

## ORIGINAL ARTICLE

# Iodine transfer dispersion polymerization with $\text{CHI}_3$ and reversible chain transfer-catalyzed dispersion polymerization with *N*-iodosuccinimide of methyl methacrylate in supercritical carbon dioxide

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Iodine transfer dispersion polymerization (dispersion ITP) with  $\text{CHI}_3$  and reversible chain transfer-catalyzed dispersion polymerization (dispersion RTCP) with *N*-iodosuccinimide of methyl methacrylate were performed successfully in supercritical carbon dioxide medium. Both polymerizations proceeded smoothly to ~80% conversion in 6 h and yielded the polymeric product as a powder after venting the reactor. In both syntheses, the number-average molecular weights ( $M_n$ ) increased with greater conversion. The ratio ( $M_w/M_n$ ) was maintained at comparatively low values throughout the polymerizations; the values of  $M_w/M_n$  were lower in the dispersion RTCP (1.3–1.4) than the dispersion ITP (1.5–1.7). A chain extension test using styrene indicated that the poly(methyl methacrylate) prepared by dispersion ITP and dispersion RTCP had high degrees of livingness (71 and 74%, respectively).

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**Keywords:** ITP; RTCP; supercritical carbon dioxide

## INTRODUCTION

Supercritical carbon dioxide ( $\text{scCO}_2$ ) has attracted attention as a new class of environmentally friendly reaction medium over the last few decades.  $\text{CO}_2$  changes from the gas or liquid state to the supercritical state ( $\text{scCO}_2$ ) at the critical point ( $T_c = 31.1^\circ\text{C}$ ,  $P_c = 7.38\text{ MPa}$ ), and the solvent properties of  $\text{scCO}_2$  can be adjusted by changing the temperature or pressure. Moreover,  $\text{scCO}_2$  has several advantages as a polymerization medium because it is nonflammable, nontoxic and easy to separate from the reaction products after polymerization.<sup>1,2</sup>

Several types of polymers containing siloxane or fluorocarbon segments are known to be soluble in  $\text{scCO}_2$  and useful as colloidal stabilizers.<sup>2–4</sup> Other polymers exhibit low solubility in  $\text{scCO}_2$ , although most monomers can be dissolved in  $\text{scCO}_2$ . Thus, most polymerizations in  $\text{scCO}_2$  are carried out with a precipitation polymerization system or a dispersion polymerization system.<sup>3,5,6</sup> We previously reported the preparation of poly(methyl methacrylate) (PMMA) particles by dispersion polymerization in  $\text{scCO}_2$  using a polydimethylsiloxane (PDMS)-based azoinitiator (VPS-0501) as an inistab (initiator + stabilizer).<sup>3</sup>

Controlled/living radical polymerization (CLRP) is a powerful method for the synthesis of polymers that have a narrow molecular weight distribution (MWD) and predictable molecular weight. Various CLRP techniques have been developed, such as, nitroxide-mediated radical polymerization (NMP),<sup>7–10</sup> atom transfer radical

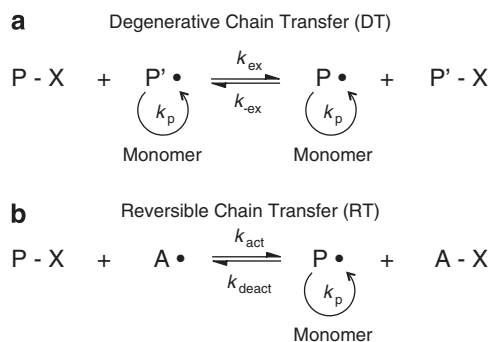
polymerization (ATRP),<sup>10,11</sup> reversible addition-fragmentation chain transfer<sup>12,13</sup> and organotellurium-mediated living radical polymerization (TERP).<sup>14–21</sup>

