Macromol. Symp. **2004**, *206*, 79–92

A New Tool for the Study of Polymerization under Supercritical Conditions – Preliminary Results

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Summary: Efficient stirring is needed to realize heat flow analysis with a thermally homogeneous medium. Because dispersion polymerization with supercritical fluids can be destabilized under stirring, a preliminary target has been to find a compromise between synthesis and basic reaction calorimetry requirements. This paper describes the use of poly (dimethylsiloxane) macromonomer with a molecular weight 5000 g/mol as stabilizer for the dispersion polymerization of methyl methacrylate in supercritical carbon dioxide. The effect of stirring speed and stabilizer concentration has been examined. This study has shown that poly (methyl methacrylate) can be produced at high yield and molecular weight using 10 wt % (respect to monomer) poly (dimethylsiloxane) macromonomer at stirring speeds up to 600 rpm. A polymerization enthalpy of -57.6±2 kJ/mol has been calculated being in good agreement with previously reported data. Thus, preliminary results for the heat balance using the newly developed high pressure reaction calorimeter for supercritical fluid applications have shown the important potential of reaction calorimetry to promote supercritical fluid technologies at industrial scale allowing for the determination of kinetics and thermodynamic and safety data, respectively.

Keywords: calorimetry; carbon dioxide; dispersion; methyl methacrylate; polysiloxane; stabilization; supercritical

Introduction

The increasing interest during the last few decades in decreasing the environmental effects of the release of organic compounds (VOC's) and aqueous waste has motivated the development of polymerization in supercritical carbon dioxide ($scCO_2$)[1,2]. However, the advantages of using CO_2 are not only environmental but also chemical and economical. One of the most practical advantages is a solvent-free polymer product by simply venting the solvent. It eliminates the need for energy intensive drying and devolatilization processes. Moreover there is no chain transfer to CO_2 in free radical polymerizations. Most studies focus on supercritical carbon dioxide, which is

DOI: 10.1002/masy.200450207

a solvent environmentally harmless, accessible and inexpensive, non-toxic and non-flammable. It can easily be recycled and its critical point (T_c = 31.1 °C, P_c = 73.8 bar) can be attained economically. Due to its availability and low price, CO_2 has a potential at industrial scale. It has been noted that CO_2 behaves like hydrocarbons with respect to its capability to dissolve small molecules, and thus many monomers exhibit good solubility in CO_2 [3]. However, it is a rather poor solvent for most high molecular weight polymers [4, 5] except for some fluoropolymers and silicones. The latter are used as sterical stabilizers in the dispersion polymerization of vinyl polymers such as poly (methylmethacrylate)[6-11] and poly(styrene)[12]. As defined by Barrett [13], dispersion polymerization is a heterogeneous polymerization process, based on the formation of latex particles in the presence of a suitable stabilizer from an initially homogeneous reaction mixture. This polymerization process exhibits complex behavior in terms of particle formation, stabilization mechanism and partitioning [14, 15] of reactants between the continuous phase and polymer-particles.

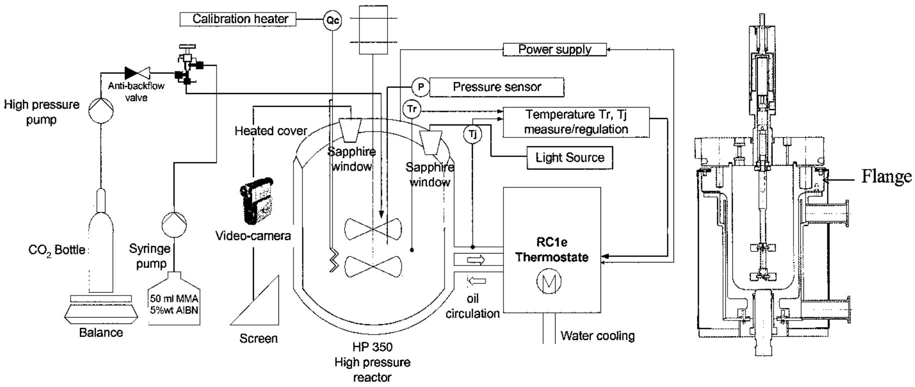
The dispersion polymerization of methylmethacrylate in supercritical carbon dioxide, using the commercially available poly (dimethylsiloxane) monomethacrylate [8, 16] (PDMS macromonomer) as dispersant, is used as model reaction. Macromonomers are polymers with a polymerizable terminal functional group being commonly used for the formation of graft copolymers. The disadvantage of such molecules is that they are chemically incorporated in the final polymer and, thus, stirring speed and stabilizer concentration will have an impact on the product quality. On the other hand, the polymerization has to be in agreement with the basic requirements of reaction calorimetry, which means having a detectable thermal signal and efficient stirring. Since efficient stirring can destabilize the dispersion, the first approach is consequently to try to find a compromise between stirring and synthesis.

