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"Living" Polymer Beads in Supercritical CO_2

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Recently, controlled radical polymerization techniques have received considerable interest because of the ability to synthesize species exhibiting precise molecular architecture.[1] The (reversible addition fragmentation chain transfer) RAFT technique allows the formation of polymers with a very narrow molecular weight distribution from a wide range of monomers.[2,3] In addition, the resulting polymer is free from undesirable metal catalysts that are present following other controlled polymerization techniques (e.g., atom transfer radical polymerization).[4] Other authors have shown that RAFT-mediated polymerizations can occur in supercritical CO_2, and product with low polydispersity (PDI), albeit low conversion, was generally observed.[5−8] Hydrophilic/CO_2-philic stabilizers were synthesized by RAFT[9,10] and in one case used in the dispersion polymerization of poly(hydroxyethyl methacrylate).[9] However, the RAFT-terminated stabilizer was not used to control the kinetics of the polymerization, and low PDIs were not observed. Our work takes a significant step further, yielding high conversion, high molecular weight polymer and living microparticles.

Supercritical fluids have emerged as acceptable replacements for organic solvents. $scCO_2$ is nontoxic, nonflammable, and inert and has an easily accessible critical point ($T_c = 31.0$ °C, $P_c = 7.38$ MPa).[11] Since the first successful radical dispersion polymerization in $scCO_2$ by DeSimone and co-workers,[12] numerous authors have reported successful polymerizations of various vinyl monomers.[13−17] While careful control of the solvent density can lead to polymer particles with well-defined morphology, simultaneous control over the polymer molecular weight remains elusive. This is a common factor in all solvents due to phase partitioning effects in the heterogeneous polymerization process.[18,19] Our strategy is to use $scCO_2$ as a solvent and plasticizing agent for the controlled/living dispersion polymerization of methyl methacrylate (MMA). The CO_2-soluble RAFT agent (α-cyanobenzyl dithionaphthylate (α-CBDN))[20] was added to the reaction vessel in varying concentrations (Table 1). The crucial aspect for a successful controlled polymerization is the requirement for the RAFT agent, or RAFT−oligomer species, to acquire sufficient mobility within the polymer particle over all conversion ranges. This was successfully facilitated by $scCO_2$. We present results demonstrating both high conversion and high molecular weight while maintaining very good control over the PDI of the resultant polymer particles.

To date, successful control over the molecular weight in dispersion polymerizations has been inhibited by the poor diffusion of the controlling agent in the polymer particle.[21] A few reports have recently appeared in which stabilizers have been synthesized with an anchoring nitroxide[22] or ATRP[23] initiator for use in $scCO_2$. In these cases, the controlling agent is confined to the surface of the particle. For free RAFT agents, we show that the excellent mass transfer properties of $scCO_2$ sufficiently plasticize the polymer, leading to effective chain transfer within the particle.

The polymerization was conducted in $scCO_2$ using 5 wt % stabilizer (PDMS-MA, 10 kDa). This stabilizer has been shown to be particularly effective in stabilizing polymer dispersions in $scCO_2$.[24] All reactions were performed at 65 °C and 27.6 MPa (4000 psi) (see Supporting Information). Conventional dispersion polymerization in $scCO_2$ in the absence of RAFT results in polymer with high molecular weight and a broad molecular weight distribution after only 10 h reaction time (Table 1, entry 1, and Figure 1). The addition of a 1:1 molar ratio of α-CBDN to initiator resulted in a retarded rate of polymerization and a polymer product with lower molecular weight and conversion. Entries 1−6 in Table 1 show the progressive increase in molecular weight of the polymer particle as a function of reaction time. In all reactions the polydispersity is less than about 1.2, and SEM micrographs showed the

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Table 1. RAFT-Mediated Polymerization of MMA in scCO$_2$

entry	time/h	[AIBN]:[αCBDN]	M_n[b]	M_w[b]	PDI	M_{nt}[c]	conversion[d]/%	appearance[e]
1	10	1:0	73 000	189 000	2.59	50 000	99	powder
2	10	1:1	3 800	4 100	1.09	4 250	17	liquid + solid
3	11	1:1	8 600	9 400	1.10	9 250	37	viscous liquid + solid
4	12	1:1	18 600	21 800	1.17	18 750	75	tacky solid
5	14.5	1:1	22 900	27 700	1.21	23 500	94	powder
6	18	1:1	28 800	34 300	1.19	24 750	99	powder
7[f]	14.5/24	1:1	62 000	90 000	1.45	70 500	99	powder
8[g]	24/48	1:1	34 000	48 000	1.41	40 100		powder

[a] Reactions performed with MMA (1.56 M), RAFT (6.23×10^{-3} M), and 5 wt % PDMS (wrt monomer) in 60 mL autoclave at 65 °C and 27.6 MPa, unless otherwise stated. [b] Calibrated with poly(styrene) standards in THF using a refractive index detector. [c] Theoretical molecular weight. [d] From ^{1}H NMR. [e] Appearance upon opening autoclave. [f] Entry 5 (1 g) redispersed with 3 mL of MMA and AIBN in scCO$_2$. [g] Performed in modified 20 mL autoclave (28 mol % PSTY in final copolymer).

