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In situ synthesis of fluorinated diblock copolymer nanoparticles via RAFT dispersion polymerization in supercritical carbon dioxide

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Abstract. Synthesis of the fluorinated diblock copolymer nanoparticles of poly(dodecafluoroheptyl methacrylate)-*b*-poly(methyl methacrylate) (PDFMA-*b*-PMMA) by RAFT dispersion polymerization is performed in supercritical carbon dioxide. Fluorinated macro-RAFT agents were first prepared via RAFT solution polymerization and characterized by NMR and GPC. The RAFT-terminated poly(dodecafluoroheptyl methacrylate) (PDFMA) homopolymers actually act as in situ stabilizer for the subsequent synthesis of the PDFMA-*b*-PMMA block copolymer nanoparticles by RAFT dispersion polymerization while exhibiting good control on the well defined spherical particles formation. SEM images show that the average size of these synthesized diblock copolymer nanoparticles was 425 nm with a narrow size distribution (1.13), which are close to the literature data for conventional MMA dispersion polymerization with a fluorinated CO₂-philic stabilizer in ScCO₂.

1. Introduction

It is well known that amphiphilic AB diblock copolymers can self-assemble to form sterically stabilized nanoparticles in selective solvent for one of the two blocks [1, 2]. Usually, the formation strategy of diblock copolymer nanoparticle is through the micellization of amphiphilic block copolymer in the block selective solvent [3, 4]. However, this micellization strategy suffers from the drawbacks of the time consuming multiple steps and the post-polymerization techniques such as solvent or pH-switching or thin film rehydration. Recently, many academic groups have examined the use of polymerization-induced self-assembly (PISA) techniques for the synthesis of amphiphilic diblock copolymer nanoparticles in situ using either emulsion or dispersion controlled radical polymerization, particularly reversible addition–fragmentation chain transfer (RAFT) [5-7]. This PISA strategy now provides robust synthetic methods for the synthesis of diblock copolymer nanoparticles.

Supercritical carbon dioxide (ScCO₂) was a superior solvent for carrying out polymerization reactions owing to its low-cost and its multitudinous environmental benefits [8-11]. In addition, the separation of solvent from polymer product is easy because CO₂ reverts to the gaseous state upon depressurization, thus eliminating energy intensive drying steps. The use of ScCO₂ for the preparation of block copolymer with controlled radical polymerization has been summarized [12]. This method for fluorinated polymer synthesis in scCO₂ is an effective technique, particularly [13-15]. Moreover,



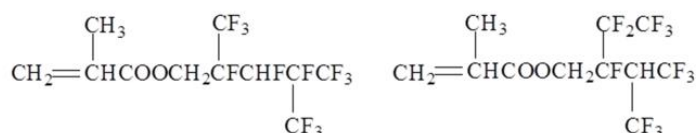
desired block copolymer structures with very high blocking efficiencies can be obtained for the ScCO_2 -induced plasticization of polymer [16].

A lot of scientists have carried out the PISA strategy for the in situ synthesis of diblock copolymer nanoparticles in water or non-aqueous (such as alcohols and alkanes) media [17, 18]. However, attempts in ScCO_2 fluorinated diblock copolymer particles synthesis are few [19, 20]. Therefore, we studied the in situ synthesis of fluorinated diblock copolymer nanoparticles in ScCO_2 using a fluorinated macro-CTA agent as the stabilizer. Our results clearly demonstrate that well-defined spherical nanoparticles with a narrow size distribution were formed via the PISA strategy.

2. Experimental section

2.1. Materials

Dodecafluoroheptyl methacrylate (DFMA, >96%, the structure of two isomers of this monomer was shown in scheme 1) was purchased from XEOGIA Fluorine-Silicone Chemical Co. Ltd (Harbin, China), and methyl methacrylate (MMA, >99%) was purchased from Sigma-Aldrich both of them passed through basic alumina column to remove inhibitor. The initiator 2,2-azobisisobutyronitrile (AIBN) was purchased from Kermeland recrystallized from methanol prior to use. The RAFT agent S-1-dodecylS'-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (DDMAT) was synthesized using the published procedure[21]. All other chemical agents were used directly.



Scheme 1. The structure of two DFMA isomers.

