Advanced Calorimetric Techniques in Polymer Engineering

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Summary: In polymer synthesis, reaction calorimetry (RC) is an appropriate technique for on-line process monitoring, since polymerization reactions are highly exothermic. Measurements are noninvasive, rapid, and straightforward. Nowadays RC is the technique recognized as the most powerful way to study such process in near-to-the-industrial conditions. Our approach was focused on temperature oscillation calorimetry (TOC). Two different reaction calorimeters were used, *i.e.* a isoperibolic calorimeter and a Calvet type high sensitivity differential calorimeter, respectively. A special attention was paid to the interpretation of the measured signals in order to obtain reliable calorimetric data. The evolution of heat transfer coefficient *UA* was followed by performing appropriate Joule effect calibrations, before and after the reaction. A convolution differential method of the measured heat flow by the generated one was used for determining the time constants and deconvoluting the measured heat flow.

Keywords: heat of reaction; heat transfer coefficient; polymerisation; reaction calorimetry; temperature oscillation

Introduction

To identify optimal operating conditions of a chemical process, knowledge of kinetic and thermodynamic parameters for the most important main and side reactions is needed. A conventional method for investigating a reaction during process development is reaction calorimetry (RC).[1] RC, accepted as the most powerful way to study the process in near-to-the-industrial conditions, allows a wide spectrum of operation conditions and measurements.

The first objective of this work was to develop a small scale isoperibolic calorimeter aimed to be used for studying polymerizations. In the isoperibolic mode the surroundings of the reaction mass (usually a jacket) are maintained at constant temperature. Exothermic or endothermic changes produce a temperature increase or decrease in the reactor. The basic equation of RC is the heat balance of an exothermic reactor with external cooling jacket, under the hypothesis of perfect mixing in the reactor and in the jacket:

$$C_P \frac{dT_r}{dt} = UA(T_j - T_r) + Q_{chem} + Q_{loss} + P_{stirrer} \quad (1)$$

In the simplest case, the heat transfer coefficient, *UA,* is assumed as constant and is obtained by carrying out an initial calibration experiment with a calibration heater. When the heat loss, Q_{loss}, and the power dissipated by the stirrer, $P_{stirrer}$, are known or negligible, Equation (1) allows the evaluation of the heat of reaction in isothermal conditions.[2] The increase in viscosity during polymerization is almost negligible in suspension and moderate in heterogeneous bulk polymerizations but significant changes occur in homogeneous bulk or solution polymerization.[3] This is why the homogeneous solution polymerization of acryamide was chosen as model

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to illustrate the performances and the limits of RC. A special attention was paid on the interpretation of the measured signals in order to achieve reliable calorimetric data. Thus, the evolution of the heat transfer coefficient was followed by performing two calibration experiments, before and after the reaction; the two values of the heat transfer coefficient are subsequently interpolated, by obtaining the desired *UA(t)* profile. In addition, a differentiation method based on the convolution of the measured heat flow by the generated one was used for determining the time constants and deconvoluting the measured heat flow. The second objective was to develop the Temperature Oscillation Calorimetry (TOC) technique particularly in a small volume (9 ml) reactor using a Calvet-type differential calorimeter. The aim of this calorimetric technique is to obtain on-line the parameters involved in the heat balance of the reaction mass during a chemical reaction.

Experimental Part

Acrylamide (AM), potassium permanganate, potassium persulfate, ascorbic acid and oxalic acid, used for polymerizations, were provided by Fluka Chemika, France and were used without further purification.

