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Comparing Methods for Calculating the Heat Flow Rate of Reactions in Different Bench-Scale Calorimeters

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Summary: A transfer function of the *RC1e*™ (*Mettler-Toledo*) calorimeter was obtained by calibration with a heating cartridge. With this function it was possible to determine the heat flow rate and total heat of different polymerization reactions. The calorimeter operates in isothermal as well as in isoperibolic mode. Additionally, 1-vinyl-2-pyrrolidone and acrylic acid were polymerized in a three-neck flask. In this common laboratory device the heat flow rate was obtained by using a transfer function calculated by calibration with a heating cartridge. Thus, the heat of polymerization can be obtained without using a calorimeter and without solving the heat balance equation.

Keywords: calorimetry; isoperibolic; isothermal; reaction calorimeter; transfer function

Introduction

Polymerization reactions carried out in an industrial scale include risks due to their exothermic character. Therefore, it is necessary to know the reaction enthalpy of a given monomer and the course of the polymerization reaction already at an early stage of product development. Bench-scale reaction calorimetry in the laboratory and on-line heat balance of production-scale polymerization reactors are well-established methods of monitoring polymerization reactions. However, cost and efforts for lab-scale calorimetry are still significantly high.

Using a simple laboratory set-up for carrying out new polymerization recipes and still getting some calorimetric data like the generated heat flow rate or the total heat production at an early stage of product design would be of advantage. In a conventional bench-scale calorimeter such data can be obtained by solving the heat balance equation of the calorimeter. For this, precise measuring of reactor and jacket temperature is essential. Additionally, the overall heat transfer coefficient and the heat exchange area of the reactor must be known. For a laboratory device like a flask, these values are commonly unknown. The application of the transfer function of the used device is one way to get information about the heat flow rate of a polymerization.

A transfer function describes how a released heat flow rate is transformed into a temperature curve. A transfer function can be gained from calibration with a heating device like a heating cartridge. Therefore, it is not required to know e.g. the overall heat transfer coefficient. To calculate the transfer function the heat flow rate curve of the calibration and the resulting temperature curve are *Fourier* transformed and divided by each other. This operation is called deconvolution. The also *Fourier* transformed temperature curve of the polymerization is than divided by the transfer function giving the heat flow rate of the reaction by reconvolution.

In a previous work it was shown, that the transfer function of an isoperibolic calorimeter with ballast vessel can be used for

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calculating the heat flow rate of a polymerization reaction by deconvolution.[1]

The purpose of the presented work is to expand the earlier described method to another calorimeter (the *RC1e*™ from *Mettler-Toledo*) and then testing this method with a simple laboratory set-up consisting of a three-neck flask and an oil bath.

Experimental Part

Calorimetric Measurements

The calorimetric measurements were performed in an *RC1e*™ reaction calorimeter from *Mettler-Toledo*. As reactor the HP-60 was used. This is a metal reactor with a pressure range up to 60 bar and a maximum volume of 1.8 L. Under reaction conditions the usable volume is between 0.5 and 1.5 L. Reactor temperature (T_R) is measured with Pt-100 resistance temperature sensors. The calorimetric signals are recorded by a computerized measuring unit (*RD*-10 from *Mettler-Toledo*) and the transformed data are saved via PC. The used stirrer, a PARAVISC™ impeller (*EKATO*), was driven by an electronically controlled motor, which is separated from the stirrer via a magnetic coupling. For good mixing the stirring rate was 200 rpm. A heating cartridge with a power output of approximately 25 W, installed in the reactor, was used for calibration. Optionally, the reactor cap is heatable by a separated thermostat (*Julabo*) to reduce heat loss due to condensation of solvent vapor. The *RC1e*™ can operate in isothermal and isoperibolic mode. The working principle of the *RC1e*™ is described in literature.[2] In both modes, the given monomer (acrylic acid (AA), 1-vinyl-2-pyrrolidone (NVP)) was polymerized in solution. In order to determine monomer conversion samples were taken during the reaction run and analyzed by gas chromatography (GC).