Iodine transfer polymerization (ITP) is another CLRP technique. In ITP, the degenerative chain transfer of iodine allows for controlled polymerization (Scheme 1a).<sup>22,23</sup> ITP can be carried out without metallic substances and under mild conditions. However, because of the low exchange frequency ( $k_{ex}$ ), the preparation of polymers with narrow MWDs by ITP is more difficult than with other CLRP techniques. Goto and colleagues developed the reversible chain transfer-catalyzed polymerization (RTCP) technique (Scheme 1)<sup>24</sup> in which a very small amount of nontransition metal catalyst (such as a compound containing germanium,<sup>25,26</sup> tin,<sup>25,26</sup> phosphorus<sup>25–27</sup> or nitrogen<sup>24,28</sup>) was added to an ITP system. In RTCP, the catalyst induces reversible chain transfer reactions that are faster than the degenerative chain transfer of iodine; the MWDs of polymers prepared by RTCP are narrower than for polymers prepared by ITP.<sup>29</sup>

The application of CLRP to environmentally friendly heterogeneous systems was also attempted.<sup>30–32</sup> In our previous works,<sup>33–41</sup> several CLRP techniques (NMP, ATRP and TERP) were applied successfully to systems dispersed in aqueous and  $\text{scCO}_2$  solvents. More recently, the RTCP synthesis of styrene with a germanium catalyst was performed successfully in a dispersion polymerization system in  $\text{scCO}_2$ .<sup>42</sup>

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**Scheme 1** Iodine transfer polymerization (a) and reversible chain transfer-catalyzed polymerization (a, b).

In this work, ITP with  $\text{CHI}_3$  and RTCP with *N*-iodosuccinimide (NIS) of methyl methacrylate (MMA) are applied to dispersion polymerization systems (dispersion ITP and dispersion RTCP, respectively) in  $\text{scCO}_2$ , to extend the range of applications of monomers and catalysts in  $\text{scCO}_2$ .

## EXPERIMENTAL PROCEDURE

### Materials

MMA and styrene (Mitsubishi Chemical, Tokyo, Japan) were purified by distillation under reduced pressure in nitrogen atmosphere. Reagent grade 2,2'-azobis(isobutyronitrile) (AIBN) (Wako Pure Chemical Industries, Osaka, Japan) was purified by recrystallization with methanol. VPS-0501 (Wako Pure Chemical Industries), iodoform ( $\text{CHI}_3$ ; Nacalai Tesque, Kyoto, Japan) and NIS (Aldrich Chem, St Louis, MO, USA, 95%) were used as received. Industrial grade  $\text{CO}_2$  with a purity of 99.5% was used (Kobe Sanso, Kobe, Japan).

### Dispersion ITP of MMA in $\text{scCO}_2$

A typical dispersion ITP procedure for MMA in  $\text{scCO}_2$  was as follows: MMA (5.0 g, 50 mmol), VPS-0501 (125 mg, 25  $\mu\text{mol}$ ; azo content of whole VPS-0501), AIBN (72 mg, 440  $\mu\text{mol}$ ) and  $\text{CHI}_3$  (197 mg, 500  $\mu\text{mol}$ ) were added to a 25-ml stainless steel reactor. A vacuum was applied, and the reactor was pressurized with liquid  $\text{CO}_2$  to 9 MPa at room temperature using a high pressure pump. The reactor temperature was raised to 80 °C by immersing it in a temperature-controlled water bath with magnetic stirring at 200 r.p.m.; during immersion, the pressure increased to  $\sim 30$  MPa. The polymerization was stopped by cooling the reactor in a water bath, and the  $\text{CO}_2$  was vented slowly. The conversion was measured by gravimetry. At low conversions, the reaction mixture was dissolved in toluene, and the polymer product was collected by filtration after precipitation in an excess of *n*-hexane.

### Dispersion RTCP of MMA in $\text{scCO}_2$

Dispersion RTCP of MMA in  $\text{scCO}_2$  was carried out with NIS (1.5 mg, 7  $\mu\text{mol}$ ) under the same conditions as the dispersion ITP in  $\text{scCO}_2$ . The polymer particles were obtained at high conversions and observed with a scanning electron microscope (JSM-6510, JEOL Ltd., Tokyo, Japan) after centrifugal washing three times with *n*-hexane.