The schematic set-up of the reaction isoperibolic calorimeter is shown in Figure 1(a). The reactor is a 100 mL flask with a jacket and a lid with five ports. The flask jacket is connected to a thermostatic bath whose temperature is maintained within $\pm 0.1\,^{\circ}C$ with a Vertex (model V9610) PID controller. One temperature sensor (Pt100) is placed in the reactor and two more at the jacket inlet and outlet, respectively. An additional J-type thermocouple (1 mm external diameter) is placed in the space between the lid and the liquid's surface. The thermocouple is in intimate contact with the feeding tube and consequently with liquid containing the initiator solution. Since, usually, the temperature of the dosing liquid is bellow the reaction temperature, the decrease of temperature to the thermocouple serves as trigger for the start of reaction as well as to correct the Q_{chem} by the heat exchanged with the reaction mass during reagents dosing, Q_{Doss} in Equation (1). The reactor also holds the calibration heater (electric resistance of 15 Ω) powered by a 30V/1A power supplier via a power amplifier connected to one of the analog outputs of the data acquisition board (a PCI-441D model from Datel Inc., USA). We developed a *LabVIEW*® (National Instruments) program to generate a desired voltage which is applied to the resistor during the pre-established calibration periods. In semibatch operation mode the reagent is fed over a period with a peristaltic pump (MasterFlex C/L, Barnant Company, USA) with a pre-calibrated feeding rate. The duration of feed is controlled by the software through a computer controlled relay. The whole application is controlled by a single *LabVIEW* program running on computer. The program allows direct interaction to all devices connected to the system as well as automatic handling of a pre-defined recipe. The main task of the *LabVIEW* program is to acquire the data of all sensors and devices as well as to control the stirrer speed and the power dissipated by the calibration heater. Both tasks are performed by the same PCI-441D precision sensor input and multi-functional I/O board. The two analog outputs are used to control the stirrer speed and the power dissipated by the calibration heater, respectively.

A schematic view of the Calvet type high sensivity differential calorimetric assembly is given in Figure 1(b). It consists of a BGR-Tech scanning transitiometer[4] connected to a Hüber unistat ultracryostat, model 390w. The connection between the cryostat and the heating-cooling shield of the calorimetric block is made *via* two flexible thermoisolated hoses. The transitiometer itself is constructed as a twin calorimeter with a variable volume. It is equipped with high-pressure vessels, a *pVT* system, and *LabVIEW*-based virtual instrument (VI) software. Two cylindrical calorimetric detectors ($\phi = 17$ mm, $l = 80$ mm)

