REACTION CALORIMETRY APPLIED TO THE DISPERSION POLYMERIZATION OF METHYL METHACRYLATE IN scCO$_2$

Sophie Fortini, Frédéric Lavanchy, Thierry Meyer*
Institute of Chemical Sciences and Engineering, Swiss Federal Institute of Technology,
CH-1015 Lausanne, Switzerland
*Corresponding author. Tel.: +41 21 693 3614; fax: +41 21 693 3190
E-mail address: thierry.meyer@epfl.ch

Reaction calorimetry is an efficient tool used to obtain kinetic, thermodynamic and safety data. A new instrument, composed of a 1.3 liter high pressure reactor coupled with a Mettler-Toledo RC1*e* thermostat unit, is developed for the investigation of chemical reactions under supercritical conditions. The dispersion polymerization of methyl methacrylate in supercritical carbon dioxide is used as a model reaction. Poly(methyl methacrylate) can be produced at high monomer conversion, with high molecular weight polymer and narrow particle size distribution powder, using 10 wt% poly(dimethylsiloxane) monomethacrylate (respect to monomer) as stabilizer under efficient stirring up to 600 rpm. A polymerization enthalpy of -54.3 ± 3 kJ mol^{-1} is calculated being in agreement with previously reported data. This reveals and confirms the potential of reaction calorimetry for the study and promotion of supercritical processes. Moreover, the effect of stirring speed and stabilizer concentration on the heat flow measurement is examined.

INTRODUCTION

Reaction calorimetry is a common tool based either on heat flow or heat balance measurements. The main applications of reaction calorimetry are the determination of kinetics parameters, the calculation of thermodynamic parameters, data evaluation for process safety and optimization [1]. A reaction calorimeter, RC1*e*-HP350, developed in collaboration with Mettler-Toledo GmbH, allows investigating chemical reactions under supercritical conditions. The set up gives the opportunity to work at larger scale with reaction conditions close to those of industrial reactors. Because it is important for polymer industries to find alternative process routes decreasing the impact of solvent emissions to the environment, the development of polymerization processes in supercritical carbon dioxide (scCO$_2$) becomes of great interest. Many monomers exhibit good solubility in scCO$_2$ [2]. However, it is a rather poor solvent for most high molecular weight polymers except for some fluoropolymers and silicones [3-5]. The latter are used as sterical stabilizers in the dispersion polymerization of vinyl polymers such as poly(methylmethacrylate) [6-8]. The dispersion polymerization of methyl methacrylate in scCO$_2$, using the commercially available poly(dimethylsiloxane) monomethacrylate (PDMS macromonomer) as stabilizer is used as model reaction. The preliminary calorimetric results, as the enthalpy of polymerization, will serve to validate the heat transfer model and to illustrate the great potential of reaction calorimetry as a thermo-analytical tool.

MATERIALS AND METHODS

Carbon dioxide (purity 99.9%, Carbagaz, Switzerland) is delivered using a bottle mounted on a balance (Mettler-Toledo GmbH, Switzerland) and connected to a CO_2 pump (NWA GmbH, Germany). The stabilizer ($M_W \cong 5000$ g mol^{-1}) supplied by ABCR (Germany), the thermal initiator (2,2'-azobis(isobutyronitrile), AIBN) supplied by Fluka, and the monomer (methyl methacrylate, MMA) supplied by BASF (Germany) are used without further purification. For all the experiments the procedure is the following: The reaction vessel is charged with monomer (202 g) and the required amount of stabilizer, then closed and filled with CO_2 (around 800 g.). When the reaction temperature is reached (80°C), a 50 ml MMA solution containing 5.1 wt% AIBN is added into the reactor under pressure using a syringe pump (100 DX, ISCO Inc.). The final ratio of AIBN/MMA is 1 wt% for all the experiments. After 4 hours, the reactor content is cooled, the CO_2 vented and the polymer collected. The stirring is assured by a three-stage Ekato MIG® at 200, 400 and 600 rpm. The conversion of methyl methacrylate is evaluated gravimetrically. The polymer obtained is characterized in terms of molecular weight distribution (TDA 300, Viscotek), particle size distribution (Mastersizer 2000, Malvern Instruments), and morphology by electron microscopy.

