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Reaction Calorimetry for the Development of Ultrasound-Induced Polymerization Processes in CO_2-Expanded Fluids

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Summary: A strong viscosity increase upon polymerization hinders radical formation during an ultrasound-induced bulk polymerization. Since CO_2 acts as a strong anti-solvent for most polymers, it can be used to reduce the viscosity of the reaction mixture. In this work, a process for the ultrasound-induced polymerization in CO_2-expanded fluids has been developed. Temperature oscillation calorimetry has been applied to study the influence of CO_2 on the viscosity during the ultrasound-induced polymerization. In contrast to polymerizations in bulk, the results show that a low viscosity is maintained during polymerization reactions in CO_2-expanded methyl methacrylate (MMA). As a consequence, a constant or even increasing polymerization rate is observed when pressurized CO_2 is applied. Moreover, the ultrasound-induced polymer scission in CO_2-expanded MMA is demonstrated, which appears to be a highly controlled process. Finally, a preliminary sustainable process design is presented for the production of 10 kg/hour pure PMMA (specialty product) in CO_2-expanded MMA by ultrasound-induced initiation.

Keywords: cavitation; molecular weight distribution; pressurized carbon dioxide; radical polymerization; ultrasound

Introduction

The chemical effects of ultrasound arise from cavitation, i.e. the collapse of microscopic bubbles in a liquid. Upon implosion of a cavity, locally extreme conditions in the bubble occur (5000 K and 200 bar)[1] and high strain rates are generated outside the bubble ($10^7\ s^{-1}$).[2] Monomer molecules are dissociated by the high temperatures inside the hot-spot, whereas polymer chains are fractured by the high strain rates outside the cavitation bubble.[3–5] Since the radicals are generated in-situ by ultrasound, no initiator or catalyst is required to perform an ultrasound-induced polymerization. An additional advantage of this technique is the intrinsic safe operation, because turning off the electrical power supply will immediately stop the radical formation and consequently the polymerization reaction.

Viscosity is an important factor during ultrasound-induced bulk polymerizations as the long polymer chains formed upon reaction cause a drastic increase in the viscosity of the reaction mixture,[6] thereby hindering cavitation and consequently reducing the production rate of radicals.[7] Precipitation polymerization forms a potential solution to this problem, because a constant viscosity and hence a constant radical formation rate can be maintained. In this perspective, high-pressure carbon dioxide is an interesting medium as most monomers have a high solubility in CO_2, whereas it exhibits an anti-solvent effect for most polymers.[8]

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Up till now ultrasound is rarely studied at higher pressures, because in most cases a high static pressure hampers the growth of cavities. Recently, we have shown that cavitation is possible in pressurized CO_2.[9] Unlike ordinary liquids, carbon dioxide has a high vapor pressure, which counteracts the static pressure.[10] Cavitation is possible if the difference between the static and vapor pressure is smaller than the maximum acoustic pressure that can be applied.[11] Dense-phase fluids (with a strong emphasis on CO_2) provide possibilities for the development of sustainable polymer processes.[12,13] Additionally, ultrasound combined with high-pressure carbon dioxide allows the development of clean routes to produce polymers with specific properties, since no organic anti-solvents are required.

In this work, a process for the ultrasound-induced polymerization in CO_2-expanded MMA has been developed. For this purpose, ultrasound-induced polymerization and scission experiments have been performed in a RC1e HP60 reactor (Mettler-Toledo GmbH, Switzerland) extended with a Sonics and Materials VC-750 ultrasonic generator. Moreover, a preliminary process design of an ultrasound-induced polymerization process is presented for a 10 kg/h industrial plant to produce specialty PMMA.