2.2. Synthesis of fluorinated macro-CTA agent

In a typical experiment, DFMA(10.0 g, 25mmol), AIBN(0.027 g, 0.17 mmol), DDMAT (0.303 g, 0.83 mmol) and THF (30 g) were weighed into a 100 mL round-bottomed flask, respectively, and then purged with N_2 for 5 min. After purged with nitrogen, the reactor was placed in a water bath at 70 °C with continuous stirring. At the end of polymerization, the round-bottomed flask was cooled in an icewater bath to terminate the polymerization process. The product was precipitated by excess methanol, washed several times, and dried in a vacuum oven for 24 h.

2.3. Synthesis of fluorinated diblock copolymer nanoparticles

A typical procedure involved use of a 30 mL high pressure autoclave with a magnetic stirrer, which was charged with macro-RAFT agent PDFMA-DDMAT (0.495 g, 0.04 mmol), MMA (1.500 g, 15 mmol) and AIBN (0.003 g, 0.01 mmol) sequentially. The autoclave was sealed and degassed with vacuum pump for 1 min to remove oxygen. Designed amounts of CO_2 were then added into the reactor and the system was then heated up to 70 °C at 30 MPa. At the end of the reactions, the reactor was cooled in cold water, and the CO_2 was slowly vented. The polymer product was collected and weighed.

2.4. Characterization

^1H NMR spectra were measured on Advance III 400 MHz NMR spectrometer (Bruker, Faellanden, Switzerland) in deuterated acetone solvent with tetramethylsilane as the internal standard. The number-average molar weight (M_n), the weight-average molar weight (M_w) and the distribution were determined by gel permeation chromatography (GPC) with THF as the eluent. The morphology of the fluorinated nanoparticles was characterized by scanning electron microscopy (SEM) (S-2500, Hitachi Seiki Ltd., Japan). Samples were mounted on aluminum foil sputter-coated with gold before analysis. The particle size (D_n) and size distribution (D_w/D_n) was determined by counting at least 100 microspheres from the SEM micrographs by using nano-measurer.

3. Results and discussion

3.1. Synthesis of fluorinated macro-CTA agent

The RAFT solution polymerization of DFMA was performed in tetrahydrofuran (THF) at 70 °C with DDMAT as the RAFT chain transfer agent (CTA) and AIBN as the source of primary radicals. Each DFMA homopolymerization was terminated at 65-72% conversion to refrain from monomer-starved conditions, thus maintaining RAFT end-groups for PDFMA homopolymer [22]. This is usually demanded for a excellent blocking efficiency and therefore well-defined diblock copolymers.

The GPC traces (Figure 1) of the synthesized fluorinated macro-CTA agent are symmetrical and unimodal and the molecular weight of $M_{n, GPC}$ at 9.4 kg/mol with $M_{w, GPC}/M_{n, GPC}$ 1.13 is obtained. Figure 2(B) is the 1H NMR spectra of the PDFMA-DDMAT macro-RAFT agent, from which the characteristic chemical shifts due to the protons in the PDFMA units and in the DDMAT-terminated group (Figure 2(A)) are all clearly observed. Based on the characteristic chemical shift of the DDMAT terminal group at 1.35 ppm (b) and the PDFMA homopolymer backbone at 4.50 ppm (h), the molecular weight $M_{n, NMR}$ at 8.8 kg/mol of the PDFMA-DDMAT macro-RAFT agent and the polymerization degree (DP) at 21 is calculated according to equation 1. According to equation 2, the theoretical molecular weight $M_{n, th}$ of the PDFMA-DDMAT macro-RAFT agent, 9.0 kg/mol, is calculated. It is found that $M_{n, NMR}$ of the PDFMA-DDMAT macro-RAFT agent is very close to $M_{n, th}$. Three PDFMA macro-CTAs were characterized using 1H NMR spectroscopy and the DP was estimated to be 13, 21 or 31, respectively.

$$M_{n, NMR} = DP \times M_{DFMA} + M_{DDMAT}$$

$$= \frac{I_{4.50}}{I_{1.35}} \times 5 \times M_{DFMA} + M_{DDMAT} \quad (1)$$

$$M_{n, th} = \frac{[DFMA]_0 \times M_{DFMA}}{[DDMAT]_0} \times \text{conversion} + M_{DDMAT} \quad (2)$$

Table 1 summarizes these synthesized fluorinated macro-CTA agents: all records were shown to be relatively narrow molecular weight distributions ($M_w/M_n < 1.21$), which is in accord with other studies reporting desired block copolymer syntheses[19,23]. Kinetic inspections of the typical PDFMA-DDMAT macro-CTA agent synthesis using RAFT solution polymerization was conducted (Figure 3). The results of GPC analysis implied a linear evolution of molecular weight with conversion, which indicated a pseudo-living behavior throughout the polymerization.