In collaboration with Mettler-Toledo GmbH, a reaction calorimeter working up to 350 bar and 300°C has been developed for supercritical conditions (Figure 1). It is composed of a 1.3 liter high pressure stainless steel reactor HP350 (Premex Reactor AG, Switzerland) coupled with a thermostat unit (Mettler-Toledo GmbH, Switzerland). The reactor is equipped with a magnetic drive allowing the use of different stirrers' types, a 25 W calibration heater, a Pt100 reactor temperature sensor, a cover and flange temperature control and a pressure sensor.
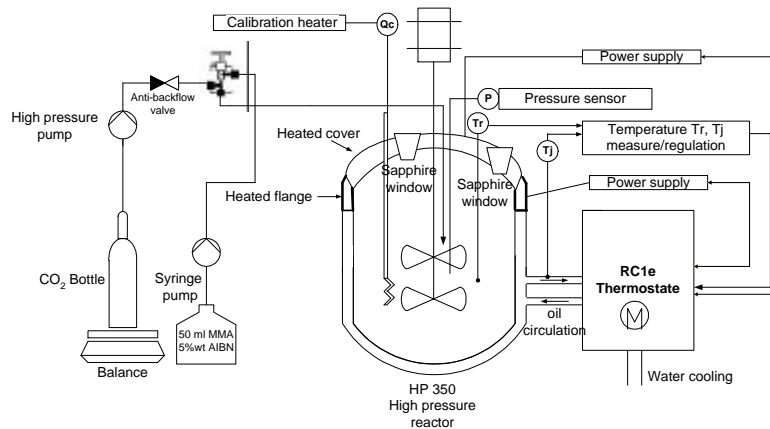

Figure 1: Technical scheme of the supercritical reaction calorimeter

The energy balance for a semi-batch process is given by [9, 10]:

$$Q_r + Q_c + Q_{stir} = Q_{acc} + Q_{dos} + Q_{flow} + Q_{loss} \tag{1}$$

where Q_r is the heat of reaction, [W]. Q_c is the heat delivered by the calibration probe, [W]. Q_{stir} is the heat input by the stirrer, [W]. Q_{acc} is the accumulation term, [W]. Q_{dos}

corresponds to the amount of heat due to addition of reactants, [W]. Q_{flow} is the heat flow through the reactor wall, [W]. Q_{loss} is the heat losses to the surroundings, [W].

The simplified heat balance equation used is:

$$Q_r = Q_{flow} + Q_{acc} = UA \cdot \left(T_r - T_j\right) + \left(m_r \cdot c_{pr} + \sum_i C_{pi}\right) \cdot \frac{dT_r}{dt} \qquad (2)$$

where U is the overall heat transfer coefficient, [W$\cdot$m$^{-2}\cdot$K^{-1}]. A is the heat exchange surface, [m^2]. T_r is the reactor temperature, [K]. T_j is the jacket temperature, [K]. m_r is the reaction mass, [kg]. c_{pr} is the specific heat capacity of the reaction mass, [J kg^{-1} K^{-1}]. C_{pi} is the heat capacity of each insert, [J K^{-1}]. The accumulation term for the reactor is taken into account in the WinRC$^{\circledR}$ software using a corrected jacket temperature in the calculation. The overall heat transfer coefficient, UA, is measured using a calibration probe delivering an amount of heat, Q_c, around 25 W and is given by eq. 3 where Q_b is the baseline term, [W]. t is the time, [s]:

$$UA = \frac{\int_{t1}^{t2}\left(Q_c - Q_b\right) \cdot dt}{\int_{t1}^{t2}\left(\left(T_r - T_j\right)\right) \cdot dt} \qquad (3)$$