Ultrasound-Induced Polymerization

In ultrasound-induced polymerization reactions, the viscosity has a large influence on the radical formation rate. Therefore, it is important to monitor the viscosity during these reactions. By coupling the overall heat transfer coefficient *U* to the viscosity of the reaction mixture, the influence of the CO_2-concentration on the viscosity of polymer solutions has been determined.[14,15]

$$\frac{1}{U} = \frac{1}{h_i} + \frac{D_i}{2k_w} \ln \frac{D_0}{D_i} + \frac{1}{h_0} \frac{D_i}{D_0} \tag{1}$$

In Equation 1 the heat transfer coefficient is based on the inside area of the reactor, for which h_i and h_o represent the partial heat transfer coefficients in the vessel and in the jacket, respectively; k_w stands for the thermal conductivity coefficient of the wall; D_i and D_o are the inner and outer diameter of the vessel.

The last two terms of Equation 1 remain constant during a polymerization reaction, because the properties of the reactor wall and cooling liquid will not change during the experiments. This is only true for low polymer concentrations present in the reaction mixture, as used for these experiment. If reactor fouling would occur at higher polymer concentration, obviously the assumption of constant properties of the reactor wall are no longer valid. However, when no fouling occurs and the last two terms of Equation 1 remain constant, *U* is an indirect measure of the viscosity of the reaction mixture, since the empirical relation for the Nusselt number (*Nu*) as a function of the Reynolds (*Re*) and Prandtl number (*Pr*) can be applied to couple h_i to the viscosity. Equation 5, which is derived from Equations 2, 3 and 4, shows the influence of the viscosity on the overall heat-transfer coefficient. An increase in the viscosity (μ) thus results in a decrease of the overall heat transfer coefficient.

$$Nu = \frac{h_i D_i}{k_i} = 0.75\,\mathrm{Re}^{2/3}\ \mathrm{Pr}^{1/3} \tag{2}$$

Where the Reynolds and the Prandtl number stand for:

$$\mathrm{Re} = \frac{\rho N D^2}{\mu} \tag{3}$$

$$\mathrm{Pr} = \frac{\mu C_p}{k_i} \tag{4}$$

$$\frac{1}{U} \sim \sqrt[3]{\mu} + \mathrm{Constant} \tag{5}$$

First some calibration experiments have been performed to determine the overall heat transfer coefficient U for polymer solutions in which no polymerization occurs. Figure 1A shows the influence of the polymer concentration (*Cpol*) and CO_2 fraction on U and consequently on the liquid viscosity. The plotted difference (ΔU) is calculated by subtracting U of the system with polymer present (*U(Cpol)*) from *U*

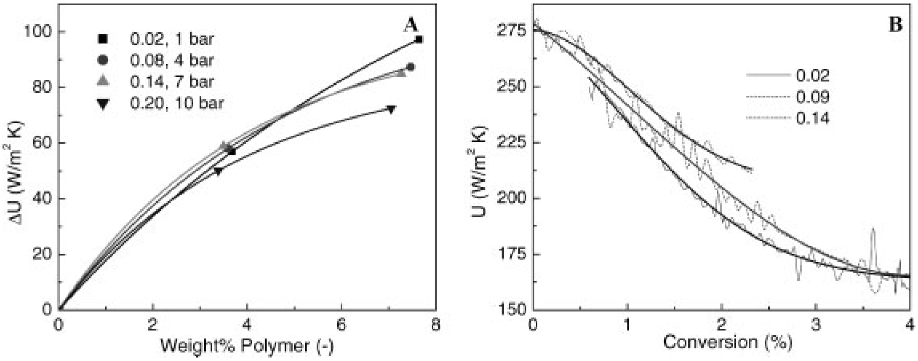

Figure 1.

