Increased Reactor Performance versus Reactor Safety Aspects in Acrylate Copolymerization

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The aim of reducing cycle times of semibatch polymerization processes requires systematic investigations of the kinetics, careful adjustment of the desired polymer properties, proper thermal reactor design and reliable reactor safety assessment [1]. As a concrete example, a semibatch copolymerization were carefully examined with respect to four different aspects. Thermo-kinetics of the reaction was investigated with isoperibolic reaction calorimetry and GC. In order to obtain reliable values for the overall heat transfer coefficient of the production scale reactor, cooling experiments were carried out with solvent and final copolymer solution as reactor content. For consistent reactor safety assessment additional investigations are necessary including case studies of breakdown incidences. These simulations were performed with a mathematical model based on the GC data and experimental vapor pressure curves. As a result of these calculations, a reduction of reaction time from 10 to 6 hours was possible. To convert into practice, it must be ensured that even in this shortened time a product of the same quality is produced.

1 Introduction

During exothermic reactions carried out in semibatch operation safeguarding considerations may frequently be in conflict with a large reactor performance. The systematic procedure for the reduction of reaction time considering safety aspects is demonstrated at the example of a semibatch copolymerization at industrial scale.

Therefore, the overall reaction enthalpy and the time dependent heat flow rate are important quantities which can be properly obtained by isoperibolic calorimetry. The chemical heat flow rates are controlled by gas chromatography and time dependent monomer concentrations become available thereby. For setup of the reactor heat balance, the cooling capacity of the production vessel must be known. This was achieved by cooling experiments in the production plant. In addition, simulations of a variety of scenarios were carried out for assessing the thermal safety of the process even in the case of a cooling failure and monomer accumulation.

The investigated reaction system is a free radical copolymerization of styrene, 2-hydroxyethyl methacrylate (HEMA), n-butyl acrylate and acrylic acid in solution. A mixture of hydrocarbon solvents, including xylene and n-butyl acetate, is used as solvent. A combination of two common peroxo-initiators with different half-life times are used as the initiator system.

2 Experimental part

All thermo-kinetic investigations of the copolymerization were carried out in an automated isoperibolic reaction calorimeter [2, 3]. The main part of this calorimeter is shown in Fig. 1.

1. cartridge heater
2. pressure sensor
3. stirrer
4. dosing pipe lines
5. Pt-100 sensor
6. magnetic stirrer

reactor vessel
ballast vessel
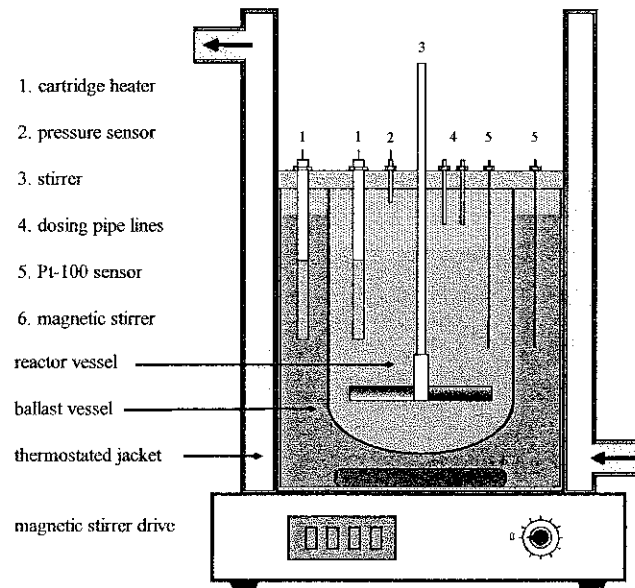thermostated jacket

magnetic stirrer drive

Figure 1: Schematic draft of the main part of the isoperibolic calorimeter CALWIN

The thermostated jacket as well as the ballast vessel are filled with Marlotherm™ oil, since the operating temperature is 140 °C. The ballast vessel is used to limit the increase in reaction temperature to a typical level of about 1 K. Therefore, reaction conditions are regarded as quasi-isothermal. The main advantage of this calorimeter design is the setup of two heat balance equations, one for the reactor