Measurements in Three-Necked Flasks

Instead of a calorimeter, a simple laboratory setup (Figure 1) was used for polymerizations. A three-necked flask of 500 or 1000 mL (A) was filled up to 2/3 of its volume with a solution of AA or NVP in water that was mixed by a magnetic stirring stick. The flask was surrounded by an oil bath (B), which was heated and also mixed by a magnetic stirrer (C). The stirring speed was 190 rpm up to 320 rpm. For calibration a heating cartridge (D) was inserted through the middle neck. Pt-100 resistance temperature sensors (E) measured temperatures in the flask and in the oil bath. The high precision measuring unit *PP2* from the company *Remü* (F) controlled the heating cartridge and the Pt-100 temperature sensors via a 12-bit analog/digital converter. Data acquisition, storage and evaluation were carried out with the aid of a PC (G). In order to determine monomer conversion, samples were taken during the reaction run and analyzed by gas chromatography.

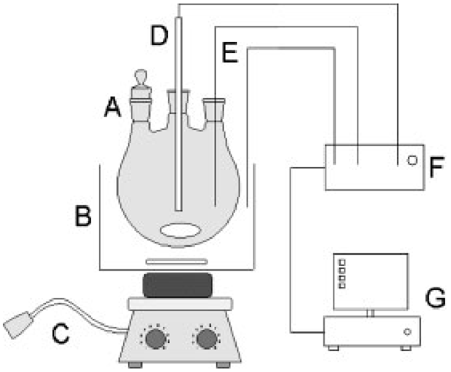

Figure 1.
Scheme of the used laboratory setup and connected peripheral units.

Experimental Procedure

The monomer solution was heated up to a certain temperature (60–65 °C). After reaching constant conditions, 500 mg of initiator (2,2′-azobis-2-amidinopropane dihydrochloride, V-50) dissolved in 4 mL of water were added. After the polymerization had taken place, the electrical heating cartridge was switched on for up to two hours dissipating a constant power input of 10 to 25 W. The amount of heat dissipated into the reactor by the heating cartridge was serving for calibration. Simultaneously, a Pt-100 temperature sensor measured the temperature in the reactor or in the three-necked flask, respectively. After switch off of the heater temperature data were continuously recorded until the temperatures in the reactor and ballast vessel reached equilibrium again and remained constant over a period of at least one hour.

Evaluation of the Measured Data

Evaluation of the experimental data was done with aid of the program *Mathematica^{TM}* 5.2, whereas measured data were subject to filtering. All temperature spikes that were outside the relevant range or which first derivate indicates an abnormal gradient were regarded as artifact and replaced by the directly preceding value.

For solving the heat balance equation of the *RC1e*$^{\text{TM}}$ in order to obtain the heat flow rate Q, the first derivatives of the measured values of T_R are needed. By common differentiation methods the signal to noise ratio is worsened. The values of Q are therefore discrete *Fourier* transformed and multiplied with a *Hanning* window function.[3,4] After this, the filtered function is transformed back into the time domain with a reduced level of noise.

Determination and Application of the Transfer Function

The transfer function of a calorimeter can be gained by calibration with an electric heater. Therefore, a certain heating profile is released into the filled calorimeter. The electric power input and the resulting temperature course are recorded and both curves are discrete *Fourier* transformed. The *Fourier* transformed temperature curve (effect) is divided by the *Fourier* transformed electric power input curve (reason) (so-called deconvolution). Afterwards, the resulting function can be retransformed into time domain. This deconvolution provides the characteristic transfer function of the calorimeter including its content.[5]

Afterwards the measured temperature curve of the polymerization is discrete *Fourier* transformed and deconvoluted with the transfer function in the frequency domain. The *Fourier* transformed heat flow curve obtained is filtered with a *Hanning* window function, too and is then transformed back into the time domain. The result in demand is the heat flow rate curve of the polymerization.