A Heat transfer coefficient difference ΔU as a function of the polymer weight percentage at different CO_2 fractions. **B** Development of the overall heat transfer coefficient U during the polymerization reactions at three different CO_2 fractions.

without polymer ($U(0)$) at a given CO_2 fraction (Equation 6). The curves in Figure 1 give the trend of the heat transfer decrease and consequently the viscosity increase (Equation 5).

$$\Delta U = U(0) - U(C_{pol}) \qquad (6)$$

According to Figure 1A, at polymer concentrations above 4 weight percent, a distinct difference between the overall heat transfer coefficients at different CO_2 fractions is obtained. This is a clear evidence for the anti-solvent effect of CO_2, since at higher CO_2 fractions ΔU is lower due to a smaller increase in viscosity. The smaller viscosity enhancement is caused by a stronger anti-solvent effect, which forces the polymer coils to be less extended in the reaction mixture.[8] It is not a dilution effect, resulting from the expansion of MMA by CO_2, as this is taken into account by the calculation of the polymer concentration. It should be noted that the anti-solvent effect in Figure 1A is most clearly visible by comparing CO_2-fractions 0.02 and 0.20 at the highest polymer concentration measured, respectively.

Figure 1B shows the development of U upon polymerization, which is determined by temperature oscillation calorimetry.[16,17] It can clearly be seen that the decrease in U is smaller and hence the increase in viscosity is lower for higher CO_2 fractions during polymerization. This is a result of the smaller gyration radius of the polymer coils due to the anti-solvent effect.[8] No precipitated polymer has been observed at the final conversion.

In Figure 2, the ultrasound-induced bulk polymerization with argon, added to saturate the cavitation bubbles, is compared to the set of polymerization reactions pressurized with CO_2 (i.e. CO_2-fraction 0.02 versus CO_2-fractions 0.08, 0.14 and 0.20, respectively). In this comparison, it is obvious from both the conversion-time history as well as the polymerization rate curves that during the ultrasound-induced bulk polymerization the reaction rate is declining, whereas the polymerization rate remains constant or even increases when pressurized CO_2 is used. The variation in calculated reaction rates for the CO_2-fractions 0.08, 0.14 and 0.20, is simply caused by the inaccuracy of determining the derivative of the conversion-time history curves. Still, Figure 2A already shows the significant difference between the decrease in polymerization rate of the experiment with CO_2-fraction 0.02 versus the maintained reaction rate for the polymerizations with CO_2-fractions 0.08, 0.14 and 0.20, respectively.

Typically, in ultrasound-induced bulk polymerizations a maximum conversion of approximately 15% can be achieved.[7] At this conversion the collapse of cavitation

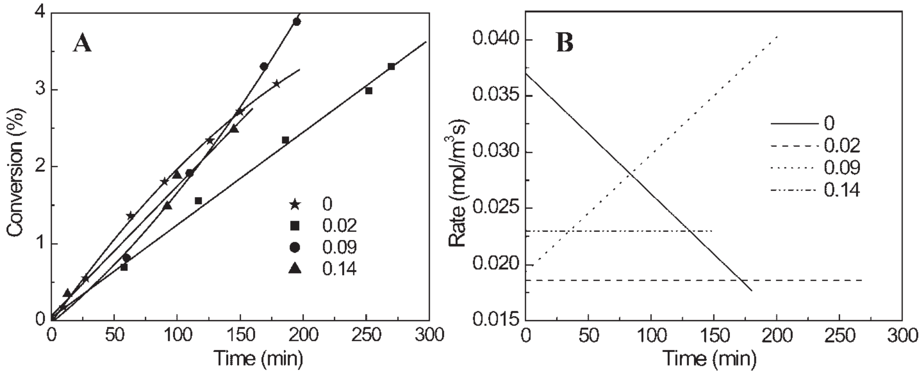

Figure 2.

Ultrasound-induced polymerizations in CO_2-expanded MMA at various CO_2 fractions. **A** Conversion-time history. **B** Reaction rates. Note that in the experiment without CO_2 present, argon has been added to saturate the cavitation bubbles.

bubbles is no longer sufficiently strong to generate radicals by ultrasound, due to the high viscosity. The decrease in viscosity by the CO_2 anti-solvent effect indicates that higher conversions in CO_2-expanded MMA as compared to bulk MMA would be possible. Moreover, at higher conversions the polymer will precipitate in the presence of an anti-solvent, due to which a constant viscosity is maintained and even higher conversions are expected.