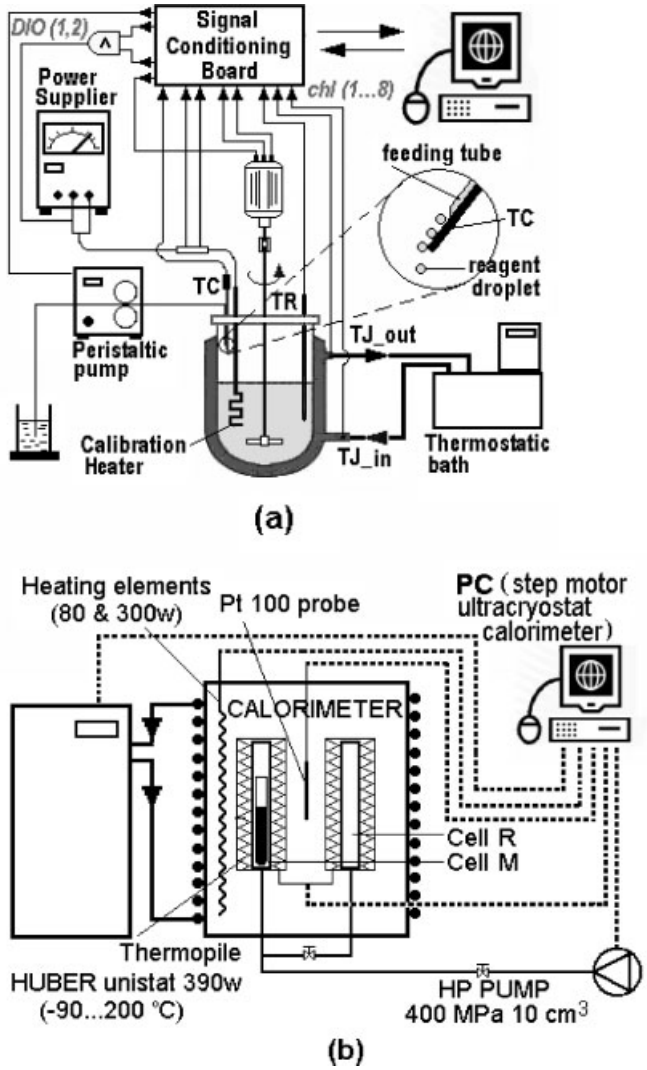

Figure 1.
Schematic view of the isoperibolic calorimeter (a) and of the assembly scanning transitiometer-cryostat (b). On the right hand part of scheme (a) a detail of the assembly thermocouple-feeding tube used as trigger for the zero moment of polymerization is given.

each made from 622 thermocouples (chromel-alumel) are mounted differentially and connected to a nanovolt amplifier, which is functioning as a non-inverting amplifier, whose gain is given by an external resistance (with 0.1% precision). The calorimetric detectors are placed in a metallic block, the temperature of which is directly controlled with a digital feedback loop of 22 bits resolution ($\sim 10^{-4}$ K), being part of the transitiometer software. The calorimetric block is surrounded by a heating-cooling jacket, which is connected to the cryostat. The calorimetric block is embedded by an additional heating-cooling shield. The temperature difference between the block and the heating-cooling shield is set to a constant value (5, 10, 20, or 30 K) and is controlled by an analogue controller. The temperature measurements, both absolute and differential, are performed with calibrated 100 Ω Pt sensors; the Pt100 tem-

perature sensor is placed between the sample and the reference cell. The heaters are homogeneously embedded on the outer surfaces of both the calorimetric block and the heating-cooling shield. The whole assembly is placed in thermal insulation enclosed in a stainless steel body and placed on a stand, which permits moving the calorimeter up and down over the calorimetric vessels. A more detailed scheme of the whole transitiometer set-up is given in Ref. 4. For studying chemical reactions, the scanning calorimeter was used as a temperature oscillation calorimeter and the high-pressure cells have been replaced by specially designed reaction cells. These cells allow stirring, different dosing profiles for one or two reactants and can accommodate a small optical probe coupled to a miniaturized spectrophotometer (for more details see Ref. 5).

Two different calibration procedures were used for the two calorimeters respectively. In the case of the isoperibolic calorimeter, the desired amount of heat (in Joules) and the suited voltage are introduced by the operator via the front panel of *LabVIEW* software. The power uptake of the heater is measured on-line, integrated over the time and compared with the required amount of heat. As soon as the two values are equal each other a digitally control relay stops the current passing through the heater. Concomitantly, the temperature difference between reaction mass temperature, T_R, and the temperature of liquid at the jacket outlet is recorded and the area under the measured peak is calculated. The ratio between the two integrals gives the overall heat transfer coefficient, UA, which is further used to obtain the heat of reaction, ΔH_R. The calibration of the scanning calorimeter was performed with the melting signal of reference substances, e.g. *n*-octane (−56.76 °C and 180.00 $J \cdot g^{-1}$), *n*-decane (−26.66 °C and 199.87 $J \cdot g^{-1}$), and distilled water (0.01 °C and 335 $J \cdot g^{-1}$). The calorimetric peaks were recorded and their integration allowed calculating the sensibility coefficient of calorimeter.

Results

As regards isoperibolic calorimetry, the radical polymerization of acrylamide in aqueous medium was chosen as model