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$$C_R \dot{T}_R = \dot{Q}_{chem} - (UA)_R (T_R - T_B) + P_{R,stirr} \qquad (1)$$

and one for the ballast vessel:

$$C_B \dot{T}_B = (UA)_R (T_R - T_B) - (UA)_B (T_B - T_J) + P_{B,stirr} \qquad (2)$$

Significant changes in overall heat transfer coefficient U due to increasing dynamic viscosity of the reaction mass [4] and occasionally reactor fouling are well known in polymerization processes. In addition, the effective heat exchange area A changes in semibatch reactors as the result of reactant feed, volume contraction due to changing densities from monomers to polymers and changes in the shape of the stirrer vortex, which varies with reactor filling height and viscosity. However, combination of these two heat balance equations eliminates the heat transfer term of the reactor $(UA)_R$ and subsequently, the calculation of the heat flow rate generated by the chemical reaction, $\dot{Q}_{chem}$ is independent from the UA term of the reactor:

$$\dot{Q}_{chem} = C_B \dot{T}_B + C_R \dot{T}_R + (UA)_B (T_B - T_J) - P_{B,stirr} - P_{R,stirr} \qquad (3)$$

The accumulation terms in Eq. (3) may be summed up as a reasonable approximation, if quasi-isothermal conditions are considered:

$$\dot{Q}_{chem} = (C_B + C_R) \dot{T}_B + (UA)_B \cdot (T_B - T_J) - P_{B,stirr} - P_{R,stirr} \qquad (4)$$

Consequently, the chemical heat generation rate can be measured without the need of measuring the reactor temperature. When both, reactor and ballast vessel temperature are known, the reactor heat transfer term $(UA)_R$ can be calculated by rearranging Eq. (2)

$$(UA)_R = \frac{C_B \dot{T}_B + (UA)_B (T_B - T_J) - P_{B,stirr}}{T_R - T_B} \qquad (5)$$

as a function of time, which offers valuable information for thermal reactor design. Data acquisition and dosing are computer based. The data acquisition and control program is based on the software TestPoint™. At the beginning of each experiment, 240.1 g of the solvent mixture were filled into the 1.1 Liter autoclave. While the system was heated up, the reactor was purged from oxygen. After determination of the stationary temperature and a first calibration, the polymerization was started by feeding of the co-monomers and initiator solution at the desired mass flow rates. The total mass of both was kept constant for all measurements at 373.8 g of monomers and 22.4 g of initiator solution. All chemicals used were of technical quality.

Total monomer conversion and co-monomer concentrations were determined by gas chromatography. The final conversion was determined for each polymerization separately. In addition, samples were taken during the entire polymerization process as the basis for calculation of co-monomer profiles. Since the reaction temperature is above the boiling point of single components, overpressure is built up inside the reactor. Therefore, sample collection had to be performed with special techniques. Samples were cooled immediately by ice and prepared for GC-measurements by dissolving approx. 500 mg of the sample in about 5 ml THF and adding 100 mg of n-butyl methacrylate as internal standard. A WGA-SB-11-FFAP

column was used for these investigations. Quantitative residual monomer determination was obtained by proper calibration for each of the co-monomers.

Large differences exist between the calorimeter autoclave and the 15 m³-production reactor with regard to the possibilities of heat removal. For evaluation of these parameters, especially the cooling capacity, cooling experiments were carried out in the production reactor. Therefore, temperature sensors were installed at the in- and outlet of the cooling water jacket in addition to one sensor measuring the reactor temperature, and a mass flow controller was built into the jacket loop as well. Since the original process control system is not suitable for export and evaluation of data, data were acquired with the aid of a personal computer and measurement electronics by HiTech Zang [5]. Heating of the reactor was conducted by medium pressure steam in a separated circle. Both, cooling and heating jackets consists of external welded half-pipes. In order to get more reliable values, two different methods were used for this determination:

Method 1: Cooling with constant temperature of the cooling water at the jacket inlet.