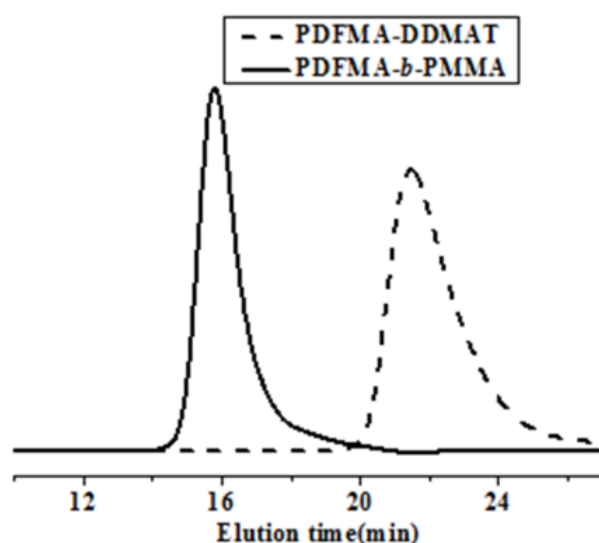


Figure 1. The GPC traces of the PDFMA-DDMAT macro-RAFT agent and the PDFMA-*b*-PMMA diblock copolymer.

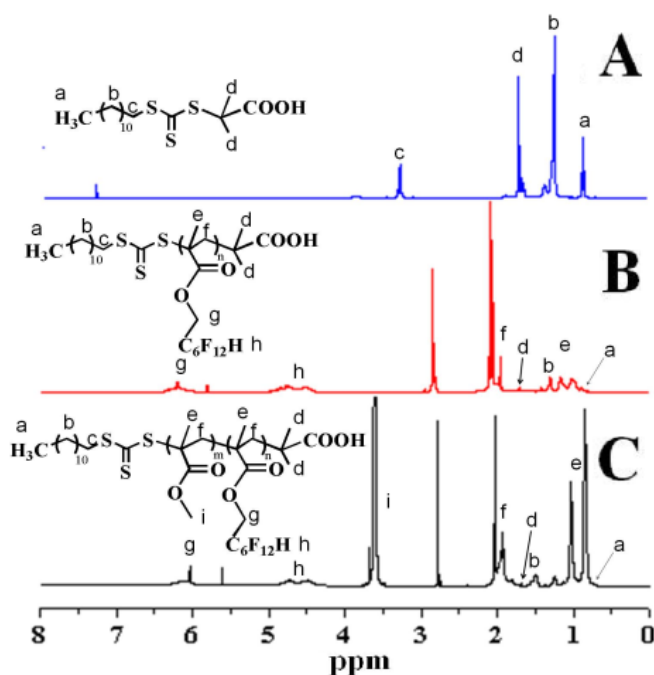


Figure 2. ¹H NMR spectra of the DDMAT agent (A), PDFMA-DDMAT macro-RAFT agent (B) and the typical fluorinated PDFMA-*b*-PMMA block copolymer synthesized by RAFT dispersion polymerization in ScCO₂.

Table 1. Summary of monomer conversions, calculated degrees of polymerization and GPC molecular weights for PDFMA macro-CTA agents synthesized by RAFT solution polymerization of DFMA in tetrahydrofuran at 70°C using AIBN. Conditions: [DFMA]₀ = 25 wt. %, DDMAT/AIBN molar ratio = 5.

Target <i>DP</i>	Conversion (wt%)	Actual <i>DP</i> by ¹ H-NMR	THF GPC /g mol ⁻¹		
			<i>M</i> _{n,GPC}	<i>M</i> _{w,GPC}	<i>M</i> _{w,GPC} / <i>M</i> _{n,GPC}
PDFMA ₂₀	68	13	5500	6300	1.15
PDFMA ₃₀	72	21	9400	10600	1.13
PDFMA ₅₀	65	31	13900	16800	1.21