### Chain extension

RTCPs of styrene in bulk systems (bulk RTCPs) were carried out as a chain extension test to estimate the degree of livingness of the two types of PMMA that were prepared by the dispersion ITP and dispersion RTCP techniques in  $\text{scCO}_2$  at 80 °C in 6 h; the products were PMMA-polystyrene (PS) block polymers (PMMA-*b*-PS). The PMMA macrotransfer agent (300  $\mu\text{mol}$ ), styrene (4.5 g, 43 mmol), AIBN (10 mg, 61  $\mu\text{mol}$ ) and NIS (4.5 mg, 20  $\mu\text{mol}$ ) were added to a glass ampoule and degassed using several  $\text{N}_2$ /vacuum cycles; then, the ampoule was sealed under vacuum. The polymerization was carried out at 80 °C while the ampoule was shaken horizontally at 60 cycles per minute (3-cm strokes). The conversion was measured by gas chromatography employing

helium as the carrier gas. *N,N*-Dimethylformamide and *p*-xylene were used as the solvent and internal standard, respectively.

### Molecular weight measurement

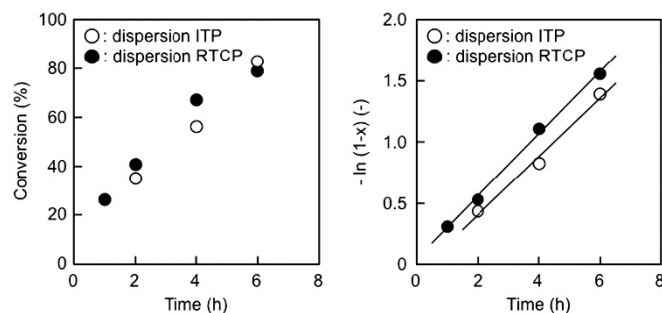
The number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ) and MWD were measured by gel permeation chromatography (GPC) with two styrene/divinylbenzene gel columns (TOSOH corporation, Yamaguchi, Japan, TSKgel GMH<sub>HR</sub>-H, 7.8 mm i.d.  $\times$  30 cm), THF as the eluent at 40 °C, a flow rate of 1.0 ml min<sup>-1</sup>, a refractive index (RI) detector (TOSOH RI-8020/21) and an ultraviolet (UV) detector (TOSOH UV-8II). The columns were calibrated with six standard PS samples ( $1.05 \times 10^3$ – $5.48 \times 10^6$ ,  $M_w/M_n = 1.01$ – $1.15$ ).

## RESULTS AND DISCUSSION

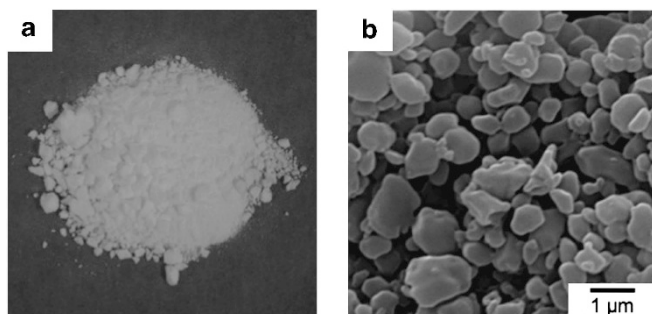
Dispersion RTCP of MMA in  $\text{scCO}_2$  was carried out using the ratio of chain transfer agent to initiator in bulk RTCP (chain transfer agent/initiator = 8/1, molar ratio) that was reported previously.<sup>28</sup> The conversion was limited to 38% for 24 h; the product, a turbid viscous solution, was obtained after venting the reactor. To rapidly perform the polymerization and obtain a powder product, the initiator level was increased to  $\text{CHI}_3/\text{AIBN} = 1/0.9$ . Dispersion ITP with  $\text{CHI}_3$  as the chain transfer agent and dispersion RTCP with  $\text{CHI}_3$  and NIS as the catalyst in  $\text{scCO}_2$  were performed at 30 MPa and 80 °C. Figure 1 shows conversion-time plots and their first-order plots for both polymerizations. Dispersion ITP and RTCP proceeded smoothly without an induction period, and the conversions after 6 h were 83 and 80%, respectively. The polymerization rates in this study were faster than the rates of analogous dispersion ITP and dispersion RTCP of styrene in previous work.<sup>42</sup> The difference in the reactions rates may be due to the difference in the propagation rate constants of MMA and styrene. As shown in Figure 1b, the first-order plots for dispersion ITP and RTCP were linear, although both polymerizations proceeded in heterogeneous systems. This finding suggests that the dispersion ITP and RTCP mainly proceeded in the particles. We do not discuss this point further in this work because no information is available about the monomer concentrations in the particles.