Usually three calibration cycles were performed during one experiment. The presented heat of reaction is the average of the values calculated from each heating cycle.

Reagents

The following reagents were used for the chemical experiments without further purification: acrylic acid (stabilized with hydroquinone monomethyl ether, *Merck*); 1-vinyl-2-pyrrolidone (NVP, *BASF AG*); 2,2′-azobis-2-amidinopropane dihydrochloride (V-50, *Wako Chemicals*); benzonitrile (*Merck*); ethanol (*Merck*). All solutions were prepared using de-ionized water.

Gas Chromatography

For analyzing the residual amount of monomer NVP in a given sample, approximately 500 mg of the sample were diluted with ethanol/water (2:1). About 50 mg of benzonitrile were added as internal standard. The residual amount of monomer was then determined using GC, a *Chrompack CP-9003* (*Varian*) with a *CP Wax 52 CB* column (50 m) and a flame ionization detector. Carrier gas was nitrogen mixed with hydrogen at a pressure of 30 kPa.
0.4 μL of the sample were brought onto the column via a split injector. The resulting chromatograms were analyzed using the software package *Maitre 2.5* (*Varian*).

Results and Discussion

Isoperibolic Operation of the *RC1e*$^{\text{TM}}$

In order to prove the applicability of the described method, different polymerization runs were carried out in the *RC1e*$^{\text{TM}}$ under isoperibolic conditions. Figure 2 shows a typical reaction run of a free radical NVP polymerization in aqueous solution. After

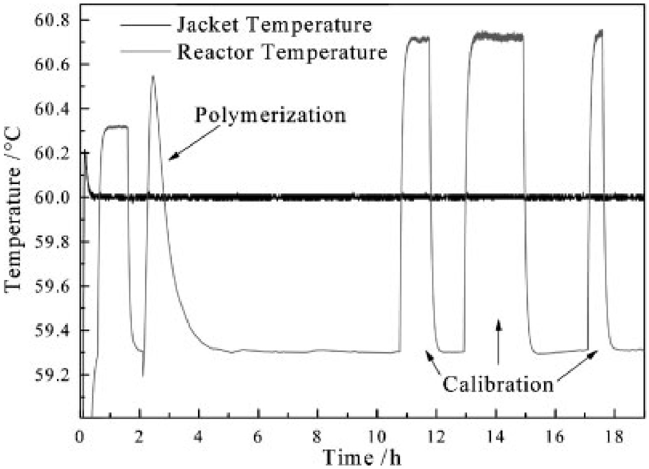

Figure 2.
Reaction run of an isoperibolic polymerization of NVP (0.94 mol in 1 L of water) with three different calibration cycles after the reaction. The jacket temperature was set to 60 °C and V-50 (1.8 mmol) was used as initiator.

the end of polymerization the heating cartridge was switched on three times for calibration. Each calibration cycle was of different length (1 h, 2 h, 0.5 h).

Subsequently, the transfer function of the calorimeter was calculated based on reactor temperature measurements during a specific heating cycle. With this function the heat flow rate curve of the polymerization was calculated from the reactor temperature curve.

For evaluating the results of this operation, the obtained heat flow rate curve was compared with the heat flow rate curve calculated from the heat balance equation of the calorimeter. In Figure 3 the heat flow curve calculated with the transfer function of the second calibration cycle and from solving the balance equation are shown. In addition the absolute differences between both curves are shown. The differences lie mostly below 1.0 W. The total amount of