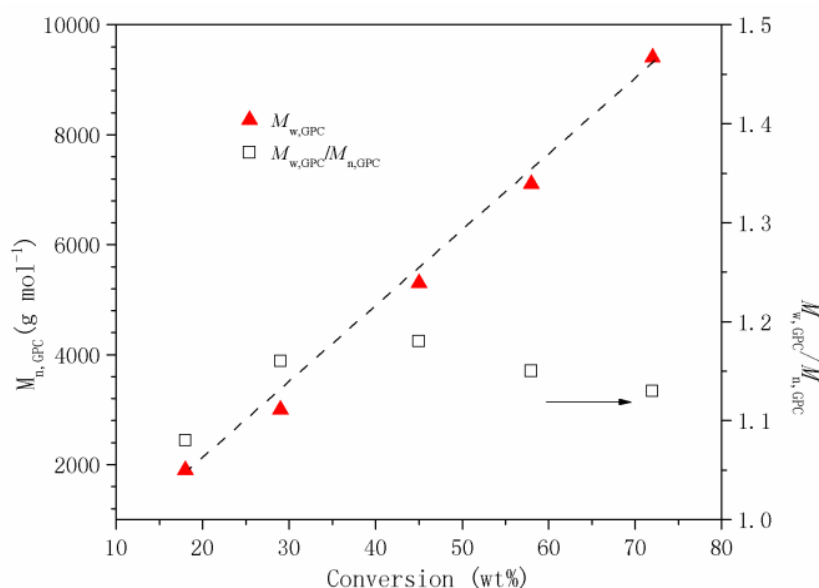


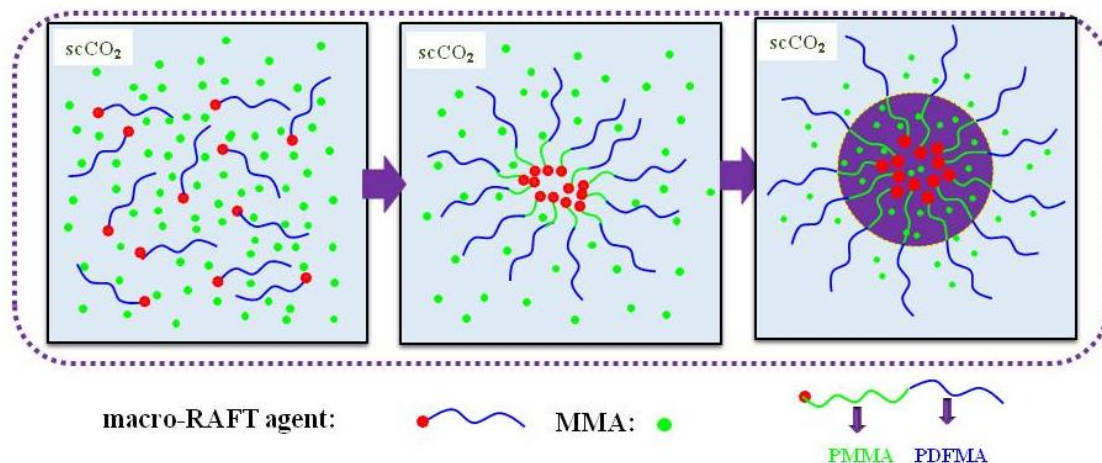
Figure 3. GPC evolution of the molecular weight *M*_{n,GPC} and the *M*_{w,GPC}/*M*_{n,GPC} value of the PDFMA-DDMAT macro-CTA agent synthesized by RAFT solution polymerization in the presence of DDMAT targeting a *DP* of 30.

3.2. Synthesis of fluorinated diblock copolymer nanoparticles

Subsequently, PDFMA-*b*-PMMA diblock copolymer nanoparticles were prepared by RAFT dispersion polymerization under $[MMA]_0:[PDFMA_{21}-DDMAT]_0:[AIBN]_0=1500:4:1$ in supercritical carbon dioxide. At the end of the reactions, the CO_2 was then slowly vented and a free flowing white powder was obtained, indicating that successful stabilization of the colloidal dispersion occurred in the RAFT polymerization.

The diblock copolymer PDFMA-*b*-PMMA was characterized by GPC analysis (Figure 1). The molecular weight $M_{n, GPC}$ of PDFMA-*b*-PMMA by GPC analysis is 38.1 kg/mol with PDI 1.24, which is similar as the theoretical molecular weight $M_{n, th}$ 37.2 kg/mol. The similar $M_{n, NMR}$ with $M_{n, th}$ and the low PDI of the PDFMA-*b*-PMMA diblock copolymer implied the good control of the polymer structure in the RAFT dispersion polymerization.

