Effect of Stabilizer Concentration, Pressure and Temperature on Polymerization Rate and Molecular Weight Development in RAFT Polymerization of MMA in $scCO_2$

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Summary: An experimental study on the effect of stabilizer concentration, pressure (100 to 500 bar), and temperature (65 to 85 °C) on polymerization rate and molecular weight development in the reversible addition-fragmentation chain transfer (RAFT) polymerization of methyl methacrylate (MMA) in supercritical carbon dioxide ($scCO_2$) is presented. AIBN was used as initiator, S-Thiobenzoyl thioglycolic acid as RAFT agent, and Krytox® 257 FSL as stabilizer. It was observed that the polymerization proceeded in a controlled manner. High conversions can be reached in reasonable times. Fairly low polydispersities (around 1.2) are possible if either pressure or temperature are increased, but better results are obtained if the polymerization proceeds at the upper temperature value of 85 °C.

Keywords: dispersion polymerization; RAFT polymerization; supercritical carbon dioxide

Introduction

Supercritical carbon dioxide ($scCO_2$) has become a very attractive medium for polymerizations and other industrial processes because of its low toxicity, reasonably low cost, mild critical point ($T_c = 31.1\,°C$, $P_c = 73.8$ bar), and environmentally benign nature.[1,2] In recent years many polymers have been synthesized in $scCO_2$, including fluoropolymers, polysiloxanes, poly(methyl methacrylate), polystyrene, and polycarbonates.[3–6] Because of the low solubility of many polymers in $scCO_2$, these polymerizations have been carried in heterogeneous processes.[7–16] Therefore, the polymerization of these monomers in $scCO_2$ usually proceeds by dispersion polymerization processes, where active polymer chains grow in the continuous phase until a critical size is reached, and then precipitate. A stabilizer is usually needed to prevent coagulation or flocculation. The stabilizers most widely used in polymerizations in $scCO_2$ contain fluorinated or siliconated groups in the CO_2-phylic portion of the molecule. These compounds are highly soluble in $scCO_2$.[17–19]

Controlled radical polymerization (CRP) processes have allowed the synthesis of polymer materials with controlled microstructures which find uses in technologically important areas, such as aerospace, nanotechnology, industrial electronics, and biomaterials.[20–23] Reversible addition-fragmentation transfer (RAFT) polymerization has proven to be one of the most effective CRP processes because of its advantages over other CRP techniques (atom-transfer radical polymerization, ATRP, and nitroxide-mediated radical polymerization, NMRP), such as the applicability of the technique to a larger range of monomer types, reaction conditions (temperature and pressure), and processes (homogeneous and heterogeneous).[5–8]

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The RAFT polymerizations of styrene and methyl acrylate (MA) in $scCO_2$ have already been reported in the literature.[24,25] However, these pioneering polymerization studies apparently proceeded in the absence of stabilizers; only low to moderate conversions were achieved, and the attained values of polydispersity (PDI) were rather high. In the case of RAFT polymerization of methyl methacrylate (MMA) in $scCO_2$, effective control was obtained by using cyano dithiobenzoates.[26,27] The reaction conditions in each of these studies were the same in all the experiments.

In this paper a different RAFT controller and a broader range of polymerization conditions were used.

Experimental Part

MMA (Sigma-Aldrich) was used as received. AIBN (Akzo Nobel Chemicals) was recrystallized twice from methanol. Carbon dioxide (Praxair, 99.99% purity) was used as received. S-(Thiobenzoyl) thioglycolic acid (Sigma-Aldrich) was used as received. Krytox® 257 FSL (DuPont) was also used as received.

The polymerizations were conducted in a 38 mL high-pressure view cell, equipped with two frontal Sapphire windows (Crystal Systems Inc.®), which allowed visual observation of the reaction mixture. A Dual Syringe Pump System (Teledyne ISCO®) was used to handle the CO_2 and bring it to supercritical conditions. The reactor was charged with monomer, initiator, RAFT agent, stabilizer and a magnetic stirring bar. Then, it was purged with a slow flow of CO_2, and pressurized with CO_2 until a given pressure, lower than the desired reaction pressure. Next, the reactor was placed into a warm water bath, and heated to the desired reaction temperature. Once this temperature was reached and controlled, pressure was increased to the desired reaction pressure by loading additional CO_2. The reaction mixture was stirred using the magnetic bar. The reaction proceeded until the desired time was reached. The product was washed with methanol, and then dried at 40 °C in an oven until constant weight. Total monomer conversion was determined gravimetrically.