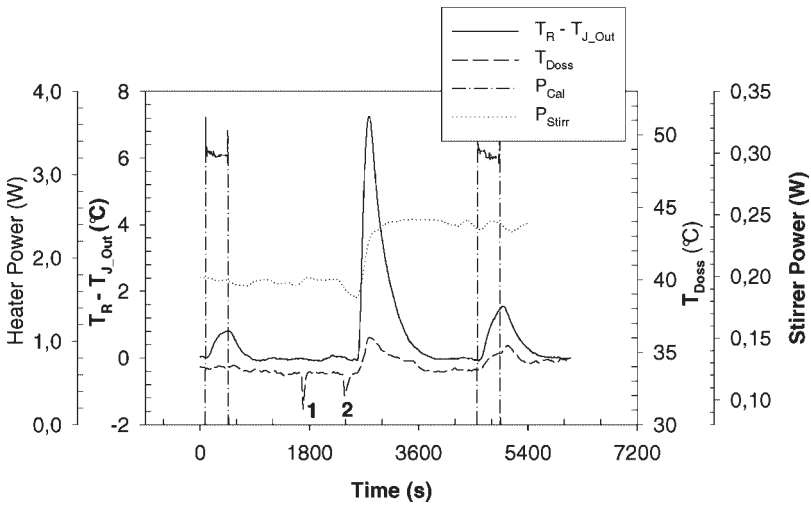

Figure 2.
Acrylamide polymerization at 39 °C with $KMnO_4/H_2C_2O_4$ redox system in 10% aqueous solution. The following data are plotted: temperature difference between reaction mass and liquid at jacket outlet, $\Delta T_R = T_R - T_{J\_Out}$, dosing temperature of initiating system, T_{Doss}, calibration power, P_{Cal}, and stirring power, P_{stirr}, respectively. For both calibrations the amount of heat dissipated by the calibration element was the same, 1200 J.

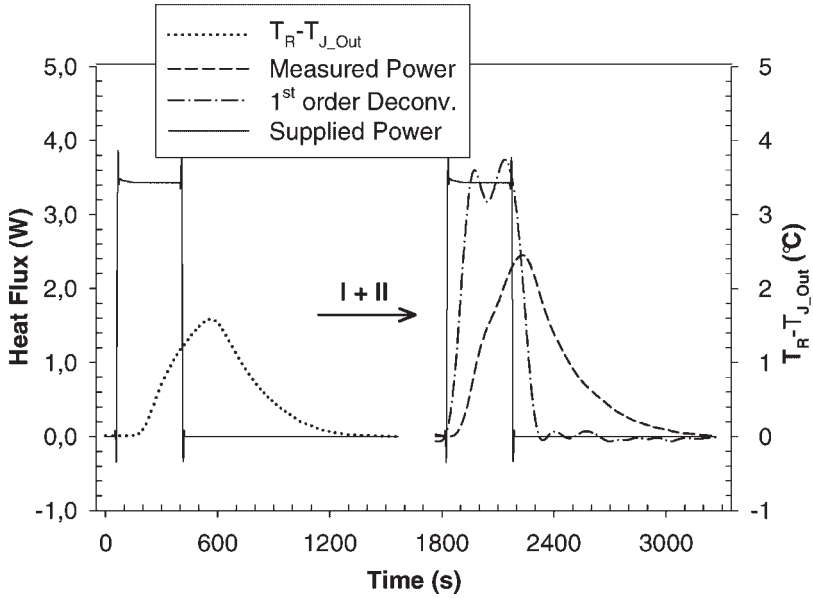

Figure 3.
Effect of heat transfer coefficient, UA, and of deconvolution on the measured increase of temperature compared with the supplied heat pulse during the calibration.

reaction, since it is known as a reproductive and easy to led process, and well describe in literature. It is also well known that the aqueous solutions of poly(acrylamide) exhibit high viscosities; the modification of viscosity during the reaction induces large changes in heat transfer coefficient. In this case, the heat of reaction cannot be computed from Equation (1), which is one of the limitations of reaction calorimetry for polymerization reactions. In the isoperibolic mode a typical polymerization run is presented in Figure 2. The reactor jacket was fixed at the working temperature; the monomer and the solvent were charged in the calorimetric vessel and as soon as the thermal equilibrium was reached the solutions of $KMnO_4/H_2C_2O_4$ redox system were fed using the dosing pump. The polymerization does not start in the presence of $KMnO_4$ (the first endothermic peak of the dosing temperature, noted by digit 1 in Figure 2, recorded by thermocouple) but it starts soon after the dosing of oxalic acid (the second endothermic peak). The maximum increase of temperature of the reaction mass ($\Delta T_R = T_R\text{-}T_{J\_Out}$) was about 7.3 °C. In addition, the stirrer power increases suddenly as soon as the polymerization begins and is maintained at constant level at the end of polymerization.

