubility of monomer), $k_{tr}$ (the rate coefficient for transfer to monomer), $\rho_{spont}$ (the rate coefficient for spontaneous, or ‘thermal’, entry of radicals into the particles), and $D_w$ (the diffusion coefficient of a monomeric radical in water). The values of $\bar{n}$ calculated using the parameters in the text and in Table 4 are given in Table 3. These values show that while the experimental values are close to those expected theoretically, there is still a significant variation. This may arise from errors in the particle sizing technique (an error of 10% in $N_p$ leads to an error of 30% in $\bar{n}$), and/or the relatively broad size polydispersity of the small latex, and does not affect the experimental comparison of techniques. In addition, the model used for these calculations is robust but imperfect,

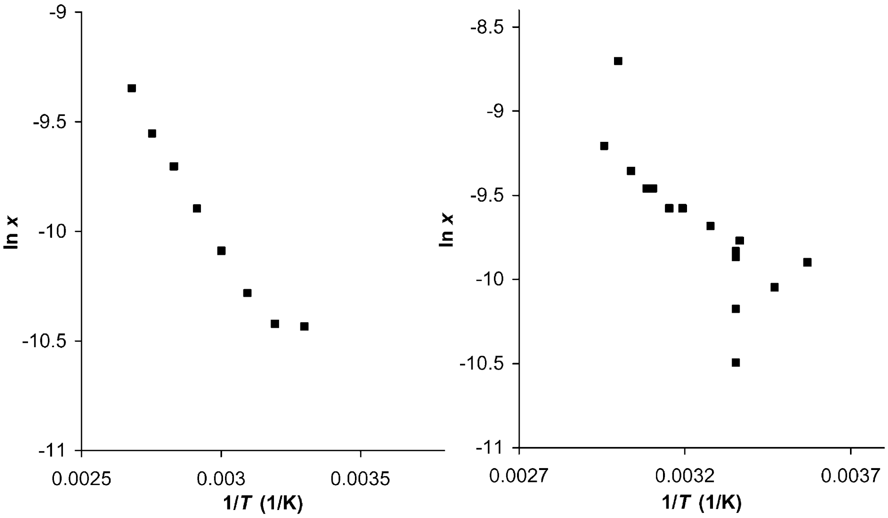

Fig. 4. Literature data [31] for molar solubility of ethyl benzene (left) and styrene (right) in water as a function of 1/T.

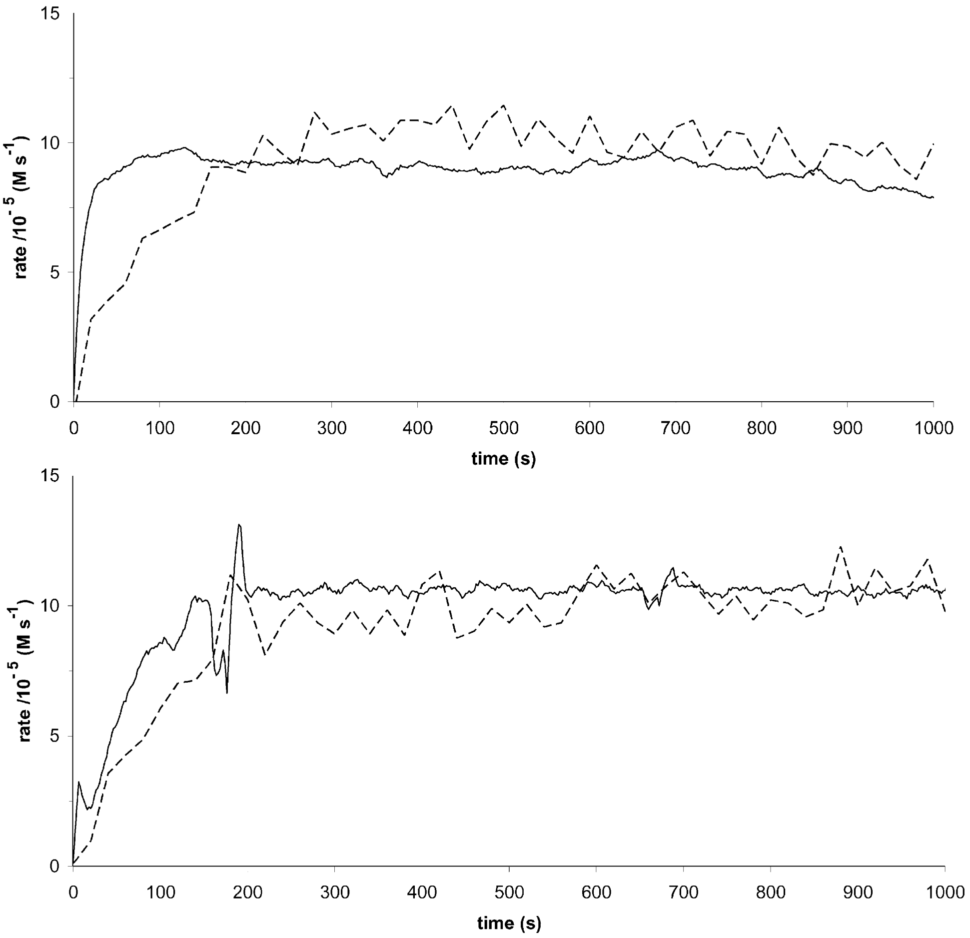

Fig. 5. Rate data from dilatometry (broken line) and from calorimetry (full line) for comparison 1 (top) and 2 (bottom) (see Table 1 for experimental conditions).

and moreover there are uncertainties in values of parameters such as $k_p^1$; the relatively small deviation between prediction and observation is typical for systems such as those studied here.

## 5. Conclusions

This work examines the methodology required for the application of reaction calorimetry to obtain accurate rate data in emulsion polymerizations, with particular attention to calibration, baseline determination, and the value of the enthalpy of polymerization. It is strongly recommended that the quenching protocol used here be employed if accurate rate data are desired. Specifically, the measurement of conversion, as required for calibration or other reason, should be measured at the end of reaction, i.e. at the end of the reaction phase, and not after the calibration period.

It is shown that $\Delta H_p$ should be determined using the apparatus and polymerization system of the study, not literature values taken from different systems by different means. A further conclusion is that there may be a significant reduction in the polymerization enthalpy in small polystyrene particles (55 nm diameter), which may be ascribed to solvation and/or surface effects.

Table 4
Values of rate parameters used in the theoretical calculation of $\bar{n}$

| Parameter | Value |
|---|---|
| $k_d$ [38] | $1.2\times10^{-6}$ s$^{-1}$ |
| $z$ [36] | 2 |
| $k_p^1$ [37] | 4 $k_p$ |
| $k_{t,aq}$ [36] | $1.75\times10^{9}$ M$^{-1}$ s$^{-1}$ |
| $C_W^{sat}$ ([33] | $4.3\times10^{-3}$ M |
| $k_{tr}$ [39] | $9.3\times10^{-3}$ M$^{-1}$ s$^{-1}$ |
| $\rho_{spont}$[a] | $4.38\times10^{-5}$ s$^{-1}$ |
| $D_W$ [40] | $1.3\times10^{-5}$ cm$^2$ s$^{-1}$ |

[a] $\rho_{spont}$ estimated from the theoretically expected entry rate due to $1\times10^{-5}$ M KPS.

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