Molecular weight development (M_n and M_w) was followed by size exclusion chromatography (SEC or GPC) using a Waters Alliance 2695 chromatograph. The GPC was equipped with a Shodex column bank from KF-801 to KF-804 and Waters 2414 refractive index, Waters 2996 PDA, and Viscotek 270D intrinsic viscosity detectors. Polystyrene standards from Polymer Standards Service Inc., ranging from MW = 392 to 3,151,000 Da were used.

Results and Discussion

Four studies are reported in this paper. The first study was focused on the effect of stabilizer initial concentration on polymerization rate (PR) and molecular weight development (MW-D) in RAFT polymerization of MMA in scCO2. Secondly, a kinetic study using a recipe based on the previous study was produced. The third and fourth studies were focused on the effects of pressure (in a range from 100 to 500 bar) and temperature (65 to 85 °C), respectively, on PR and MW-D.

Effect of Stabilizer Concentration

Although the stabilizer used by us has been used before in polymerization of MMA in $scCO_2^9$, in our system there was an additional ingredient in the recipe (the RAFT controller). Therefore, we carried out a study varying the amount of stabilizer in order to determine an adequate amount of stabilizer for our other studies. For this study, the mass of monomer was 8 g (20 wt./v-%), AIBN was used as initiator at a concentration of 0.0128M, S-Thiobenzoyl thioglycolic acid (the RAFT agent) was used at a concentration of 0.0128M, and the amount of Krytox® 257 FSL (the stabilizer) was variable. Other polymerization conditions were: T = 75 °C, P = 350 bar, and the speed of agitation was 500 rpm. The

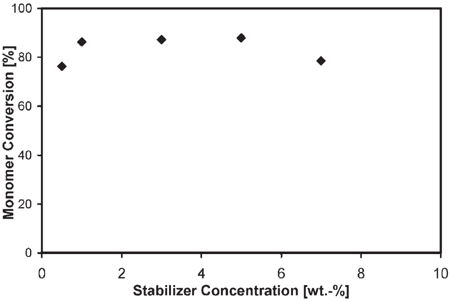

Figure 1.
Effect of stabilizer concentration on monomer conversion at 16 hours of polymerization.

polymerizations were stopped at 16 hours in the five runs of the study.

It is observed in Figure 1 that the conversion achieved at 16 hours of polymerization is rather insensitive to the amount of stabilizer used. Amounts of stabilizer as small as 1 wt.-% seem to be adequate for our system. However, a stabilizer concentration of 3 wt.-% was chosen for our remaining studies. The values of weight average molecular weight (M_w) and PDI corresponding to the cases plotted in Figure 1 are summarized in Table 1. It is observed that although low M_w values and PDIs lower than 1.5 were obtained, the degree of control attained with this RAFT agent was not very good.

Kinetic Study

The reaction conditions used for the kinetic study were the following: 20 wt./v-% (8 g) of MMA, 0.0128 M of AIBN, 0.0128 M of S-Thiobenzoyl thioglycolic acid, 3 wt.-% of Krytox® 257 FSL, T = 75 °C, and P = 350 bar.

Table 1.
Summary of conversion and MW-D data for the study on the effect of stabilizer concentration on monomer conversion at 16 hours of polymerization.