If only cooling water is responsible for changes of the reactor temperature, UA can be determined by fitting according to the course of measured reactor temperature $T_R(t)$. Eq. (6), which is derived from Newton's cooling law, is given in the VDI-Wärmeatlas [6]:

$$T_R(t) = T_{J,in} - (T_{J,in} - T_{R,0}) \cdot \exp\left\{ -\frac{\dot{m}_J c_{P,J}}{m_R c_{P,R}} \left[1 - \exp\left(\frac{-UA}{\dot{m}_J c_{P,J}} \right) \right] t \right\} \qquad (6)$$

Eq. (6) is limited to the following constraints:

- Heat transfer coefficient may be described by a suitable average value.

- Heat losses to the surroundings as well as power input by the stirrer or any chemical reaction can be neglected.

- Heat capacity of the reactor is small compared to its content.

This method was performed at the end of a polymerization run with the final copolymer solution. Hence, viscosity and any reactor fouling had production like conditions.

Method 2: Heat balance of cooling water at stationary state.

Stationary state was achieved by cooling and heating of the reactor at the same time. This ends in a thermal balance. While stationary conditions are realized, the conductive heat flow rate through the reactor wall

$$\dot{Q}_{cond} = UA(T_R - \bar{T}_J) \qquad (7)$$

should be equal to the convective heat flow rate of the cooling water through the jacket,

$$\dot{Q}_{conv,J} = \dot{m}_J c_{P,J} (T_{J,out} - T_{J,in}) \qquad (8)$$

if losses from lateral heat conduction inside the reactor wall and other secondary heat flow terms of minor importance are neglected. The reactor temperature is kept constant by heating, which equals the conductive heat flow. The overall heat transfer coefficient U is estimated by combination of Eqs. (7) and (8)

$$U = \frac{\dot{m}_J c_{P,J}(T_{J,out} - T_{J,in})}{A \, \Delta T_{LM}} \qquad (9)$$

with ΔT_{LM} describing the logarithmic mean temperature difference between reactor and cooling water jacket [7]. These measurements were carried out in the production scale reactor filled with water and solvent, respectively. In general, the reactor temperature during these tests should be as close as possible to the reaction temperature of about 140 °C. However, boiling has to be avoided, so that these measurements were limited to about 90 °C for water and about 120 °C for the solvent mixture.

3 Results and Discussion

3.1 Thermo-kinetics of the semibatch copolymerization

In order to obtain information about the chemical heat flow rate of the reaction, the measured heat flow rate has to be corrected by the convective heat flow rate, which is needed to heat up the cold added reactants to reaction temperature. Fig. 2 shows the resulting chemical heat flows rates and overall heats of reaction for different dosing periods.
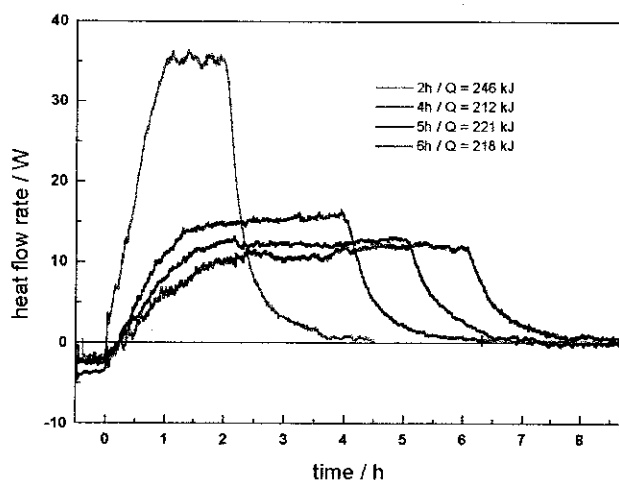

Figure 2: Heat flow rates for different dosing periods and overall heat of reaction

All experiments were reproduced with similar results. Furthermore, the measured values for the heats of reaction, which were obtained by integration of the heat flow rate curves correspond for dosing periods of 4, 5 and 6 hours with data from literature, if the overall heat of copolymerization is assumed to be additive with regard to the individual heats of homo-polymerization of the co-monomers. For known values of final monomer conversion, the fractional thermal conversion was determined by calorimetry according to Eq. (10) [8]:

$$X(t) = \frac{\int_0^t \dot{Q}_{chem} \, dt}{\int_0^\infty \dot{Q}_{chem} \, dt} \qquad (10)$$