In order to quantify the heat of reaction, the correlation between the temperature difference and the corresponding heat flux should be made. The following two steps were involved in this process: (a) the determination of the overall heat transfer coefficient, *UA*, which allows the conversion of measured increase of temperature in terms of power (I in Figure 3); and (b) the determination of calorimeter time constant, τ, and subsequently the deconvolution of thermokinetic data (II in Figure 3). In the first step, a known amount of power *P* was dissipated through the resistance of the calibration heater during a well-defined period, t_{cal}, resulting in a temperature increase. The heat generated during the calibration and the corresponding *UA* are

Table 1.
Evolution of the overall heat transfer coefficients, *UA*, of the calorimeter time constants, τ, and of heat of polymerization, ΔH_R, in function of the interpolation method used to describe the variation of *UA* during the polymerization of AM in water*

	Measured parameters	Units	Values
Overall heat transfer coefficient, *UA*	Before polymerization, UA_1	W/°C	3.409
	After polymerization, UA_2	W/°C	1.402
Time constant, τ	Before polymerization, τ_1	s	92
	After polymerization, τ_2	s	268
Heat of reaction, ΔH_R, (proportional to conversion)	kJ mol^{-1} AM		88.21

* Reaction conditions of Figure 3.

calculated as follows:

$$Q_c = P \cdot t = UA \int_0^{t_{cal}} \Delta T_R dt = UA \cdot S* \rightarrow UA = Q_c/S* \quad (2)$$

where S^* is the area of the calibration peak (°C · s). After calibration the determination of reaction heat, Q_r, is very easy: $Q_r = UA \cdot S$; where S is the integral of reaction effect. The second step, deconvolution of the calorimetric signal makes also use of the calibration signals and implies a differentiation method based on the convolution of the measured *W(t)* by the generated one $\phi(t)$ represented by the following system of linear equations:[6]

$$\phi_1(t) = \phi(t) + \tau_1 \frac{d\phi(t)}{dt}$$

$$\phi_2(t) = \phi(t) + \tau_2 \frac{d(\phi_1(t))}{dt}$$

$$\phi_n(t) = \phi(t) + \tau_n \frac{d\phi_{n-1}(t)}{t} \ldots\ldots \quad (3)$$

$W(t) = \lim_{n\to\infty} \phi(t)$ and $\tau_1, \tau_2, \ldots \tau_n$ are calorimeter time constants of successive orders. In practical cases, a limited number of linear equations is used, usually one like in the present case; that is n = 1 and the corresponding time constant is then τ_1. The effect of both heat transfer coefficient and first-order deconvolution on the shape of the heat measured during calibration is illustrated in Figure 3.

Usually, the calibration is performed before and after reaction experiment. When the difference between the areas is significant, as in the case of polymerization reactions, the two values of the heat transfer coefficient are interpolated to obtain the desired *UA(t)* profile, which is subsequently used for determination of the heat of reaction. The quality of results depends heavily on the interpolation procedure used (i.e. average value, linear with time, proportional to conversion, proportional to the power input of the stirrer). The most important parameters of the polymerization illustrated in Figure 3 are collected in Table 1. The values obtained for heat of polymerization, ΔH_R, agree well with the one reported in literature, i.e. 89.6 kJ/mol.[7]

The first selected example concerns the use of reaction calorimetry with objective to increase the polymer yield. It is know that the oxygen has an inhibiting effect in free radical polymerization; due to its presence the propagation step is prematurely stopped at relatively low conversions. Solution polymerization of acrylamide was initiated with potassium persulfate/ascorbic acid redox system, which was preferred since possible present oxygen traces in reaction medium do not inhibit the process but act as a complementary activator in the reaction of free radicals formation. The polymerizations were carried out at three temperatures, 40, 50 and 60 °C, respectively, under the presence of atmospheric oxygen (see Figure 4). After the shift to the baseline of the temperature peak corresponding to the polymerization the process was reinitialized by alternating addition of potassium persulfate and ascorbic acid.