Krytox, wt.-%	*MMA, percentage conversion*	*M_n, g mol^{-1}*	*PDI*
0.5	76.25	11,550	1.36
1	86.29	11,710	1.39
3	87.30	14,500	1.41
5	87.91	11,610	1.33
7	78.57	12,750	1.57

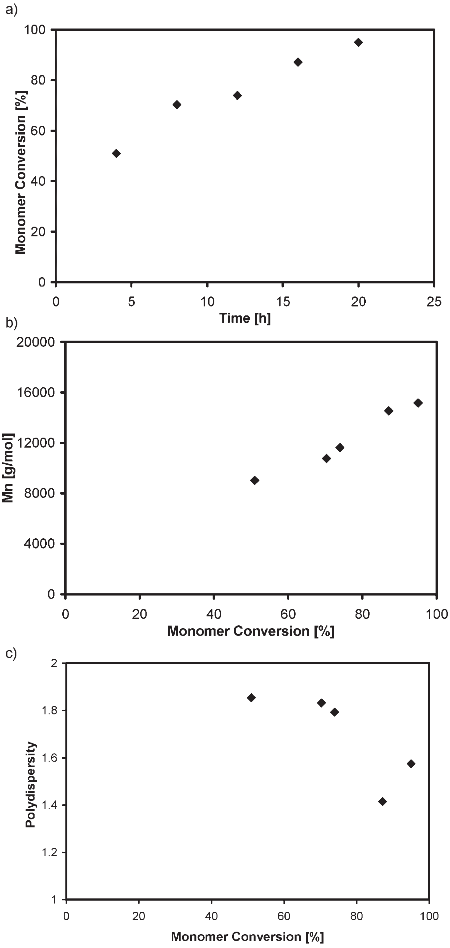

Figure 2.
RAFT polymerization of MMA in $scCO_2$ at T = 75 °C and P = 350 bar: (a) %-conversion versus time, (b) M_n versus %-conversion, and (c) PDI versus %-conversion.

It is observed in Figure 2a that high monomer conversions are achieved in less than 20 hours. The linear relationship between M_n and conversion observed in Figure 2b suggests that the polymerization proceeds in a controlled manner. However, the PDIs obtained (Figure 2c) are fairly high for a controlled system, and certainly higher than those obtained in previous studies using other RAFT agents.[30,31] Although rather high PDIs were obtained using S-Thiobenzoyl thioglycolic acid as RAFT agent (see Figure 2c), this kinetic study shows that the polymerization proceeds in a controlled manner, and that high monomer conversions are attainable in reasonable times (for a controlled polymerization). The fact that this controller is not effective for RAFT polymerization of MMA in $scCO_2$ (in the range of conditions of the present study) may not be related to the fact of carrying out the polymerization in $scCO_2$, since very good performance of this RAFT agent for dispersion polymerization of styrene in $scCO_2$ has been observed.[32] In order to determine if good control is possible using S-Thiobenzoyl thioglycolic acid for RAFT polymerization of MMA in $scCO_2$ at other polymerization conditions, other two studies at higher pressures and temperatures were conducted.

Effect of Pressure

The reaction conditions used for the pressure study were as follows: 20 wt./v-% (8 g) of MMA, 0.0128 M of AIBN, 0.0128 M of S-Thiobenzoyl thioglycolic acid, 3 wt.-% of Krytox® 257 FSL, T = 75 °C, and pressure (P) was varied from 100 to 500 bar. All the experiments of this study proceeded for 16 hours.

It is observed in Figure 3a,b that monomer conversion and M_n increase linearly with pressure. This is caused by the increased solvent power of CO_2 as density increases due to the higher pressure of the system. It is observed in Figure 3c that PDI is insensitive on pressure in the range 100 to 300 bar, but at higher pressures, the obtained PDI values decrease significantly, reaching a fairly low PDI (around 1.25) at 500 bar.

Effect of Temperature

The reaction conditions used for the temperature (T) study were as follows: 20 wt./v-% (8 g) of MMA, 0.0128 M of AIBN, 0.0128 M of S-Thiobenzoyl thioglycolic acid, 3 wt.-% of Krytox® 257 FSL, P = 300 bar, and temperature (T) was varied from 65 to 85 °C. All the experiments of this study proceeded for 16 hours.