For control of thermal conversion and to determine the maximum accumulation of monomers which is a crucial moment for reactor safety, samples were taken during the entire polymerization process and analyzed by gas chromatography. Fig. 3 shows good agreement of both, calorimetric and chromatographic data. In the beginning, calorimetry seems to be more reliable, since the gas chromatographic result depends largely on the exact sample time. On the other hand, the error of conversion determined by integration of the heat flow rate increases with time because small errors, e.g. a drift in baseline, are accumulated. Monomer conversion obtained by calorimetry presupposes unchangeable copolymer composition.
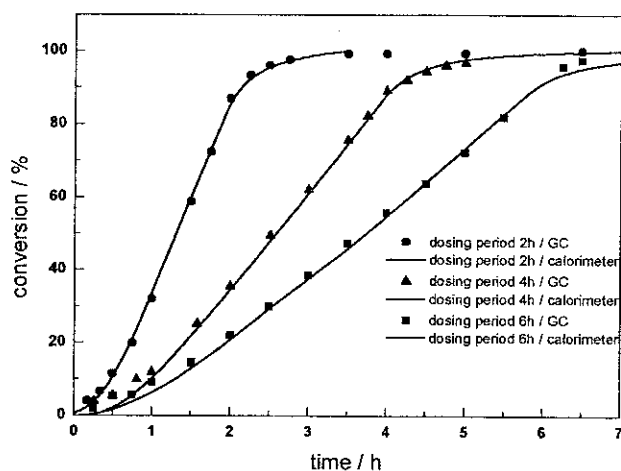

Figure 3: Comparison of overall monomer conversion obtained by calorimetry and gas chromatography

Furthermore, monomer accumulation and MTSR – values (Maximum Temperature of Synthesis Reaction) are important quantities for thermal safety assessment, as shown by Stoessel [9]. The MTSR is defined as follows

$$MTSR = T_{R,0} + \Delta T_{ad} \qquad \text{with} \qquad \Delta T_{ad} = Y_{acc} \frac{Q_R}{C_R} \qquad (11)$$

and can be calculated from gas chromatographic measurements for determination of accumulated monomer part Y_{acc} and known feed rates. Fig. 4 shows conversion, accumulation and calculated MTSR – values for dosing periods of 6, 4 and 2 hours. Monomer accumulation is increasing with reduced dosing periods as expected and reaches its maximum at about 17 % in case of a 2 hours dosing period. However, not only the co-monomer accumulation increases but overall monomer conversion and the total reaction mass as well, when co-monomer feed rates are increased. Therefore, numerator and denominator in Eq. (11) increase at the same time and the resulting maximum MTSR value for a 2 hours dosing period is only 10 K higher than for a dosing period twice as long.
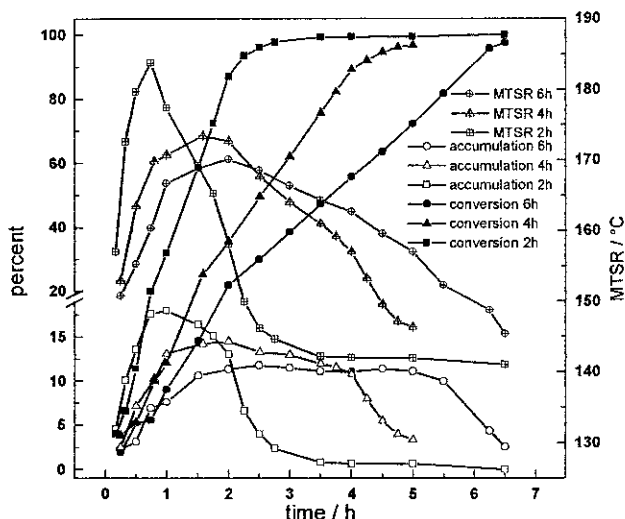
Figure 4: Monomer conversion, instantaneous monomer accumulation and MTSR values versus reaction time for different dosing periods

Nevertheless, it has to be kept in mind, that a reasonable small difference between MTSR and the desired level of reaction temperature is insufficient in order to ensure that isothermal reaction conditions may be realized.