The terms Q_{loss} and Q_{stir} in eq 1 can be taken as constant during an isothermal experiment and are introduced in the baseline, Q_b. The measurement of UA is realized at the beginning and at the end of the polymerization. The analysis may be more complicated due to the change of medium viscosity during a polymerization process. In this case, both term UA and Q_{stir} depend on the viscosity and may vary during the polymerization. The influence of Q_{stir} can be limited choosing a "proportional to conversion" baseline type. A mean value of UA is used for the heat flow term. The accumulation term in eq 1, Q_{acc}, could be neglected when working in a perfect isothermal mode. It is introduced in eq 2 in order to take into account little variations in T$_r$ at the polymerization start. During the reaction, at 400 and 600 rpm, the deviation of T$_r$ is less than a tenth of degree. It means that this term becomes negligible with respect to the heat flow term. The dosing term, Q_{dos}, can only be neglected when a small quantity is added or when T$_{dos}$ follows T$_r$.

After integration of Q_r, the reaction enthalpy becomes:

$$\Delta_r H = \frac{\int_{t0}^{tf}\left(Q_r - Q_b\right) \cdot dt}{m_{ro} \cdot X} \qquad (4)$$

where $\Delta_r H$ is the polymerization enthalpy, [J$\cdot$kg^{-1}]. m_{ro} is the initial amount of monomer, [kg]. X is the monomer conversion when the polymerization is stopped (t_f).

RESULTS AND DISCUSSION

The results for the dispersion polymerization of methyl methacrylate in $scCO_2$ at 80 °C using the PDMS macromonomer as stabilizer are summarized in Table 1:

Table 1: Experiments, conditions and results

	PDMS/MMA [wt %]	[rpm]	P_0 [bar]	P_1 [bar]	P_r [bar]	Product Quality	M_w [kg mol^{-1}]	M_w/M_n [-]	MMA Conversion [%]	D(v,0.9) [μm]
1	5	200	214	239	244	sticky solid	28	2.8	/	/
2	10	200	210	236	255	white powder	117	2.3	96	1.5
3	10	400	239	272	280	white powder	118	2.2	92	2.1
4	10	600	228	256	262	white powder	119	2.3	94	1.9
5	10	600	223	253	268	white powder	126	2.2	94	2.1

The characteristic polymerization time is 180 minutes. In Table 1, P_0 is the pressure inside the reactor before adding the mixture of MMA/AIBN. P_1 is the pressure just after the dosing of the solution and before the start of the polymerization and P_r corresponds to the pressure at the end of the reaction. A typical pressure profile is shown in Figure 3b. It is observed that the pressure first decreases till a minimum and then increases reaching a value slightly higher the initial value after the dosing but before the start of polymerization. Several authors [6, 11] observed that the pressure can either increase or decrease with time during a batch dispersion polymerization in $scCO_2$. It appears that the pressure behavior depends on the initial pressure in the system. The actual data do not allow defining a precise pressure upper limit from which a decrease in pressure is observed rather than an increase. The behavior change could be estimated between 230 and 300 bar. The pressure decrease can be understood by taking into account the change in molar volume of a vinyl monomer to the corresponding polymer. Lepiller and Beckman [11] attributed the particular pressure variation with respect to the initial pressure in the reactor, to the non ideal behavior of the ternary system monomer-CO_2-polymer.