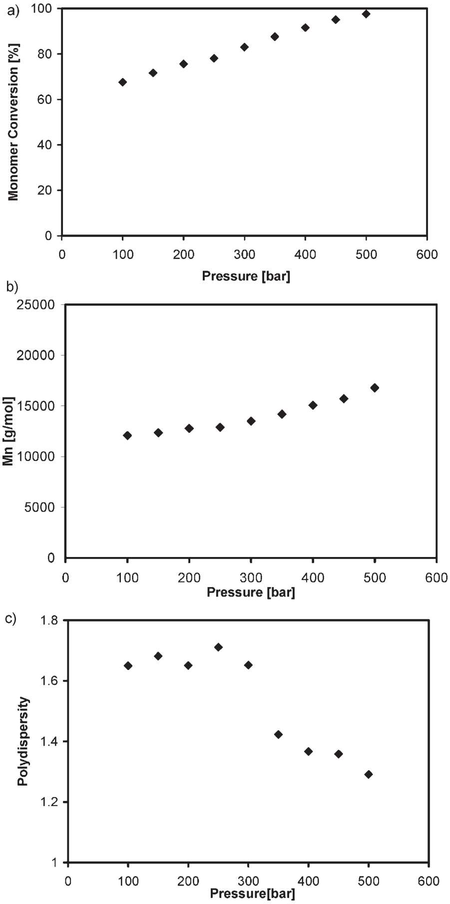

Figure 3.
Effect of pressure (T = 75 °C) on (a) %-monomer conversion, (b) M_n, and (c) PDI at 16 hours of polymerization in RAFT polymerization of MMA in $scCO_2$.

It is observed in Figure 4a,b that conversion and M_n increase moderately as temperature is increased. On the other hand, the effect of T on PDI is quite significant with PDI reaching a value lower than 1.2 at 85 °C, which was our T-upper limit in the study. This temperature effect can of course be explained by the effect of T on the individual rate constants of the reactions involved in the RAFT polymerization scheme, which has been studied in detail for conventional (in the absence of CO_2) systems.[33]

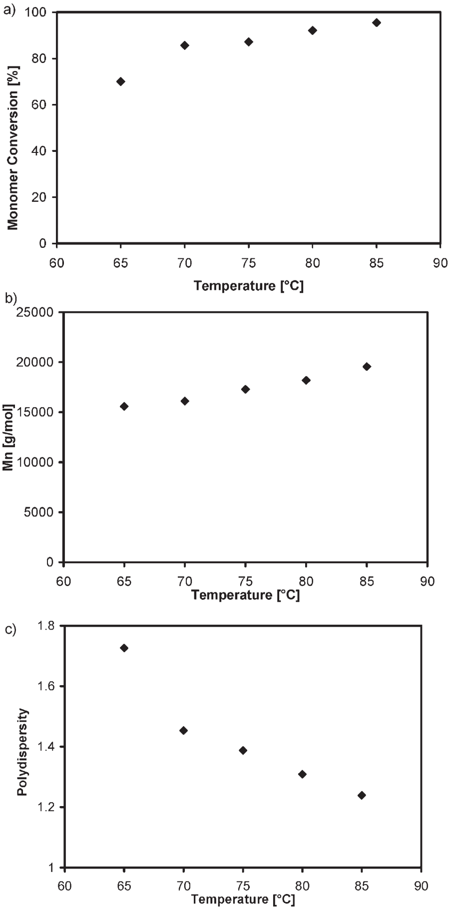

Figure 4.
Effect of temperature (at $P = 300$ bar) on: (a) %-monomer conversion, (b) M_n, and (c) PDI at 16 hours of polymerization in RAFT polymerization of MMA in $scCO_2$.

Concluding Remarks

S-Thiobenzoyl thioglycolic acid, a readily available RAFT controller, is adequate for RAFT polymerization of MMA in $scCO_2$ if the polymerization is carried out at pressures not lower than 300 psi, and temperatures no lower than 85 °C. If lower T and P are used, controlled behavior is possible, but the attained PDIs are rather high.

Although our report is not the first one addressing the issue of RAFT polymerization of MMA in $scCO_2$, we have used a different (commercially available) RAFT agent, and we have focused on the important effects of stabilizer, pressure and temperature on polymerization rate and molecular weight development, thus making our study quite complete.

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