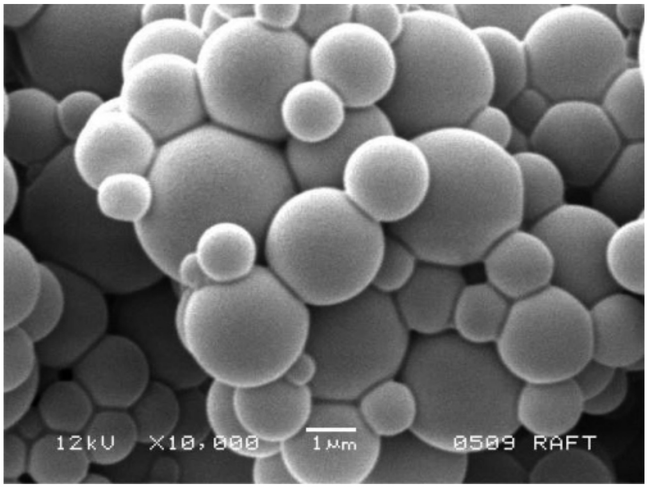

Figure 1. SEM image of microparticles formed during the RAFT-mediated dispersion polymerization of MMA in scCO$_2$. The particles have a well-defined, spherical morphology and a polydispersity <1.2.

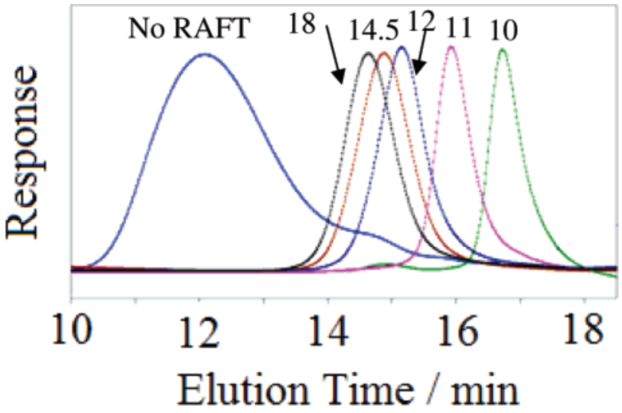

Figure 2. GPC traces for PMMA formed in scCO$_2$ at 65 °C (1:1 α-CBDN:AIBN; 5 wt % PDMS stabilizer) with polymerization times of 10, 11, 12, 14.5, and 18 h (marked on figure). A reference trace is shown for PMMA formed in the absence of α-CBDN (10 h).

formation of well-defined, micron-sized, spherical polymer particles (Figure 2). We found that the high concentration of initiator relative to RAFT did not affect the molecular weight distribution, presumably due to the slow decomposition kinetics of AIBN in scCO$_2$ compared to conventional solvents.[25]

The narrow molecular weight distribution exhibited by polymer formed in the presence of RAFT agent suggests that a high degree of control is exerted over the reaction. While the low PDI is indicative of controlled reaction conditions, the "livingness" is proven by the increase in molecular weight as a function of conversion. This is highlighted in Figure 1, in which GPC traces are shown for entries 1−6 of Table 1 (the small peak at ∼15 min is due to residual surfactant in the sample). A gradual increase in molecular weight with conversion suggests that the "livingness" of the reaction is retained throughout the whole reaction (Figure 1). Furthermore, the molecular weight of the polymer closely matches the theoretical molecular weight based on RAFT concentration.[2] Indeed, further evidence for a living polymerization is observed by reinitiation of purified PMMA with additional MMA (Table 1, entry 7). 1 g of RAFT-terminated PMMA from a previous reaction (M_n 23 kDa; Table 1, entry 5) was loaded into the autoclave with 3 mL of MMA and reacted in scCO$_2$ with additional initiator and stabilizer for 24 h at 65 °C. The GPC trace of the resultant polymer (M_n = 62 kDa) was unimodal with a narrow molecular weight distribution (Table 1, entry 7). Furthermore, the peak due to PMMA at 23 kDa was not present in the GPC trace. This suggested that chain extension was effective in scCO$_2$. Such repropagation of a RAFT-terminated polymer is a requisite characteristic of a reversible-termination mechanism. Indeed, this result provided further evidence for the "living" nature of this dispersion polymerization in scCO$_2$ and highlighted the applicability of this technique for the controlled synthesis of block copolymers exhibiting well-defined morphology.