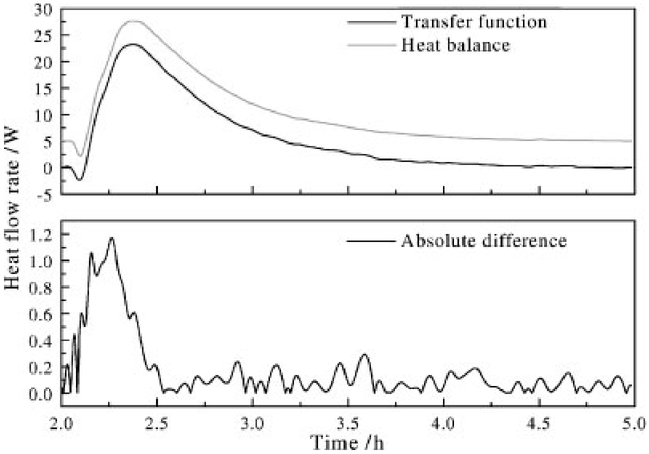

Figure 3.
Calculated heat flow rate curve with the transfer function from the second calibration cycle and from the heat balance equation along with the absolute difference between both curves. In the upper diagram, the heat balance was provided with an offset of 5 W for better visibility.

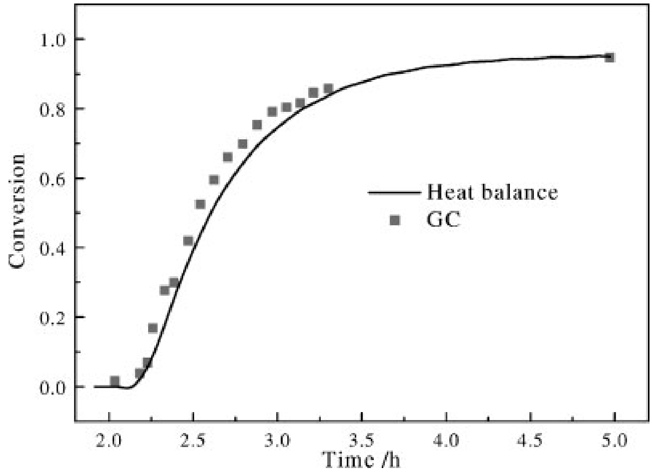

Figure 4.
Comparison of time-conversion curves of NVP polymerized under isoperibolic conditions (reaction parameters see Figure 3).

heat calculated from the transfer function (area below the curve) is 57.2 ± 0.7 kJ (63.4 ± 0.8 kJ/mol) and from the heat balance equation 57.0 kJ, corresponding to a deviation of 0.4%.

In this experiment 100 mL (0.94 mol) of NVP were polymerized. The heat of polymerization of NVP is 64.3 ± 1.9 kJ/mol.[6] Assuming complete conversion, 0.94 mol of NVP lead to an enthalpy of 60.4 ± 1.8 kJ. However, GC analysis resulted in a conversion of 96%, equivalent to an enthalpy of 58.0 ± 1.7 kJ. The measured value is just 1.4% below this value. The time-conversion curve calculated from the heat flow rate corresponds well with conversion obtained from gas chromatographic analysis (Figure 4). With the transfer function of the *RC1e*™ in isoperibolic operation mode the respective course of reaction can be derived from the temperature curve of the corresponding polymerization.

Isothermal Operation of the *RC1e*™

The other tested mode of operating the *RC1e*™ calorimeter is the isothermal

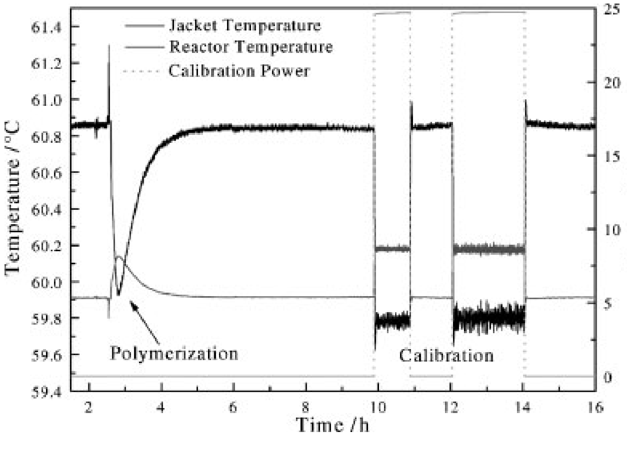

Figure 5.
Reaction run of an isothermal polymerization of NVP (0.94 mol in 1 L of water) with two different calibrations after the reaction. The reactor temperature was set to 60 °C and V-50 (1.8 mmol) was used as initiator.