3.2 Cooling capacity of the industrial reactor

In order to achieve isothermal reaction conditions, the cooling capacity of the production reactor has to be larger than the heat generation rate of the reaction during the entire process. The cooling capacity consists of the convective term (direct cooling by dosing of reactants) and the conductive heat transfer to the jacket. While the convective cooling is almost constant and can be calculated easily, the UA term of the conductive cooling changes significantly during semibatch polymerization and has to be determined experimentally. In Fig. 5 measured reactor temperatures are compared with fitted data estimated from Eq. (6). A good agreement is obvious and the correlation coefficient is calculated to be 0.9968.
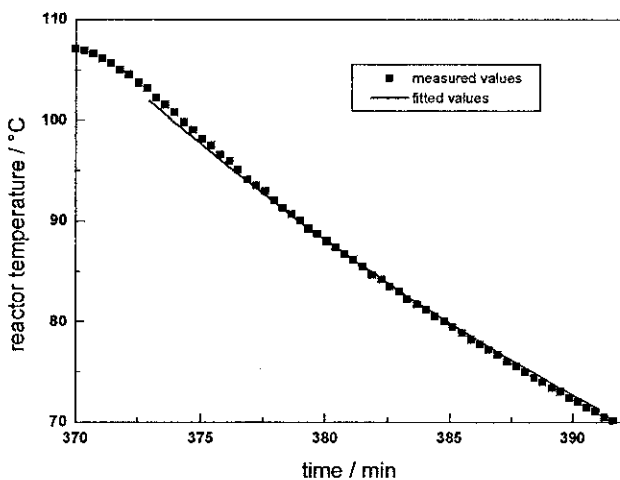

Figure 5: Measured and fitted temperatures during cooling of the production reactor

The experimentally determined overall heat transfer coefficients are

- Method 1   122 $W/m^2 K$

- Method 2   97.7 $W/m^2 K$

Since Method 2 was carried out only with pure water and solvent, the result had to be recalculated considering the difference in viscosity by using the heat transfer characteristic (Nusselt equation). With regard to numerous assumption and approximations made for the calculations and the significant different measurement conditions, the difference between both estimates of about 20 % seems to reasonable small.

3.3 Heat balance

Since the measured heat flow rate scales with the reactor volume, measured data are normalized to 1 kg of reactor content for better comparison and summarized in Tab. 1. In addition, the corresponding cooling capacities are listed. A simple comparison of maximum and removable heat flow rates for each dosing period shows that for dosing periods of 6 and 4 hours isothermal reaction conditions can be realized.

Table 1: Produced and removable heat flow rates for different dosing periods

dosing period h	max. heat flow rate W/kg	conductive cooling capacity kW	convective cooling capacity kW	overall cooling capacity kW	removable heat flow rate W/kg
6	19	238.2	70	308.2	25.4
4	25.2	238.2	105	343.2	28.3
2	55	238.2	209.6	447.8	36.9

Subsequently, isothermal conditions can not be realized during the entire process for a dosing period of only 2 hours.

3.4 Simulation of cooling failures

For an extended reactor safety analysis of the polymerization process the statement of isothermal reaction conditions at normal operating conditions is insufficient. In addition, the effects of possible breakdowns, especially cooling failures, on the large scale reactor have to be calculated in order to prevent thermal runaway situations. Consequently, a variety of breakdown incidences and resulting scenarios have been simulated on the basis of deterministic mathematical models, which help to identify critical effects on the thermal safety of the polymerization process. In fact, some different failures, e.g. a broken stirrer shaft, can be simulated with the same model as a cooling breakdown. The following conservative assumptions were made:

- produced heat is completely used to rise the temperature of the reactor content (adiabatic reactor behavior)

- pressure over the reaction mass can be estimated from Clausius – Clapeyron equation.