Figure 2 shows the optical and scanning electron microscope (SEM) photographs of PMMA prepared by dispersion RTCP in  $\text{scCO}_2$  for 6 h. After the  $\text{CO}_2$  was vented, the PMMA was obtained as a white flowing powder (Figure 2a). The product was washed with *n*-hexane to remove excess VPS-0501. An SEM photograph (Figure 2b) shows that the PMMA was in the form of submicrometer-sized and micrometer-sized nonspherical particles.

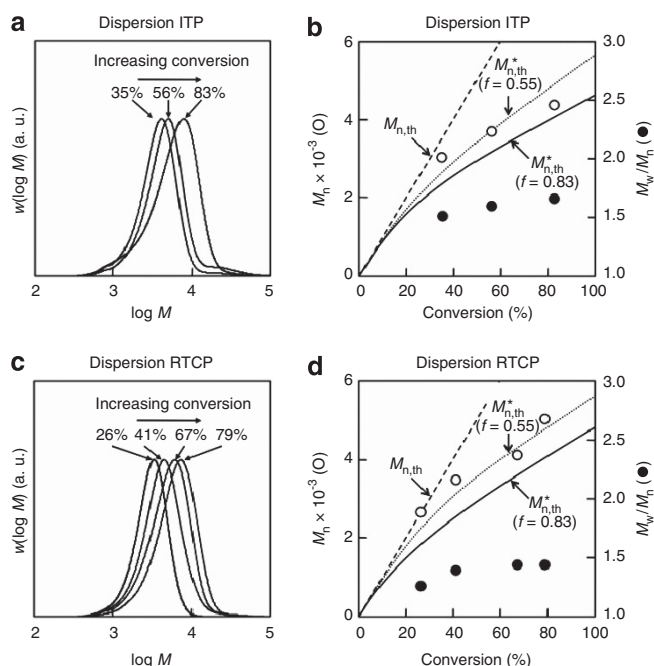
Figure 3 shows the MWDs,  $M_n$ , and  $M_w/M_n$  of PMMA prepared by the dispersion ITP and the dispersion RTCP with NIS in  $\text{scCO}_2$  at



**Figure 1** Conversion-time plots (left) and their first-order plots (right) (where  $x$  stands for conversion) for dispersion ITP (open circles) and dispersion RTCP with NIS as a catalyst (closed circles) of MMA in  $\text{scCO}_2$  at 80 °C and 30 MPa.  $\text{MMA}/\text{CHI}_3/\text{AIBN}/\text{NIS} = 100/1/0.9/0$  (ITP) or  $0.014$  (RTCP), molar ratio.



**Figure 2** Photograph (a) of PMMA-I prepared by dispersion RTCP of MMA with NIS in scCO<sub>2</sub> at 80 °C and 30 MPa for 6 h, and scanning electron microscope photograph (b) of the particles after centrifugal washing with hexane. A full color version of this figure is available at *Polymer Journal* online.