In order to promote such a technology at industrial scale, thermodynamical and kinetic data have to be determined. The employed set up allows a scale up with reaction conditions close to those of industrial reactors [17]. Reaction calorimetry is based on the measurement of heat flows and finds most of its application in the determination of kinetic parameters, safety studies and process optimization [18] as well as phase equilibrium and phase transition studies [19]. The set up is a new concept of reaction calorimetry, developed with Mettler-Toledo GmbH (Switzerland), especially for the analysis of supercritical fluids with respect to reaction kinetics and thermodynamic data.

Description of the RC1*e* reaction calorimeter

The Mettler-Toledo RCI*e* reaction calorimeter is a bench scale calorimeter based on the work of Regenass [18, 20]. Its basic set up is depicted in Figure 1 (a) and (b). The reactor is surrounded by a jacket where silicon oil flows at high flow rate. With this reactor it is possible to work in three different operating modes: *adiabatic*, where the jacket temperature (T_j) is adjusted in such a manner that there is no heat transfer through the reactor wall (heat of reaction conserved); *isoperibolic*, where the jacket temperature is kept constant and the reaction temperature (T_r) follows the reaction profile; and *isothermal*, where the desired reaction temperature is set to a constant value and T_j is changed automatically to maintain T_r at the specified value. All the experiments of this study are performed in isothermal mode.

The system is composed of: a metallic reactor/thermostat unit (RC1e), a dosing controller (RD10), a computer and a pressure unit. The reaction vessel (HP 350, Premex, Switzerland) is a high pressure autoclave made of high strength stainless steel and allows operating up to 350 bars and 300 °C. The total reactor volume is 1.15 liters (V_r). A magnetic coupling allows stirring from 0 to 3000 rpm. A safety rupture disc prevents any damage due to excessive pressure. The software (WinRC-NT) displays and stores the measured data on-line by the RC1/RD10 during the experiment. It also transfers set points and safety parameters to the RC1/RD10. The thermostat unit controls the reaction temperature by pumping silicon oil through the double jacket of the reactor. The oil circulation system is divided into two separate parts: the heated circulation with electrical heating and the cooling circulation with an external coolant. The experimental values of the various parameters (T_r, T_j, rpm, pressure) are transferred to the computer at least every two seconds, allowing the calculation of other parameters (Q_r, Q_{flow}, dT_r/dt, etc).



(a) (b)

Figure 1: (a) High pressure reaction calorimeter and (b) technical scheme of the reactor

The technical challenge of supercritical reaction calorimetry is, different from normal liquid calorimetry, that all the available reactor volume is filled by the supercritical media. This means that the total heat transfer area is not only the perfectly controlled jacked wall but also the cover and the flange. Therefore, the metallic cover was equipped by an electrical heating and a PT100, allowing the set point to be directly adjusted to the on-line measured reaction temperature. Temperature differences and heat flows between the cover and the reaction medium can, thus, be avoided. Moreover, in purely isothermal mode, the metallic flange could be assumed to be at reaction temperature. If not, it could be separately thermally controlled to follow the reaction temperature

Energy balance

The most fundamental assumptions are that reactor and jacket temperature are homogeneous, and that the reaction system is perfectly mixed. The energy balance for a semi-batch process is given by:

$$Q_r + Q_{acc} + Q_c = Q_{dos} + Q_{flow} + Q_{loss} - Q_{stir} \qquad (1)$$

Qr is the heat generation of the reaction (equation 2), [W]. Q_{acc} is the accumulation term (equation 3), [W]. The term Q_c is the heat delivered by the calibration probe, [W]. Q_{dos} corresponds to the amount of heat due to addition of reactants (equation 4), [W]. Q_{flow} is the heat flow through the reaction wall, [W]. Q_{loss} is the heat losses to the surroundings, [W]. Q_{stir} is the heat input by the stirrer, [W].