The experiment realized with 5 wt % PDMS macromonomer leads to a sticky solid of low molecular weight, broader molecular weight distribution and low monomer conversion. The dispersion polymerization is already destabilized at stirring speed of 200 rpm. A heat transfer analysis shows that 200 rpm is a lower limit in order to have a thermally homogeneous medium [10]. It is known that dispersion polymerizations in $scCO_2$ can be destabilized under efficient due to additional termination mechanism by interaction with the reactor metallic wall [12] or due to shear forces. With 10 wt % PDMS macromonomer (see experiments 2-5 in Table 1) the polymerizations yield a fine white powder with high molecular weight at monomer conversion around 94% (mean value). The spherical morphology of the polymer is observed by SEM micrographs (Fig. 2a) validating the measurement of the particle size distribution obtained by laser diffraction technique. The term D(v, 0.9) in Table 1 means that 90% of the particles have a diameter under the given value. Figure 2 (a) and (b) represents the particle morphology and particle size distribution for the polymerization n° 3 in Table 1.
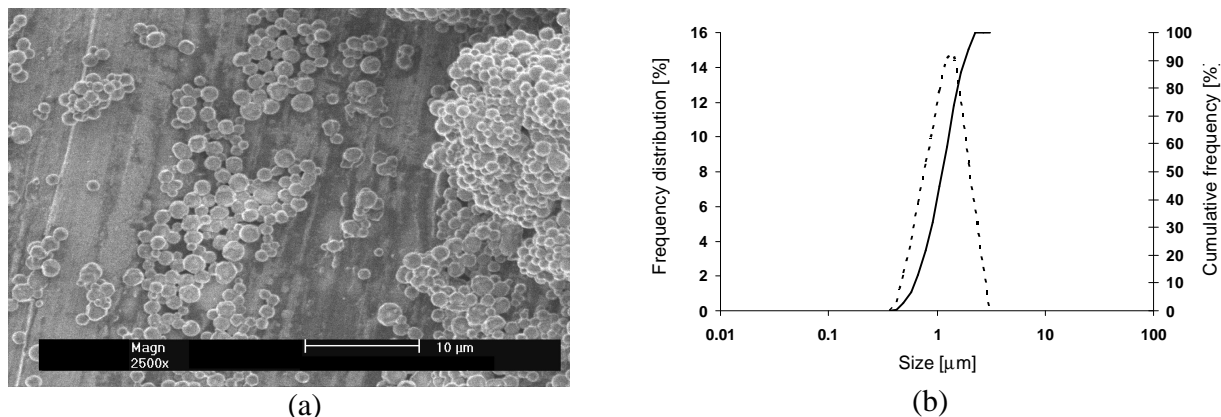
Figure 2: (a) SEM micrograph and (b) Particle size distribution of PMMA produced at 400 rpm

At commercial scale, stirring is essential to ensure thermal homogeneity and to avoid thermal runaway. With 10 wt% PDMS macromonomer the dispersion polymerization of MMA in scCO$_2$ can be realized under efficient stirring speed up to 600 rpm.
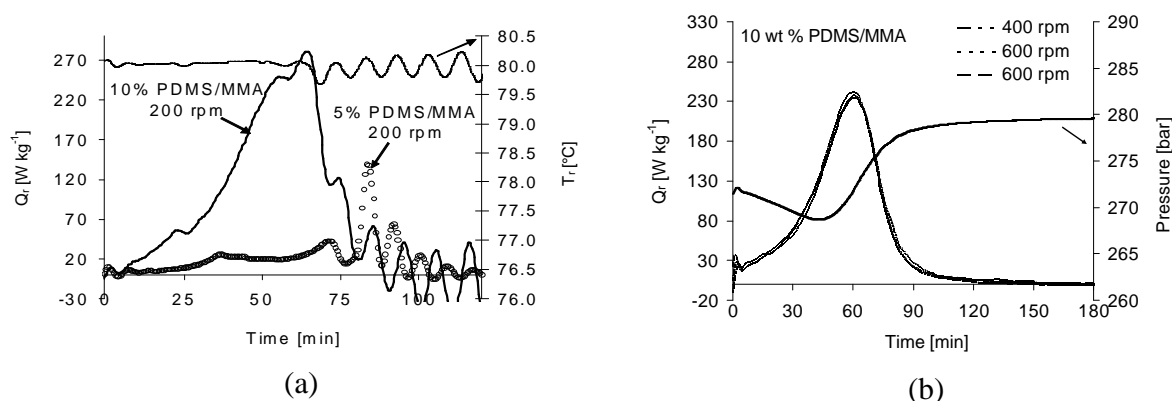