**Figure 3** MWDs (a, c),  $M_n$  and  $M_w/M_n$  (b, d) of PMMA measured with GPC (RI detector) at different conversions of dispersion ITP (a, b) and dispersion RTCP with NIS (c, d) of MMA in scCO<sub>2</sub> at 80 °C and 30 MPa.

various conversions. In both polymerizations, the MWD shifted to higher molecular weight side with increasing conversion (Figures 3a and c). The  $M_w/M_n$  ratio was maintained relatively low even for high conversions (Figures 3b and d). These results indicate that ITP with CHI<sub>3</sub> and RTCP with NIS of MMA were applied successfully to dispersion polymerization system in scCO<sub>2</sub>. The  $M_w/M_n$  values from the dispersion ITP ( $M_w/M_n = 1.4\text{--}1.6$ ) were higher than the values from the dispersion RTCP ( $M_w/M_n = 1.3\text{--}1.4$ ) throughout the polymerization procedures. These results indicate that the nitrogen catalyst worked effectively even in scCO<sub>2</sub>.

In Figures 3b and d, the  $M_n$  values increased with conversion, but they deviated from the theoretical values for  $M_n$  ( $M_{n,th}$ ) that were predicted by equation (1).

$$M_{n,th} = \frac{[M]_0 MW_M \alpha}{[CHI_3]_0} \quad (1)$$

where  $[M]_0$  and  $[CHI_3]_0$  are the initial concentrations of monomer and transfer agent, respectively.  $MW_M$  is the molecular weight of the

monomer, and  $\alpha$  is the monomer conversion. This equation can be applied when the ratio of initiator concentration to chain transfer agent concentration is low and the number of polymer molecules generated from the initiator radical can be neglected. However, in this study, the ratio of initiator to chain transfer agent is high, and the effect of the initiator radical cannot be neglected. Therefore, equation (1) was modified to derive equation (2).

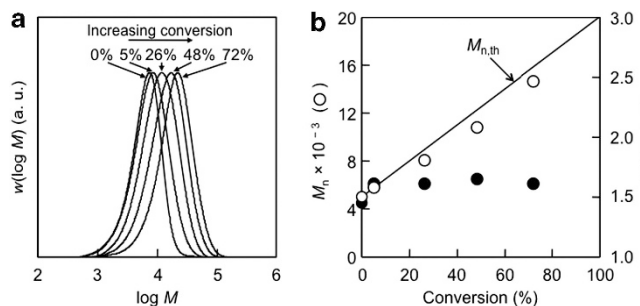
$$M_{n,th}^* = \frac{[M]_0 MW_M \alpha}{[CHI_3]_0 + 2f[AIBN]_0 \left[ 1 - \frac{[AIBN]_t}{[AIBN]_0} \right]} \quad (2)$$

where  $f$  is the initiator efficiency,  $[AIBN]_0$  is the initial concentration of initiator and  $[AIBN]_t$  is the concentration of initiator at time  $t$ . As  $f$  for AIBN in scCO<sub>2</sub> was reported as 1.5 times higher than in general organic solvents,<sup>43</sup> the value of 0.83 was used for  $f$  in this calculation. The decomposition rate constant ( $k_d$ ) of AIBN used for the calculation ( $5.49 \times 10^{-5} \text{ s}^{-1}$ ) was obtained based on the information that (a) the  $k_d$  value of AIBN in scCO<sub>2</sub> (21 MPa, 79 °C) was 2.5 times lower than in benzene at the same temperature under atmospheric pressure<sup>43</sup> and (b) the  $k_d$  value of AIBN in toluene at 80 °C was  $1.37 \times 10^{-4} \text{ s}^{-1}$ .<sup>44</sup> As the result, the  $M_n$  plots were between  $M_{n,th}$  from equation (1) (broken lines in Figures 3b and d) and  $M_{n,th}^*$  ( $f = 0.83$ ) from equation (2) (solid lines in Figures 3b and d). When 0.55 was used in place of 0.83 for  $f$  in the calculation of  $M_{n,th}^*$  for the dispersion ITP and RTCP, the  $M_n$  plots were in good agreement with  $M_{n,th}^*$  (dotted lines in Figures 3b and d). Similar results were obtained in our previous work<sup>42</sup> in which PS particles were prepared by dispersion ITP (using benzoyl peroxide (BPO) as the initiator and CHI<sub>3</sub> in scCO<sub>2</sub>) and dispersion RTCP (with BPO, CHI<sub>3</sub> and germanium (IV) iodide as the catalyst in scCO<sub>2</sub>). When 0.65 (BPO) was used in place of 1 for the value of  $f$  in the calculation of  $M_{n,th}^*$ , the results were in good agreement with the  $M_n$  values. In the previous work, we decreased the value of  $f$  value for BPO based on the primary radical termination. The further decrease of the value of  $f$  for AIBN in the current work might be based on the 'cage effect' in addition to the primary radical termination, although it was reported that  $f$  for AIBN increased in a homogeneous scCO<sub>2</sub> system<sup>43</sup> as described previously. In this study of dispersion polymerization systems, the value of  $f$  for AIBN in particles (where the viscosity is relatively high) may be lower than in a homogeneous scCO<sub>2</sub> medium.