The heat release by polymerization reaction is defined by the equation 2, where $V_{continuous\ phase}$ is the total volume of the reactor in this case, V_r, [m^3]; ($-\Delta H_r$) is the heat of polymerization of the monomer used [J/mol]; and R_p is the global rate of polymerization [mol/(m$^3 \cdot$ s)].

$$Q_r = V_{continuous\ phase} \cdot (-\Delta H_r) \cdot R_p \qquad (2)$$

The accumulation term Q_{acc} is defined by equation 3 and corresponds to the heat needed to change the internal temperature T_r [K] of the media by a certain amount dT_r/dt [K/s]. m_r is the reaction mass [kg] and c_{pr} the specific heat capacity of the reaction mass [J/(kg$\cdot$K)]. This term can be neglected as soon as the system is working in a pure isothermal mode which is the case for all the presented experiments.

$$Q_{acc} = m_r \cdot c_{pr} \cdot \frac{dT_r}{dt} \qquad (3)$$

The calibration probe delivers an amount of heat Q_C that is measured on-line and has a value around 25 W. It is used to measure the overall heat transfer coefficient, UA, before and after the polymerization through equation 4. Calibration is applied during 10 minutes during which the internal temperature T_r is kept constant.

$$UA = \frac{\int_{t1}^{t2} (Q_c - Q_b) \cdot dt}{\int_{t1}^{t2} (T_r - T_j) \cdot dt} \qquad (4)$$

where Q_b is the baseline term, which will be discussed later, and T_j is the jacket temperature [K].

The dosing term, defined by the equation 5, is the amount of heat absorbed or released due to the addition of a reactant at a different temperature than the reaction mass:

$$Q_{dos} = \frac{dm_d}{dt} \cdot c_{pd} \cdot \left(T_r - T_{dos}\right) \qquad (5)$$

where dm_d/dt is the mass flow of dosing [kg/s]; c_{pr} is the specific heat of the added substance [J/(kg·K)]; T_r is the current temperature of the reactor contents [K]; T_{dos} is the temperature of the added substance (entered as a fixed value or measured by RD10). There are three main situations where the dosing term Q_{dos} can be neglected: if the reaction starts “far after” the introduction of the reactant, if T_{dos} is not “too different” from T_r, or if the dosing mass is small enough compared to the reaction mass m_r. It has been observed during all the presented isothermal experiments that the dynamic of the system is sufficiently fast to compensate the addition of a small quantity of cold reactant. Thus, the dosing term can be neglected for the studied cases.

The term Q_{flow} in eq. (1) is the heat flow through the reactor wall:

$$Q_{flow} = U \cdot A \cdot (T_r - T_j) \qquad (6)$$

where U is the overall heat transfer coefficient [W/(m^2·K)]; A is the heat exchange surface [m^2]; T_j is the jacket temperature [K]. As soon as supercritical fluid occupies all the volume available, the heat exchange area corresponds to its maximum geometrical value.

The two terms Q_{loss} and Q_{stir} in equation 1 are normally constant during an isothermal run and can be combined in the baseline term Q_b. This means the integration of a heat production peak or a calibration peak already takes into account the heat losses and the heat of stirring as soon as stirrer speed and temperature do not change. However, the measure of UA before and after the reaction or taking into account a constant baseline (Q_b) are sufficient for reactions with only small changes of physical-chemical properties. For polymerizations, this assumption is limited as the viscosity can change significantly during the process, depending, for example, on the polymer concentration. Thus, the two terms Q_{stir} and UA which are directly dependent on the viscosity of the media can change during the polymerization process. A further development of the system and general objective will be to measure UA on line during the polymerization.

From eq. (1) and (2) it can be seen that the reaction rate is related to the evolution of the measured heat. For single reactions or one dominant reaction, as is the propagation reaction in free radical or chain polymerization processes, Q_r is directly proportional to the measured heat. For complex systems, where consecutive or parallel reactions with similar thermal contributions occur, the signal corresponds to the addition of all heat contributions, i.e the macrokinetic. The final and simplified heat balance equation used in this paper is given in equation 7 and takes into account all the previous remarks:

$$Q_r = Q_{flow} \qquad (7)$$

Experimental

Stabilizer (PDMS macromonomer, $M_W \cong 5000$ g/mol), supplied by ABCR (Germany), initiator (2,2'-azobis(isobutyronitrile), AIBN), supplied by Fluka, and monomer (methylmethacrylate, MMA), supplied by BASF (Germany), were used without further purification. Carbon dioxide of purity 99.9% is supplied by Carbagaz (Switzerland). The bottle is mounted on a balance (Mettler-Toledo GmbH, Switzerland) with an extended precision of 0.1 g over the range of 0-12.8 kg and is connected to a pump (NWA GmbH, Germany). This precision balance is necessary to achieve an accurate control of the injected CO_2 amount. There are two sapphire windows fixed on the reactor cover in order to have a visual access to what is happening inside the reactor: an endoscope from FiberOptic AG (Switzerland) equipped with a miniature digital camera as well as a light source are fixed on those windows. The camera is connected to a tactile screen (Pro-Face GmbH, Deutschland) from which pictures can be transferred to a computer for further treatment. The typical reaction procedure is the following: For all polymerizations in Table 1, the reaction vessel is charged with monomer (200g) and the required amount of stabilizer, then closed and filled with CO_2 (around 800 g). The temperature is raised to 80°C. At this temperature, a solution of 50 ml MMA containing 5.1 wt % AIBN is introduced in the reactor under pressure using a syringe pump (100DX, ISCO Inc.). The final ratio of AIBN/MMA is 1 wt % for all the experiments. At the end of the reaction, the reactor contents are quenched by cooling and CO_2 venting. Global product yield and the quantity of PDMS monomethacrylate chemically incorporated in the final product are evaluated gravimetrically. Extraction experiments of PDMS macromonomer with hexane (Reactolab SA, Switzerland) are carried out to distinguish between the amounts of PDMS monomethacrylate physically and chemically incorporated in the final product. After drying the polymer, four samples (0.2 g) of each experiment are prepared in small test tubes for centrifugation and left under stirring with hexane for one hour and then centrifuged for 15 min at 9000 rpm. The solution of hexane containing the extracted PDMS macromonomer is removed carefully and the samples are dried. It is possible to calculate the amount of PDMS macromonomer chemically incorporated in the final product from the mass balance for the dried product. The polymer is characterized in terms of molecular weight by triple detection size exclusion chromatography (TDA 300, Viscotek), particle size distribution (Mastersizer2000, Malvern Instruments) and morphology, respectively, by electron microscopy (SEM). Reactions were carried out at different stabilizer concentrations and different stirring speeds. The stirrer used (Figure 2) is the triple stage Ekato MIG® (Schneider AG, Switzerland).

Figure 2: Triple stage Ekato MIG®

This type of stirrer is particularly designed to homogenize heterogeneous liquid-liquid, solid-liquid or gas-liquid mixtures at low shear.

Results and Discussion

The preliminary results for the methylmethacrylate polymerization in supercritical CO_2 using commercially available poly (dimethylsiloxane) macromonomer are presented in Table 1. The lower limit of stirring speed was chosen to be 200 rpm, since a previous heat transfer analysis showed this stirring speed to be the lowest to obtain a thermally homogeneous medium [21]. The latter analysis was realized by means of the Wilson plot method [22].

Table 1: Experiments, conditions and results

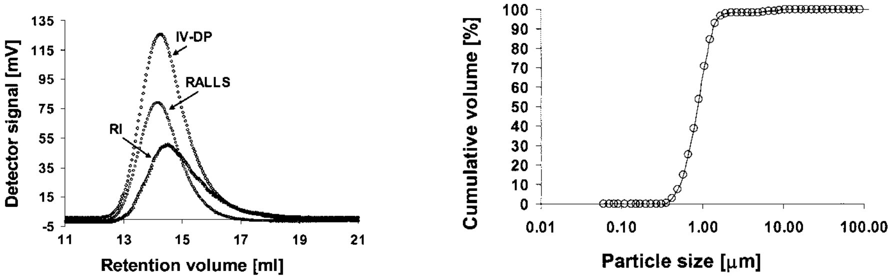
	PDMS/MMA wt %	[rpm]	P_0 [bar]	P_r [bar]	Yield [%]	M_w [kg/mol]	PDI	Product	dp (SEM) [μm]	D(v,0.9) [μm]	Span [-]	wt % PDMS incorporated
1	5	200	214	244	/	28	2.8	Sticky solid	/	/	/	/
2	10	200	210	255	95	114	2.0	White powder	0.5-1.8	1.3	0.9	3.7
3	10	400	239	280	93	112	1.9	White powder	/	2.1	1.3	4.3
4	10	600	228	262	94	120	2.0	White powder	1.2-2.3	1.9	1.1	4.8
5	10	600	223	268	95	131	2.0	White powder	/	2.1	1.1	4.3

The characteristic time of polymerization was 150 min and the reaction temperature was maintained at 80 °C. In Table 1, P_0 corresponds to the pressure of the reactor before adding the mixture of MMA and AIBN, i.e. before the beginning of the polymerization. P_r corresponds to the pressure at the end of the polymerization. The pressure profile is shown in Figure 5 (b).