Ultrasound-Induced Polymer Scission

Besides polymerization, ultrasound-induced polymer scission reactions have been investigated. Ultrasound-induced polymer scission is a well-controlled process, as fracture occurs approximately in the middle of the chain, see Figure 3. A mechanism is proposed for this non-random fracture behavior,[18] from which it can be concluded that complete stretching of the polymer chains is required before breakage can occur. The developed model, which is a combination of strain rate and drag force calculations, predicts a limiting molecular weight and a quadratic dependence of the polymer molecular weight on the scission rate, which have experimentally been confirmed. The developed degradation model is also capable to describe the effects of various process variables on cavitation-induced polymer scission, such as the lower scission rate at a higher liquid viscosity.

At increasing polymer concentration, the scission process becomes less effective and eventually stops. This is a drawback for the development of a scission process based on ultrasound, because concentrated polymer systems are favored in industry. The addition of an anti-solvent for the polymer can prevent the increase in viscosity at higher polymer concentrations. To determine the influence of CO_2 as an anti-solvent on the ultrasound-induced scission rate,

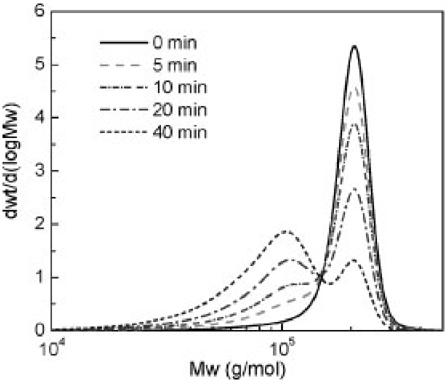

Figure 3.

Highly controlled ultrasound-induced polymer scission of 0.1 wt% PMMA in MMA in the presence of the radical scavenger 1,1-diphenyl-2-picrylhydrazyl (DPPH) to prevent further polymerization of the formed macro-radicals.

ultrasonic scission experiments of PMMA have been performed in bulk MMA as well as in CO_2-expanded MMA. Modeling the experimental time-dependent molecular weight distributions (MWD) has revealed the scission kinetics at different polymer concentrations and CO_2 fractions.[19] The model is composed of a dynamic bubble simulation and a bead-rod model. The dynamic cavitation calculations predict that total stretching of a polymer chain is possible during explosive growth and collapse of a cavitation bubble in microseconds. This is a prerequisite for scission at the polymer chain center. With the bead-rod model a limiting molecular weight of 6^*10^4 g/mol is calculated for PMMA dissolved in MMA, which has been experimentally confirmed. An almost squared dependence of the molecular weight on the scission rate is obtained from the measured time-dependent molecular weight distributions. Moreover, the general degradation model is capable to describe the effects of various process variables on cavitation-induced polymer scission.

Preliminary Process Design

Applications of ultrasound in processing and synthesis are widespread on laboratory scale. However, no industrial plant in which ultrasound initiates a polymerization reaction has been built so far. This is a consequence of the relatively low energy efficiency (10^{-5} J/J) for the generation of radicals in the ultrasound process,[20] which results in a high electrical power consumption. For the development of an economically feasible bulk process (larger than 5000 kg/h), the energy conversion still needs to be improved. For specialty products, however, it is expected that an ultrasound-based process can be viable. A product with a high-added value has thus to be produced, e.g. polymers for biomedical applications. These types of polymers have stringent demands concerning impurities, such as catalyst and initiator traces, residual monomer and organic solvents. With the ultrasound-induced polymerization process in CO_2, no initiators and organic solvents are required. In this work, a preliminary process design has been developed to produce 10 kg/hour pure PMMA (specialty product) in CO_2-expanded MMA by ultrasound-induced initiation, which has resulted in the clean, closed-loop process shown in Figure 4.[21]