The second example illustrates how RC can be used to evaluate the minimal temperature at which an initiating system

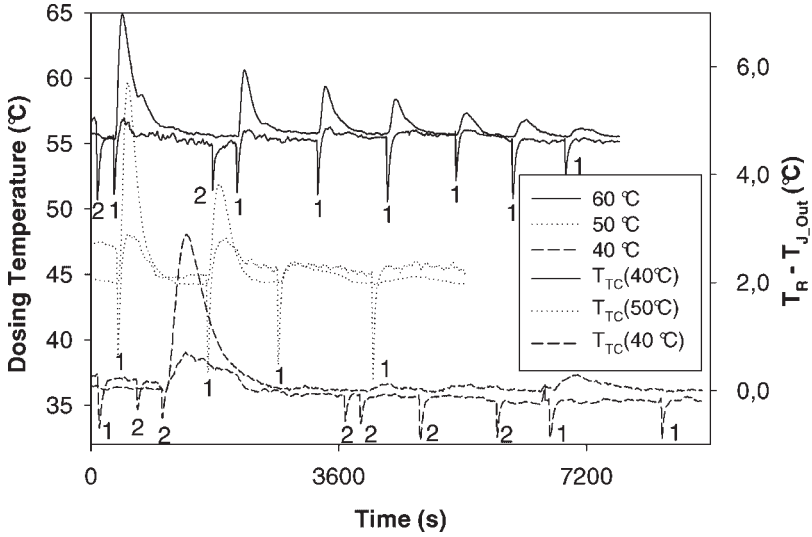

Figure 4.
Acrylamide polymerization at different temperatures with $K_2S_2O_8$/ascorbic acid redox system in 7.5% aqueous solution. The curves with exothermic peaks correspond to the increase of temperature due to the polymerization, while those having endothermic peaks are related to the dosing of initiator systems. The digit '1' denotes the moment of adding of potassium persulfate and the digit '2' the moment of adding of ascorbic acid.

becomes efficient (Figure 5). The experiment was carried out by scanning the temperature from 25 to 53 °C with a scanning rate of 0.2 °C/min. After the first calibration, at constant temperature (25 °C), the components of redox system, potassium persulfate (endothermic peak '1') and ascorbic acid (endothermic peak '2'), were fed in the system. As is seen in Figure 5, the polymerization started at about 32.8 °C and the stable dynamic baseline was reached after 18 min, at about 41.2 °C; in this case,

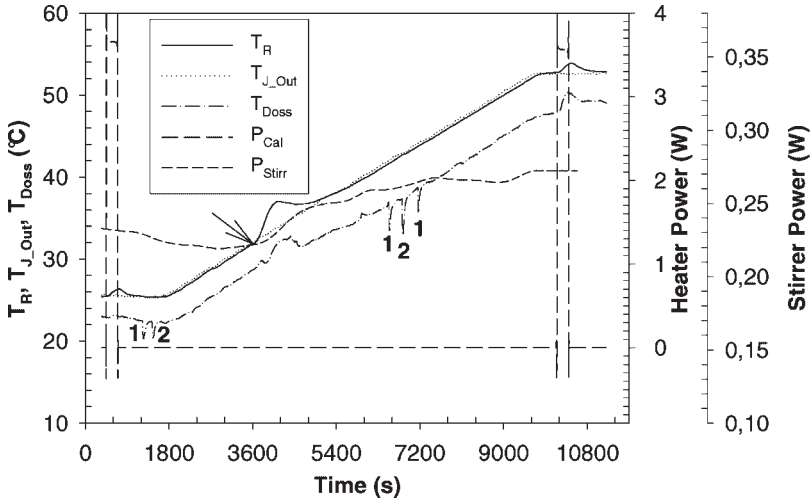

Figure 5.
Plots of raw data acquired during acrylamide polymerization in temperature programmable ramp mode with potassium persulfate/ascorbic acid redox system.

the maximal increase of reaction mass temperature, $\Delta T_R\text{-}max$, was about 3.5 °C. Subsequent addition of potassium persulfate or ascorbic acid did not restart the polymerization, which means that all the monomer was already converted into high polymer.