The first experiment conducted with 5 wt% PDMS macromonomer (with respect to the monomer) lead to a sticky solid of low molecular weight and broad molecular weight distribution at low monomer conversion. The mechanism responsible for the destabilization under stirring is still under discussion. This phenomenon could have its origin in radical quenching that occurs at the metal surfaces of the reaction vessel, introducing additional termination mechanisms [23], which lead to a low molecular weight product. Moreover, particle coagulation and polymer precipitation could also be caused by a destabilization of the dispersion under shear forces due to mechanical energy dissipation. As soon as the dispersant acts mainly as a sterical stabilizer, the number of molecules at the surface of the growing polymer particles must be sufficient. Equilibrium between initiator, monomer and stabilizer quantities needs to be respected. Another possible explanation is that as soon as the system leaves the state of equilibrium, polymerization takes place also in the continuous phase, $scCO_2$, in considerable quantities. Morbidelli et al [14] have shown that for their system a certain amount of low molecular weight polymer is produced in the continuous phase parallel to the main polymerization occurring in the dispersed particles.

The experiments conducted with 10 wt% PDMS macromonomer at stirring speeds of 200, 400 and 600 rpm (see experiments 2-5 in Table 1) yield a fine white powder with high molecular weight at monomer conversions about 95% and a well defined spherical morphology observable by SEM micrograph. Molecular weights are lower than the ones published by Giles et al [16] where the experiments were realized in the absence of stirring. The quantity of PDMS macromonomer chemically incorporated is of the same order of magnitude.

The advantage of particle characterization using the particle sizer instrument is that the sample can be identified by its particle size distribution. This information is generally used by manufacturers to guarantee the specification of powders. The term D (v, 0.9) in Table 1 means that 90% of the particles have a diameter under the given value. Figure 3 shows, as example, the molecular weight (a) and particle size (b) distributions obtained for the polymerization n° 2:



(a) (b)

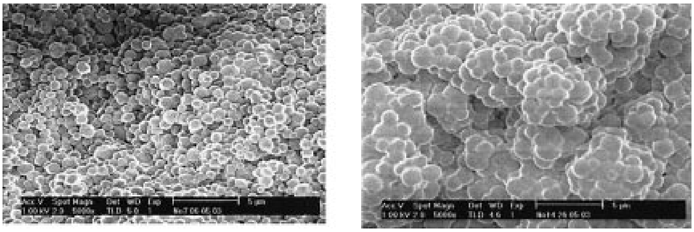
Figure 3: (a) Triple detection size exclusion chromatography of polymerization n° 2, IV = intrinsic viscosity, RALLS = right angle laser light scattering, RI = refraction index and (b) Particle size distribution of polymerization n° 3

Moreover, in Table 1 the span term gives an indication of the width of particle size distribution and is given by:

$$Span = \frac{D(v,0.9) - D(v,0.1)}{D(v,0.5)} \ [-] \tag{8}$$

In spite of what is expected from liquid dispersion theory, the experiments with higher stirring speeds do not result in narrower particle size distributions. Furthermore, it has to be considered that the stirring speeds might be too small to see an effect on the particle size distribution. In fact supercritical CO_2 has a two orders of magnitude lower viscosity than water and one order of magnitude lower than organic solvents. This implies that shear forces due to stirring are less efficient as to the production of droplets or particles, respectively.