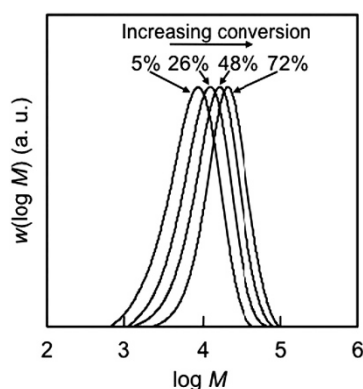
To estimate the livingness of PMMA prepared by the dispersion ITP and the dispersion RTCP with NIS in scCO<sub>2</sub>, bulk RTCPs were performed with styrene for chain extension tests of the two types of the PMMA at 80 °C. These reactions were carried out at a typical ratio of chain transfer agent to initiator (PMMA macrotransfer agent/AIBN = 5/1) in CLRP. The polymerizations proceeded smoothly, and the conversions were ~70% within 8 h. Figure 4 shows the MWD (by RI detector),  $M_n$  and  $M_w/M_n$  at various conversions of the bulk RTCP of styrene for the chain extension test. The RI detector can detect all of the polymer chains. The MWD shifted to the higher molecular weight side with increasing conversion (Figure 4a). The  $M_n$  value linearly increased with conversion and was in good agreement with  $M_{n,th}$  (Figure 4b). A similar result was obtained with the bulk RTCP with PMMA macrotransfer agent prepared by dispersion ITP in scCO<sub>2</sub>. These results indicate that the chain extension tests proceeded in a controlled manner, and the livingness of the PMMAs prepared by the dispersion ITP and the dispersion RTCP in scCO<sub>2</sub> was maintained.

Figure 5 shows the MWD measured by GPC with the UV detector and an incident wavelength of 254 nm. The UV detector detects polymer chains that contain styrene units (PMMA-*b*-PS, PS) but not





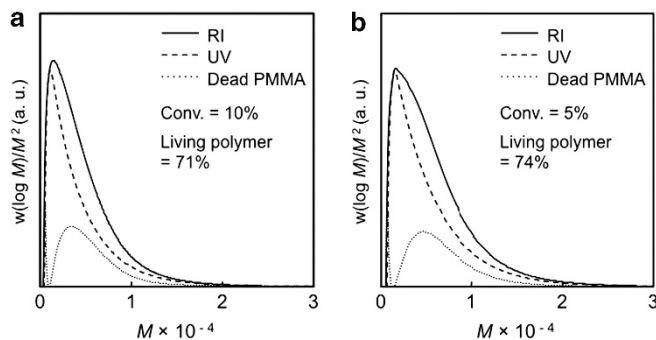
**Figure 4** MWD (a),  $M_n$  and  $M_w/M_n$  (b) of PMMA-*b*-PS measured with GPC (RI detector) at different conversions of bulk RTCP of styrene at 80 °C for chain extension with PMMA-I macrotransfer agents prepared by the dispersion RTCP with NIS as catalyst of MMA in  $scCO_2$  at 80 °C and 30 MPa. Styrene/PMMA macrotransfer agent/AIBN/NIS = 700/5/1/0.3, molar ratio.