Figure 3: (a) Effect of PDMS concentration and (b) of stirring speed on the heat flow analysis

Figure 3 (a) shows that the profile of the heat released by the polymerization is dependent on the stabilizer concentration which has a direct influence on the dispersion stability. At 5 wt% PDMS macromonomer, the reaction rate and monomer conversion are low. Figure 3 (b) shows that with 10 wt% PDMS macromonomer the heat released by the polymerization does not depend on stirring speed. Moreover, it appears that the reaction calorimeter gives results with excellent reproducibility. Comparing Figure 3 (a) and (b) respect to stirring speed, it is observed that 200 rpm is a lower limit of stirring speed. In this case, the heat transfer is not efficient enough and the reaction calorimeter cannot control the reactor temperature precisely and quickly enough. Clearly, it is better to work at 400 or 600 rpm for quantitative analysis. The integration of the thermal curves allows calculating a mean value for the enthalpy of polymerization of -54.3 ± 3 kJ mol^{-1} being in agreement with literature value of -57.8 kJ mol^{-1} obtained in conventional solvents. Despite the high reproducibility of the experiments, the uncertainty of 3 kJ mol^{-1} on the enthalpy value comes from the integration methods employed (i.e. selected baseline, UA values utilization, etc.).

CONCLUSIONS

The poly(dimethylsiloxane) monomethacrylate with a molecular weight of 5000 g mol^{-1} is a suitable stabilizer for the dispersion polymerization of methyl methacrylate in scCO$_2$ under efficient stirring. The polymerization is taken as a model reaction for the development of supercritical reaction calorimetry. The measured enthalpy of polymerization is in agreement with previously reported data. The high reproducibility indicates that the reaction calorimeter operates accurately. Respect to the heat balance, evaluation and exploitation of parameters as the overall heat transfer coefficient and the heat dissipated by the stirrer could be improved. However, the results presented reveal the great potential of supercritical reaction calorimetry for the thermodynamic and kinetic study of chemical reactions under supercritical conditions

REFERENCES

[1] REGENASS, W., Journal of Thermal Analysis, Vol. 49, **1997**, p. 1661

[2] HYATT, J. A., Journal of Organic Chemistry, Vol. 49, **1984**, p. 5097

[3] DESIMONE, J. M., GUAN, Z., ELSBERND, C. S., Science, Vol. 257, **1992**, p. 945

[4] RINDFLEISCH, F., DI NOIA, T. P., McHUGH, M. A., Journal of Physical Chemistry, Vol. 100, **1996**, p. 115581

[5] GILES, M.R., HAY, J. N., HOWDLE, S. M., WINDER, R. J., Polymer, Vol. 41, **2000**, p. 6715

[6] HSIAO, Y.L., MAURY, E.E., DESIMONE, J.M. et al., Macromolecules, Vol. 28, **1995**, p. 8159

[7] O'NEILL, M.L., YATES, M.Z., JOHNSTON, K.P. et al., Macromolecules, Vol. 31, **1998**, p. 2838

[8] O'NEILL, M.L., YATES, M.Z., JOHNSTON, K.P. et al., Macromolecules, Vol. 31, **1998**, p. 2848

[9] FORTINI, S.,LAVANCHY,F.,MEYER, T., Macromolecular Symposia,Vol. 206, **2004**, p.79

[10] LAVANCHY, F., FORTINI, S., MEYER, T., Organic Process Research & Development, **2004**, in press,

[11] LEPILLEUR, C., BECKMAN, E.J., Macromolecules, Vol. 30, **1997**, 30, 745-756

[12] CHRISTIAN, P., GILES, M.R., HOWDLE, S.M. et al., Polymer, Vol. 41, **2000**, p. 1251