The advantage of temperature oscillation calorimetry (TOC) is illustrated in relation with the problem of a correct calorimetric evaluation despite the variation of the heat transfer value. This technique makes only use of the reactor energy balance and determines already during the reaction the heat transfer value from forced temperature oscillations. This new method to determine the chemical heat flow simultaneously to a changing heat transfer value requires only the use of a mathematical procedure for evaluation of measured data.[8] As indicated before, a highly sensitive Calvet-type differential calorimeter (*BGR-Tech*, Poland) was used to perform TOC measurements. The desired oscillations of temperature were obtained by imposing a sinusoidal variation of the set-point of calorimetric block by means of an external temperature control system. The evaluation of energy balance [Equation (1)] was performed in two steps. In the first step the heat transfer value *UA* was calculated from temperature oscillations. In the second step the reactor energy balance without oscillating heat contribution was considered and the chemical heat flow, Q_{Chem}, was calculated from Equation (1). Given that Equation (4) is the general expression for an oscillating signal, and considering only the influence of oscillating terms on energy balance the equations for *UA* [Equation (5)] and heat capacity c_p [Equation (6) were obtained:[9]

$$X = A_x e^{i(\omega t + \varphi_x)} \tag{4}$$

$$UA = \frac{A_Q}{A_T}\cos(\varphi_Q - \varphi_T) \tag{5}$$

$$mc_p = \frac{A_Q}{\omega A_T}\sin(\varphi_Q - \varphi_T) \tag{6}$$

The values of phase and amplitude for each signal during the course of chemical reaction can be obtained applying the Fourier transform technique on each measured signal.

Undoubtedly, scanning calorimetry allows to perfectly controlling throughout the experiment the imposed temperature modifications. The versatility of the technique permits for example to stop, restart or impose any type of temperature profiles, in other words to monitor an ongoing reaction. As an example, the neutralization reaction of H_2SO_4 (0.5 N) with NaOH (0.5 N) was selected as model reaction, which is known as highly exothermic reaction (-139.1 kJ mol^{-1}). Typically, the masses inside the reactor were around 50–55 cm^3 of the acid solution in which the NaOH solution was added at 0.5 cm^3 min^{-1}. The dosing period of NaOH was 80 min. The raw data handling is given elsewhere.[10] The reaction conditions were

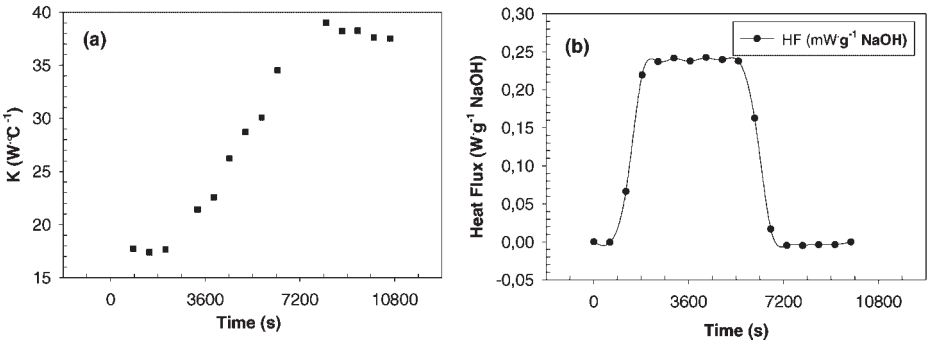

Figure 6.
Heat transfer (a) and heat flux (b) evolution during the neutralization reaction at 30 °C.