The resulting pressure is calculated from temperature-pressure-measurements and adaptation to the Clausius – Clapeyron equation (Fig.6), which shows excellent conformity with experimental results. The overall heat of vaporization (50 kJ/mol) needed to achieve this conformity of the adaptation seems to be a little high in comparison with data from literature for o-xylene (41,8 kJ/mol [10]).
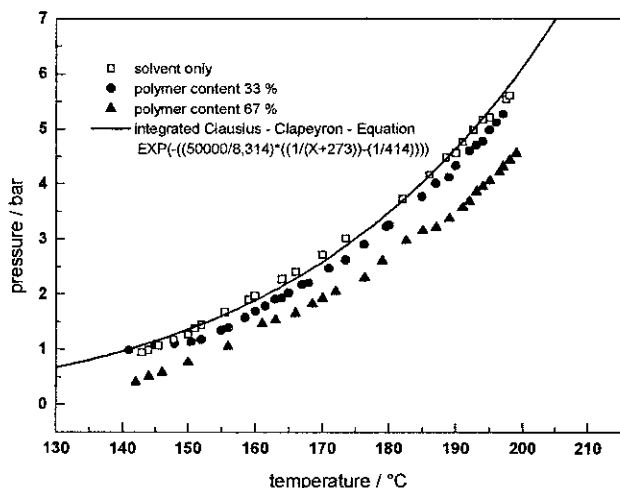

Figure 6: Temperature - pressure measurement for different polymer contents

As expected from Flory-Huggins theory, the resulting pressure decreases with increasing volume fraction of polymer contained in the solvent. Again the worst case, pure solvent, is used for further simulation. Severe breakdowns incidences are cooling failures which are investigated predominantly. Two different scenarios are presented here:

- Scenario 1 is based on a stopped reactants dosing if the cooling breaks down.

- Scenario 2 simulates an unstopped dosing even when a cooling breakdown occurs.

Scenario 1

Fig. 7 shows the adiabatic runaway behavior of the production scale reactor in case of a an immediate stop of monomer and initiator feeding pumps when the breakdown in reactor cooling occurs. The time chosen for the cooling breakdown is the moment of maximum co-monomer accumulation, which represents the worst case study with respect to reactor safety. Since the reactor stays within its characteristic design limits of 3 bar even if the cooling failure appears at this most critical point in time, the process will be safe as far as thermal aspects are considered, if the dosing period is not shorter than 4 hours.
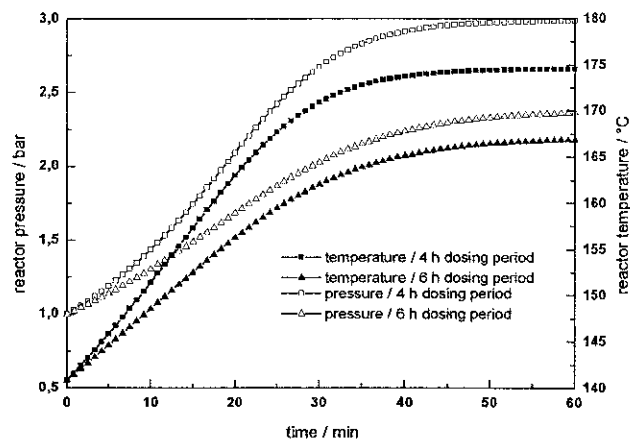

Figure 7: Simulated temperature and pressure curves for adiabatic reactor behavior for different dosing periods when dosing is stopped after cooling failure