The MMA fed to the reactor is converted to PMMA till a conversion of 15%. The product stream (2) consisting of PMMA, MMA and CO_2, is sprayed into the extraction column, in which it is contacted with supercritical CO_2 counter currently. The PMMA precipitates and the MMA dissolves in the supercritical phase. This extraction process is better known as the Supercritical Anti-Solvent process

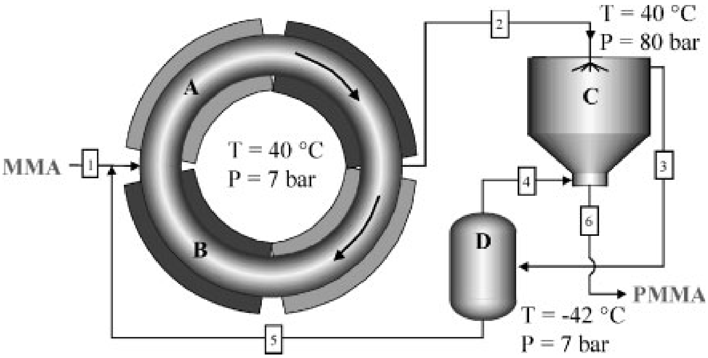

Figure 4.

Process flow diagram of the ultrasound-induced polymerization of MMA in CO_2-expanded MMA; with cavitation (A) and cooling areas (B) in a loop reactor, an extraction column (C) and a separation unit (D).

(SAS).[22] Typically, residual monomer concentration in the final product can go down to 10 ppm,[23] because of the significant extraction capacity of CO_2 for MMA. However, in literature no references have been found that describe the extraction of large amounts of MMA from PMMA. Therefore, it is assumed that 20 times (molar basis) the amount of CO_2 is required to produce pure PMMA. The resulting MMA/CO_2-stream from the SAS-column (3) is separated in a flash-drum (D) into almost pure CO_2 (4) and MMA (5). The flash-drum is operated adiabatically at 7 bar, resulting in an operation temperature of $-42\,^\circ C$. The cold CO_2 stream has to be recompressed to 80 bar before it can be reintroduced into the extraction column, which requires a compressor of 24 kW. By compression, the CO_2 is heated to $180\,^\circ C$, which has to be cooled down to $40\,^\circ C$. The cold MMA stream (5) can be added directly at multiple places into the loop reactor, which already results in a cooling capacity of approximately 30 kW.

Conclusions and Outlook to the Future

In this study, the potentials and challenges of ultrasound-induced polymerization and scission reactions in high-pressure fluids have been explored. It can be concluded that ultrasound allows producing well-defined polymers in CO_2-expanded fluids without using additional chemicals. Still, the energy consumption and the relatively low polymerization rates make it a relatively expensive way to produce polymers. An improved energy efficiency and polymerization rate would enable a larger application potential for ultrasound-induced polymerization processes than specialty polymers only. Although no large-scale industrial polymerization processes based on ultrasound exist yet, commercial applications in other fields such as ultrasound cleaning and sterilization prove that ultrasound is a readily available technique. Nevertheless, the application of ultrasound for polymerization purposes requires a thorough multidisciplinary understanding of ultrasound parameters, liquid properties and polymerization kinetics, for which reaction calorimetry has proven to be a indispensable tool.

Notation

μ	Viscosity (Pa s)
ρ	Density (kg/m^3)
C_p	Specific heat capacity (J/kg K)
D	Impeller diameter (m)
D_0	Outer diameter of reactor (m)
D_i	Inner diameter of reactor (m)
h_i	Partial heat transfer coefficient reactor (W/m^2 K)
h_0	Partial heat transfer coefficient jacket (W/m^2 K)
k_i	Conductivity of liquid inside reactor (W/m K)
k_0	Conductivity of liquid inside jacket (W/m K)
k_w	Conductivity of reactor wall (W/m K)
N	Stirrer speed (s^{-1})
Nu	Nusselt number (–)
Pr	Prandtl number (–)
Re	Reynolds number (–)
U	Overall heat transfer coefficient (W/m^2 K)

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