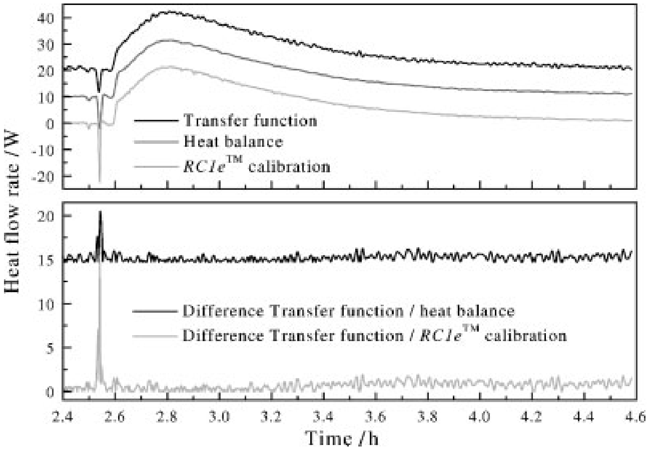

Figure 6.

Calculated heat flow curve with the transfer function from the second calibration cycle, from solving the heat balance equation and from the internal *RC1e*^{TM} calculation along with the absolute difference of the curves (reaction parameters see Figure 5). In the upper diagram, the heat balance was provided with an offset of 10 W and the transfer function with an offset of 20 W for better visibility. In the lower diagram the upper black line was provided with an offset of 15 W.

one. Figure 5 shows a typical reaction run of a NVP polymerization. At the end of polymerization, the heating cartridge was switched on two times for means of calibration. Each calibration cycle was of different duration (1 h, 2 h).

Just like for the proceeding conditions, the transfer function was calculated, however, not using the reactor temperature but the jacket temperature. With the transfer function the heat flow rate curve of the polymerization was calculated from the jacket temperature curve.

The resulting heat flow curve was compared with that calculated from the heat balance equation. Additionally, a heat flow curve is calculated with the aid of the *RC1e*^{TM} software package based on solving

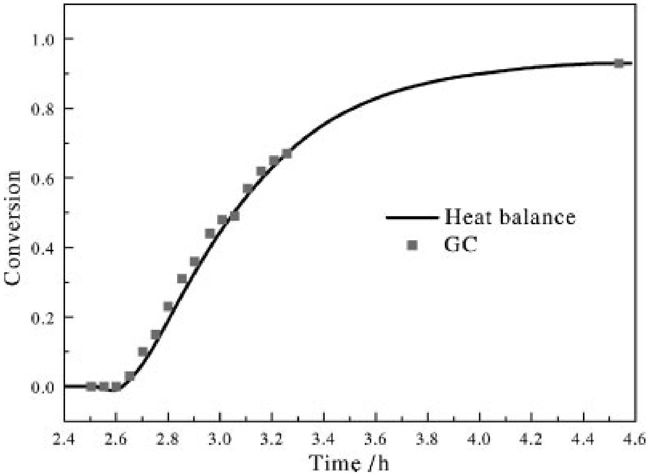

Figure 7.

Comparison of time-conversion curves of NVP polymerized under isothermal conditions (reaction parameters see Figure 5).