Scenario 2

Unstopped dosing of reactants without any jacket cooling leads to temperature and pressure curves as shown in Fig.8. The remaining dosing period is set to 4 hours for both feed rates, which means that in case of 4 hours dosing period, the polymerization runs at "adiabatic" conditions right from the beginning. Independently of the dosing period, the plant exceeds its design limits in both cases. In case of the shorter dosing period, a slight decrease of temperature and pressure can be observed during the first hour. This effect results from the direct cooling by cold reactants fed into the reactor. When the reaction starts, most of the accumulated monomer will be converted into copolymers in a very short period of time of approx. 30 minutes. Subsequently, temperature and pressure climb up steeply, which makes it even more difficult to stop the reaction and cool down the reactor before its design limits are exceeded and reactor venting will occur.
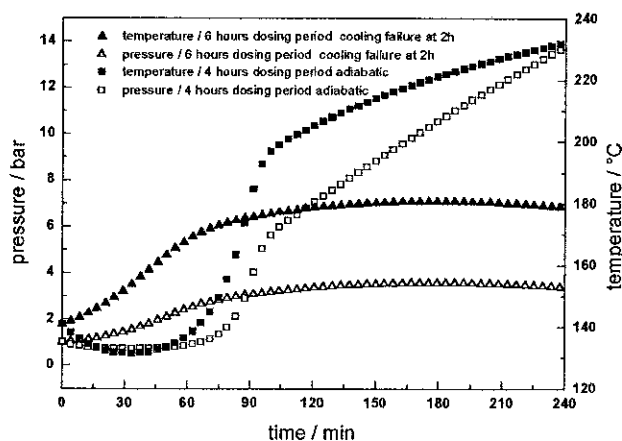

Figure 8: Simulated temperature and pressure in case of "adiabatic" reactor behavior for different dosing periods with ongoing dosing after cooling failure

3.5 Largest controllable batch reactions

The reaction is carried out in semibatch operation mode. Therefore, the mass of the reactor content increases constantly with reactant feedings and in particular, the amount of accumulated monomer is enlarged accordingly. The increase in molar number of monomers results in an increase in latent heat, which may exceed the reactor design limits. For these investigations again two scenarios can be distinguished.

The largest controllable batch reaction with a cooling failure at the same time is defined by the resulting adiabatic temperature rise. It must be restricted to 40 K, since a MTSR over 180 °C would lead to pressures above 3 bar. Fig. 9 shows the maximum amount of accumulated monomer, which can be accepted in comparison with the measured amount.
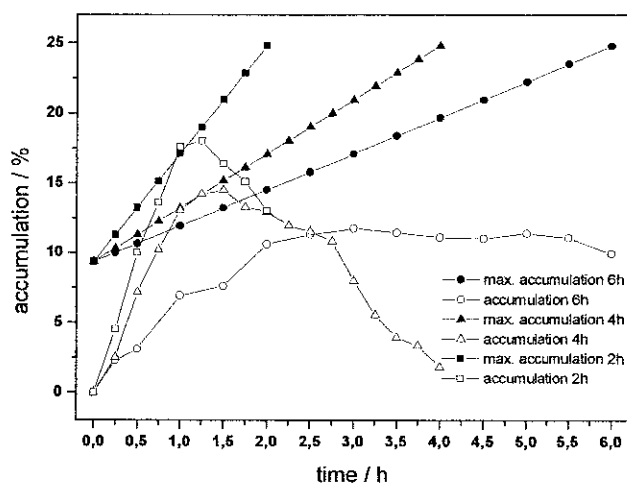

Figure 9:   Comparison of acceptable and measured accumulation

While for a dosing period of 6 hours, there is always a large difference between the maximum acceptable accumulation and the measured one. This difference becomes smaller with reduced dosing periods. The accumulation at 4 hours dosing period even reaches the maximum tolerable accumulation. Any further reduction of dosing periods leads, e.g. in the case of 2 hours, to a small period of time, where the monomer accumulation exceeds the acceptable amount. Because of the fast increase in mass, this period is surprisingly short, but it is not acceptable with regard to reactor safety.

The determination of the maximum acceptable latent heat is more difficult in the case of a working jacket cooling. Calculations for these scenarios rely on the experimentally determined cooling capacity and subsequently, they have the same error margin. These scenarios simulate the effect of uncontrolled fast dosing of monomers or ineffective initiator while the cooling is still operating. Since isothermal conditions can not be ensured for a dosing period of 2 hours anyway, these scenarios concentrate exclusively on dosing periods of 4 hours. Fig. 10 shows the thermal behavior of the production reactor for different levels of monomer accumulation. The temperature is calculated from the start of the reaction while the dosing of