This technique is also suitable for the synthesis of block copolymers. Following the polymerization of MMA, styrene and AIBN were injected into the autoclave through a high-pressure injection port without the need to depressurize the system (20 mL autoclave). This ensured that the particulate nature of the preformed PMMA was not altered by the introduction of styrene monomer. After reaction of the styrene (48 h) a polymer powder was recovered (Table 1, entry 8). GPC revealed a unimodal distribution with M_n of 34 kDa and PDI of 1.41 upon copolymerization of MMA with styrene. SEM showed that the spherical morphology was retained in the copolymer (Supporting Information). This is the first report of block copolymers being formed using free RAFT agent in a dispersion polymerization.

One issue with RAFT agents for commercial use is the color of the resultant polymer. Apart from the aesthetic disadvantage, a degree of toxicity arises from the RAFT agent. Additionally, the mechanism of RAFT polymerization means that the controlling agent is not recovered at the end of the process. We have adopted a technique proposed by Perrier for the removal of the RAFT agent.[26] In our case, the challenge was to remove the color while maintaining the morphology of the particles.

In a typical RAFT-mediated dispersion polymerization of MMA in scCO$_2$, the polymer exhibits a strong pink color due to the dithioester moiety. In order to remove the end group while maintaining the particulate morphology of the particles, a 20:1 excess of initiator (AIBN) compared to RAFT agent was added to the reaction vessel at the completion of the polymerization step. The particles were stirred under polymerization conditions for 12 h (65 °C at 4000 psi) (see Supporting Information). The

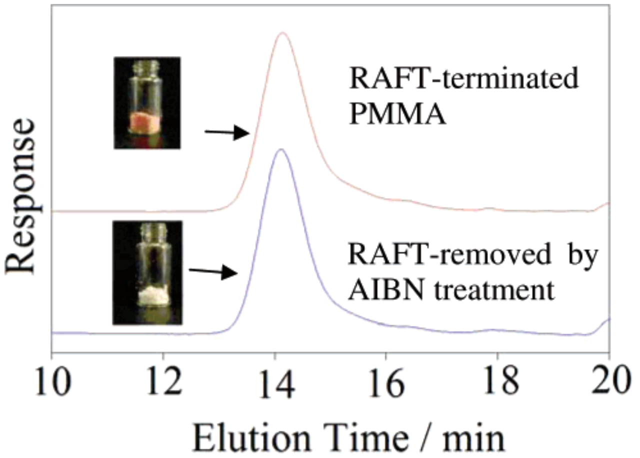

Figure 3. GPC trace of PMMA microparticles formed by RAFT-mediated polymerization in $scCO_2$, before and after removal of the RAFT end group. Photographs of the powder are included to show that the microparticles change from pink (when terminated by RAFT) to white (when RAFT agent is removed).

particles were then washed with $scCO_2$ in order to remove the RAFT end groups from the reactor. The flushed eluent was collected as a viscous pink liquid and confirmed by NMR to be a complex mixture of PMMA oligomers and RAFT components. The resulting polymer powder was white, thus suggesting the removal of the dithioester end groups (Supporting Information). NMR analysis showed that RAFT groups were now absent from the polymer, suggesting that the removal was complete; the doublet at 7.96 ppm from the naphthyl group adjacent to the dithio moiety was absent in the spectrum following the RAFT removal. Importantly, GPC analysis showed that the polymer molecular weight and polydispersity were not affected by the process (Figure 3), and the SEM confirmed the particulate nature of the particles was retained. The success of this process is attributed to the excellent transport of the AIBN radicals throughout the system by the $scCO_2$. The recovery of colorless particles that retain their molecular and morphological characteristics makes this technique more valuable for commercial applications—for example, retention of morphology would be important for the coatings industry or for the development of well-defined core−shell type materials.

We have demonstrated successful RAFT-mediated polymerizations in $scCO_2$ in which polymer was synthesized to high conversion and high molecular weight. Furthermore, polymer particles of well-defined morphology have been produced with a narrow molecular weight dispersity. Our approach has been extended to the synthesis of well-defined block copolymers. Indeed, the versatility of the RAFT system employed and the advantages of $scCO_2$ predispose this technique to a wide variety of applications. Further development of this method and investigation of the block copolymer phase behavior in the particles are currently underway in our laboratory.

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Supporting Information Available: Experimental procedure for homopolymer and copolymer synthesis, in addition to a procedure for removal of RAFT end group; SEM image of copolymer particles. This material is available free of charge via the Internet at http://pubs.acs.org.

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