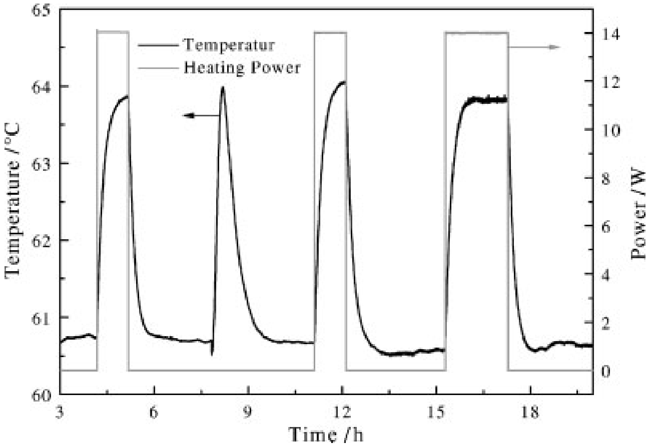

Figure 8.
Reaction run of NVP (0.47 mol in 750 mL of water) polymerization in a three-neck flask with one calibration before and two different calibrations after the reaction. The jacket temperature was set to 61 °C and V-50 (1.2 mmol) was used as initiator.

the heat balance equation. This curve was also compared with the curve from the transfer function. The results are shown in Figure 6. Only while initiator is added, the curves deviate significantly. The reason for this divergence is the filtering operation applied to the transfer function that broadens the signal. This leads to an average value. The total calculated heat from the transfer function is 54.3 ± 0.3 kJ (57.8 ± 0.3 kJ/mol). The value from the balance equation is 53.9 kJ and from the internal *RC1e*™ calculation 53.9 kJ as well. The maximal deviation is 0.7% based on the *RC1e*™ calculation.

Here again, 100 mL of NVP were polymerized. With a total conversion of 93% calculated from GC measurements the total amount of heat should be 56.2 ± 1.7 kJ, however, the measured value from the transfer function is 4% below. Figure 7 shows the time-conversion curve calculated from the heat flow curve using the transfer function and conversion values calculated off-line from GC measurements.

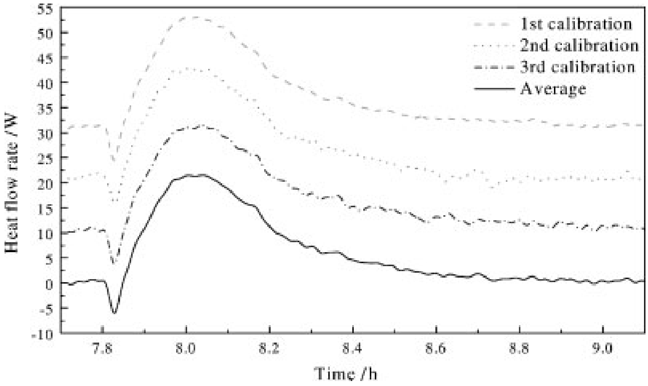

Figure 9.
Heat flow rate curve of the NVP polymerization in a three-neck flask calculated via the transfer function gained from the first, second and third calibration cycle and the average of them (reaction parameters see Figure 8). The heat flow rates calculated from the calibrations were provided with an offset for better visibility.

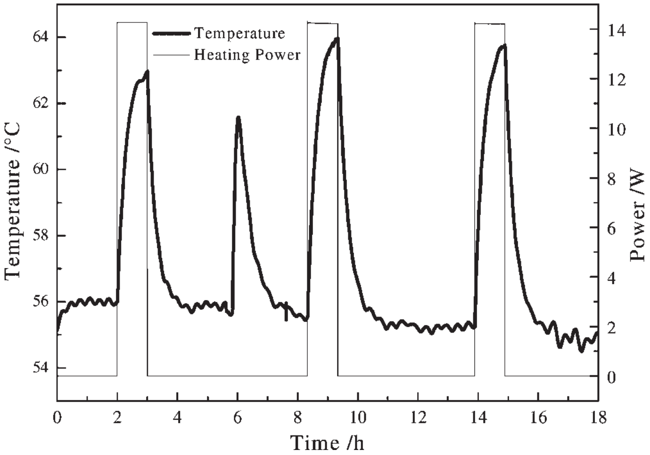

Figure 10.
Reaction run of an AA polymerization (0.29 mol in 750 mL water) with three heating cycles for calibration. The polymerization was performed in a three-neck flask. The jacket temperature was set to 56 °C and V-50 (1.0 mmol) was used as initiator.