reactants continues. Isothermal conditions at 140 °C were assumed until the reaction actually starts.
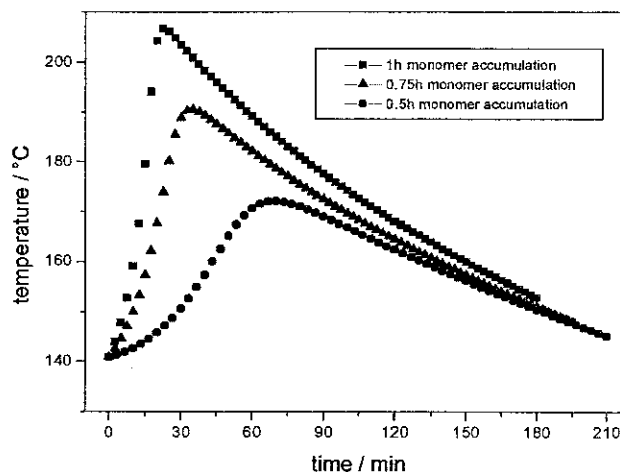

Figure 10:   Temperature curves for different monomer accumulation times

For an accumulation level of 12.5 % of total monomer which corresponds with half an hour of dosing without any reaction the resulting temperature curve reaches its maximum after about 1 hour at approx. 172 °C and stays below 180 °C, which represents the reactor design limit. In contrast, the reaction of monomer accumulated in 0.75 h already exceeds this reactor safety limit and has to be avoided. In addition, the temperature climb up is significantly faster and reaches its maximum of 190 °C already after about 30 minutes. As expected, the temperature increases even more rapidly, if monomer accumulation during 1 hour is assumed.

3.6 Product quality

If safety aspects do not prevent a reduction in reaction time, then a product of at least the same quality must be produced. In general, shorter dosing periods result in higher molar masses due to an increase in monomer concentrations. This effect was observed in the present investigation as well. Two possible measures may compensate this. Changes in the dosing profiles or shifts in the dosing times will establish the former product quality. A change in the recipe, e.g. the use of a different initiator system, can be a suitable alternative that worked well in the presented investigations.

4 Conclusions

For dosing periods from 6 to 4 hours the reactor will remain within its design limits, if reactant feedings are blocked when the jacket cooling breaks down. Since pressure may rise up to 3 bar in the case of adiabatic behavior, any further reduction of the dosing period with increasing latent heat should be avoided. 4 hours seems to be the lower limit of the dosing period under the constraints respected.

In combination with a reduction of 2 hours of consecutive batch reaction time, the total reaction time can be reduced from

10 to 6 hours. The overall reactor performance is increased by about 11 % without additional investments. An equivalent product quality can be obtained by optimization of the recipe within the reduced reaction time. Additional time may be saved by an initial charge of co-monomers which shortens the time to reach quasi-stationary state during the dosing period and adiabatic reaction conditions after the end of monomer dosing. Since production costs may vary not only with reduced reaction time (e.g. if different chemicals must be used) overall economic views have to compare the cost advantage of technical optimization with the new, possibly changed raw material costs in order to evaluate the minimum production costs.

Subscripts

0	initial value
acc	accumulation
B	ballast vessel
chem	chemical reaction
cond	conductive
conv	convective
in	inlet
J	jacket
out	outlet
R	reactor, reaction

5 Symbols used

A	[m^2]	heat exchange area
C	[J/K]	effective heat capacity
cP	[kJ/kgK]	specific heat capacity
MTSR	[K]	Maximum Temperature of Synthesis Reaction
m	[kg]	mass
$\dot{m}$	[kg/h]	mass flow rate
Pstirr	[J]	power input by the stirrer
Q	[kJ]	overall heat of reaction
$\dot{Q}$	[J/s]	heat flow rate
U	[W/(m^{2}K)]	overall heat transfer coefficient
T	[K]	temperature
$\dot{T}$	[K/s]	time derivative of temperature
t	[s]	time
ΔTad	[K]	adiabatic temperature rise
ΔTLM	[K]	logarithmic mean temperature difference
X	-	conversion
Yacc	-	accumulated monomer part

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