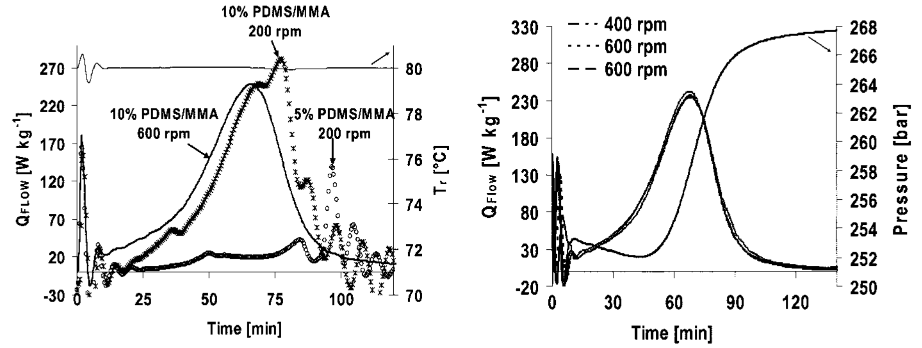
At commercial scale, stirring is essential to ensure thermal homogeneity and to avoid thermal runaway. For 10 wt % PDMS macromonomer, the dispersion polymerization of MMA in $scCO_2$ can be realized under efficient stirring. Experiments 4 and 5 were performed using a stirring speed of 600 rpm. The effect of stirring on product morphology is shown on Figure 4. The polymer particles produced at 600 rpm are more agglomerated compared to those produced at 200 rpm (see Figure 4 (a) and (b)). Future experiments at higher speeds will reveal if 600 rpm is an upper limit for the stability of the dispersion polymerization at 10 wt % PDMS macromonomer.



(a) (b)

Figure 4: (a) SEM micrographs of PMMA produced at 200 rpm and (b) 600 rpm

For this preliminary approach, the overall heat transfer coefficient was measured before the addition of the AIBN-MMA solution (e.g. in absence of any reaction) and at the end of the polymerization. The next challenge will be to develop a methodology allowing the accurate measurement of the overall heat transfer coefficient according to the evolving physical and chemical properties. Methods such as oscillating calorimetry with supercritical fluid or heat-loss number [24] could help solving this problematic.



10 wt% PDMS/MMA

(a) (b)

Figure 5 (a) and (b): Effect of PDMS macromonomer concentration and stirring speed on the heat flow analysis (Q_{FLOW}) of the dispersion polymerization of MMA in $scCO_2$, T_r = 80°C and AIBN/MMA = 1 wt %

It was observed that the heat released by the polymerization reaction is dependent on the stabilizer concentration since the latter has a direct influence on the stability of the dispersion and hence on the MMA conversion. With 5 wt% stabilizer, the polymerization rate was very low and the polymerization was less effective (see Figure 5 (a)). For a stable dispersion with 10 wt% PDMS macromonomer, it appeared that the stirring speed did not influence the global heat released by polymerization (see Figure 5 (b)). However, it was observed that the shape of the thermal curve obtained was smoother at stirring speeds higher than 200 rpm. This is due to the fact that the reaction calorimeter cannot control the reactor temperature precisely enough due to the less efficient heat transfer but also due to the control parameters of the reaction temperature (slave) and jacket temperature (master). Clearly, it is better to work at 400 or 600 rpm for quantitative thermal analysis. After all, Figure 5 (b) shows that the reaction calorimeter allows for good reproducibility. Both curves at 600 rpm have identical shape. By integration of the thermal curves, the enthalpy of polymerization could be calculated. The measured value was -57.6±2 kJ/mol, which is in good agreement with the literature value of -57.8 kJ/mol for conventional solvents [25]. This result is very important and shows the potential of reaction calorimetry for determining kinetic and thermodynamic data for supercritical fluid processes.

Conclusions

It has been shown that poly (dimethylsiloxane) monomethacrylate with a molecular weight of 5000 g/mol is a suitable stabilizer for the dispersion polymerization of methylmethacrylate in supercritical carbon dioxide under efficient stirring.

In order to use all the potential of reaction calorimetry for the promotion of supercritical fluid polymerizations at industrial scale, a compromise between thermal homogeneity, good heat transfer and product quality was found. The studied polymerization is taken as model reaction for the development of supercritical reaction calorimetry. The effect of stabilizer concentration and stirring speed was studied. The enthalpy of polymerization was determined, and was in good agreement with previously reported data. Results were very reproducible indicating that the reaction calorimeter is operative.

The realization of supercritical polymerization calorimetry is characterized by several technical difficulties. Most of the complications are related to the fact that the physical-chemical properties of the reaction medium change during the polymerization. This implies, for example, that the evolution of the overall heat transfer coefficient during the measurement has to be taken into account. Another important term in the heat balance that must be accurately defined is the heat input dissipated by the stirrer. Its contribution to the heat balance should not be neglected.

This work has clearly shown that it is possible to carry out calorimetric studies in $scCO_2$. Reaction calorimetry can, thus, be employed to obtain kinetic and safety data on polymerization in supercritical carbon dioxide.

Acknowledgment

The Swiss Commission for Technology and Innovation n° 5254.1 and Mettler-Toledo GmbH are gratefully acknowledged for their support.

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