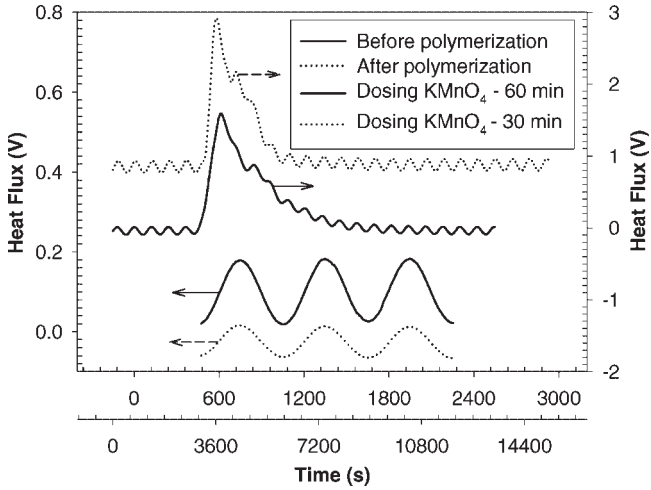

Figure 7.
Heat flow evolution during the acrylamide polymerization with $KMnO_4/H_2C_2O_4$. The dosing periods of KMnO4 were 60 min (full line) and 30 min (dotted line) respectively. The decrease of amplitude of the calorimetric signal due to the increase of viscosity during polymerization is shown on the lower part.

as follows: reaction temperature 30 °C, amplitude of temperature oscillations 0.25 °C, period of oscillation 10 min, and temperature of the cooling liquid in the jacket of the calorimetric block 0 °C. After mathematical treatment both the heat transfer coefficient, *UA*, and the heat of neutralization, Q_{Chem} are obtained (Figure 6). As expected, the overall heat transfer coefficient, *UA*, increases almost linearly during the experiment, since the wetted surface area, *A,* in the reactor increases during the dosing period. Thus, the *UA* increased from 17 to about 35 $W\,°C^{-1}$ during the dosing period and the integration of heat released during the neutralization yielded an enthalpy of -133.5 kJ mol^{-1} which is close to the literature values.

TOC was also used to perform the polymerization of acrylamide (7.5% aqueous solution). In this case, the reaction temperature was 40 °C, the amplitude of temperature oscillations 0.25 °C, the period of oscillation 10 min, and the temperature of the cooling liquid in the jacket of the calorimetric block 10 °C. In a typical experiment, 4 ml of aqueous solution of acrylamide were added in the reaction cell together with the corresponding amount of oxalic acid (30 μl aq. soln. 10% w/w). After establishing the thermal equilibrium the temperature oscillation was imposed and after 6 periods the solution of the second redox initiator component ($KMnO_4$, 50 μl aq. soln. 5% w/w) was fed over a period. The feeding period of $KMnO_4$ (see Figure 7) controls both the amplitude and the span of calorimetric peak, i.e. the rate of polymerization at a given temperature, the higher the amount of initiating species the higher is the polymerization rate. The decrease of amplitude of the calorimetric signal from 0.1 to about 0.0375 V was due to the large increase of viscosity during the solution polymerization which, in turn, induces the decrease of heat transfer coefficient.

Conclusion

Relatively new calorimetric techniques, temperature oscillation calorimetry (TOC) and scanning transitiometry, have been employed to perform chemical reactions. TOC allows obtaining on-line parameters involved in the heat balance of the reaction

mass during a chemical reaction. Using a Calvet-type differential calorimeter (scanning transitiometer), in which the temperature of the reaction mass is kept at a constant set-point value, TOC provides reliable results of the reaction power of polymerization reactions. In addition, it was proved that a simple isoperibolic RC can be successfully used to increase the yield or to assess the efficiency of initiators in the near-to-the-industrial conditions if a special attention is paid to the baseline determination (*UA*) and to the deconvolution of measured heat flux.

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