The chemical composition of the PDFMA-*b*-PMMA fluorinated block copolymer was determined by 1H NMR spectroscopy (Figure 2C). The signals at 4.5-4.9 ppm is due to the $-O-CH_2-R_f$ group; and signals at 5.9-6.4 ppm can be assigned to the $-CHF-$ and $-CH(CF_3)_2-$ group of DFMA[19]. By comparison with Figure 2A and Figure 2B, clearly, the emergent signals at 3.3-3.9 ppm (i) in Figure 2C are belonged to the $-O-CH_3$ group of MMA units, which suggests that the PMMA segments are coupled with PDFMA segments and the block copolymer is successfully synthesized.



Scheme 2. Synthesis of PDFMA-*b*-PDMA fluorinated diblock copolymer nanoparticles by RAFT dispersion polymerization in $ScCO_2$.

The morphology of the PDFMA-*b*-PMMA copolymer nanoparticles synthesized through the in situ RAFT dispersion polymerization were characterized. Scanning electron microscopy (SEM) images show that well-defined spherical nanoparticles with the average size at 425 nm are obtained (Figure 4). Simultaneously, the average diameter of these nanoparticles is estimated with statistical analysis of 100 particles, and the values were shown in Figure 4. It is declared that these particles have a narrow size distribution (1.13), which are close to the literature for conventional MMA dispersion polymerization in $ScCO_2$ in the presence of fluorinated CO_2 -philic stabilizer[24,25]. Indeed, the fluorinated PDFMA-DDMAT homopolymer was used as macro-CTA and it acts also as stabilizer of the fluorinated nanoparticles formed. In this study conditions, the MMA monomer, the macro-RAFT agent and the AIBN initiator are all soluble in the $ScCO_2$ medium and a homogeneous solution at the polymerization beginning can be formed. With the propagation of the PMMA block, the block copolymer becomes insoluble and therefore self-assembles into block copolymer nanoparticles, when the DP of the PMMA block reaches a critical value (scheme 2). Owing to the CO_2 -philic PDFMA block, the synthesized block copolymer nanoparticles can be uniformly dispersed in the polymerization medium.

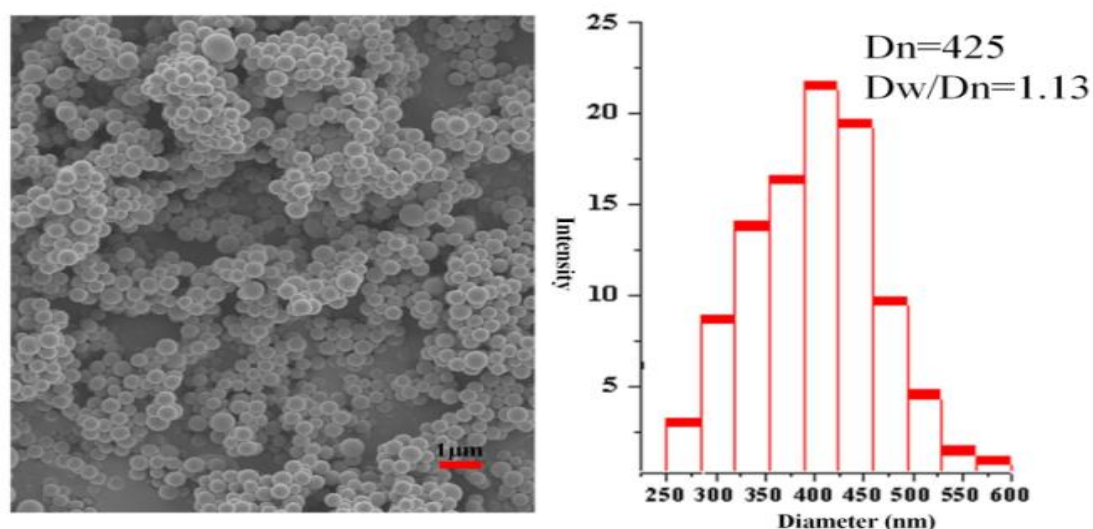


Figure 4. SEM images of the PDFMA-*b*-PMMA fluorinated block nanoparticles prepared using PDFMA₂₁-DDMAT macro-CTA.

Acknowledgements

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