Polymerization of NVP in a Three-Neck Flask

As described above, NVP was polymerized in a three-neck flask. Three heating cycles, one before and two of different length after the polymerization, were carried out for calibration (Figure 8).

In an isoperibolic calorimeter the heat of reaction is calculated from the heat balance equation in need of a constant jacket temperature. With an oil bath as jacket, heated by a magnetic stirrer, no constant temperature could be achieved. So the heat of reaction had to be calculated otherwise.

With the temperature curve of the corresponding heating cycle the transfer function of the flask was calculated, and the average of all three heat flow rate curves finally led to the heat flow rate of the reaction (Figure 9).

In this experiment 0.47 mol of NVP were polymerized. The calculated total amount

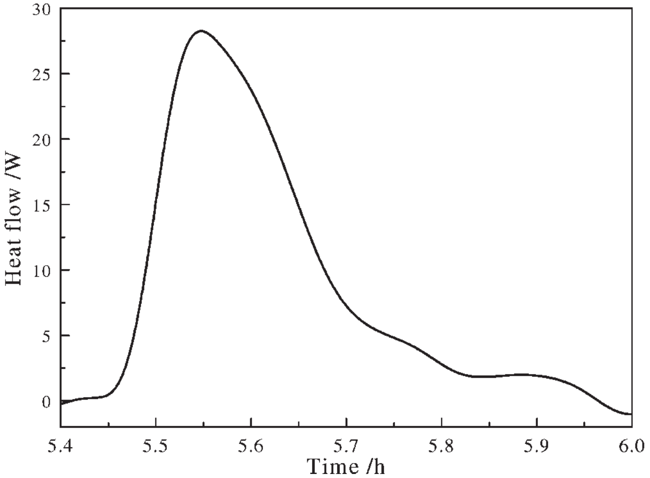

Figure 11.
Heat flow rate curve of the AA polymerization calculated with the transfer function gained from the first heating cycle (reaction parameters see Figure 10).

of heat was 29.6 ± 2.2 kJ (64.9 ± 4.9 kJ/mol). With a proofed conversion of 97% by GC the maximum amount of heat is 29.3 ± 0.9 kJ, corresponding to a deviation of 1%.

Polymerization of AA in a Three-Neck Flask

After polymerizing NVP, with AA an even faster polymerizing monomer was investigated. The heat of polymerization of AA is 77.5 kJ/mol.[7]

Figure 10 shows a free radical polymerization of 20 mL (0.29 mol) of AA in aqueous solution. Three heating cycles, one before and two after the reaction, were conducted for purpose of calibration.

The heat flow rate was determined applying the transfer function (see above) (Figure 11) and only by using a broad filter window, despite the loss of information about the course of reaction. For example, the addition of initiator is not visible as a negative peak in the heat flow curve. Additionally, the heat flow rate curve could be only achieved from the second calibration. Therefore, the gained heat flow curve is just a qualitative description and not quantitative at all. Nevertheless, the calculated amount of heat of 19.6 kJ (69.0 kJ/mol) is in the range of the assumed amount of heat of 22.1 kJ (98% conversion from HPLC measurements). The measured value from the transfer function is 13% below this value.

Conclusion

A transfer function of the *RC1e*™ reaction calorimeter was successfully calculated from a calibration cycle. With this function the heat flow rate and heat of polymerization can be determined. The method fits well for isothermal and isoperibolic operation conditions of the *RC1e*™. The heat of reaction was calculated under isoperibolic conditions with a deviation of 1.4% compared with the calculated result from GC conversion and the theoretical heat of reaction. Under isothermal conditions the deviation was 6%.

Instead of using a calorimeter it is possible to use a common laboratory device like a three-neck flask for polymerization and still obtaining the heat of reaction. For the polymerization of NVP the heat of reaction was calculated with a deviation of 1%. With AA the reaction runs faster and the heat of reaction was obtained with a deviation of 13%. Hence, the application of the described method on fast reactions is still subject of further research.

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