**Figure 5** MWD of PMMA-*b*-PS measured with GPC (UV detector) at different conversions of the bulk RTCP of styrene at 80 °C for the chain extension with PMMA-I macrotransfer agents prepared by dispersion RTCP with NIS as catalyst of MMA in  $scCO_2$  at 80 °C and 30 MPa. Styrene/PMMA macrotransfer agent/AIBN/NIS = 700/5/1/0.3, molar ratio.

PMMA. The MWDs measured with the UV detector were similar to those obtained with the RI detector (Figure 4a). This finding indicates that most of the PMMA chains formed by the dispersion RTCP with NIS in  $scCO_2$  were extended by the bulk RTCP with styrene, resulting in PMMA-*b*-PS.

To examine the ratio of living PMMA chains to all polymer chains (the PMMA livingness), the numbers of living polymer chains and the total number of polymer chains were calculated by transforming the MWDs measured with the UV and RI detectors, respectively. Figure 6 shows the number distributions (plots of  $w(\log M)/M^2$  vs  $M$ ) of products after 1 h of the bulk RTCP chain extension tests for PMMA prepared by dispersion ITP and dispersion RTCP; low conversions were assumed (PS generated from initiator radicals during the chain extension tests was neglected). Livingness percentages of PMMA for dispersion ITP and dispersion RTCP with NIS in  $scCO_2$ , calculated from the proportion of number of the living polymer chains (UV) to number of all polymer chains (RI), were 71 and 74, respectively. These values were higher than those calculated at the same initial molar ratio of AIBN and  $CHI_3$  in both polymerizations. This finding suggests that the number of polymer chains generated from initiator radicals was lower than the calculated value, which was based on primary radical termination and lower initiator efficiency than theoretically calculated value (described above). Moreover, in the dispersion RTCP in  $scCO_2$ , the livingness of PMMA



**Figure 6** Plots of  $w(\log M)/M^2$  vs  $M$  (number distributions; area normalized to unity) at 1 h of the bulk RTCPs of styrene for the chain extension with PMMA macrotransfer agents prepared by dispersion ITP (a) and dispersion RTCP (b) in  $scCO_2$  at 80 °C. Styrene/PMMA macrotransfer agent/AIBN/NIS = 700/5/1/0.3, molar ratio.

prepared in this study was higher than the livingness of PS prepared in our previous work.<sup>42</sup> As the ratio of initiator to chain transfer agent in this study was smaller in the previous work, the ratio of the number of polymer chains generated by the initiator to the number generated by the chain transfer agent was smaller than the ratio in previous work; this difference is the reason for the higher livingness observed in this study.

## CONCLUSIONS

Dispersion ITP with  $CHI_3$  and dispersion RTCP with NIS of MMA in  $scCO_2$  were carried out at 80 °C and 30 MPa. In both polymerizations, the conversion was  $\sim 80\%$  after 6 h, and the PMMA powder was obtained after the reactor was vented. The MWD of the PMMA shifted to the higher molecular weight side with increasing conversion for both methods of synthesis.  $M_n$  increased during the polymerizations while the  $M_w/M_n$  values remained low. These results indicate that the dispersion ITP with  $CHI_3$  and the dispersion RTCP with NIS of MMA were performed successfully in  $scCO_2$  systems. It was confirmed that NIS works effectively even in  $scCO_2$  by comparing the  $M_w/M_n$  values in both systems. Finally, the livingness percentages of the PMMA products were estimated to be relatively high.

## ACKNOWLEDGEMENTS

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- DeSimone, J. M., Maury, E. E., Menciloglu, Y. Z., McClain, J. B., Romack, T. R. & Combes, J. R. Dispersion polymerizations in supercritical carbon dioxide. *Science* **265**, 356–359 (1994).
- Kendall, J. L., Canelas, D. A., Young, J. L. & DeSimone, J. M. Polymerizations in supercritical carbon dioxide. *Chem. Rev.* **99**, 543–563 (1999).
- Okubo, M., Fujii, S., Maenaka, H. & Minami, H. Production of submicron-sized poly(methyl methacrylate) particles by dispersion polymerization with a poly(dimethyl siloxane)-based azoinitiator in supercritical carbon dioxide. *Colloid Polym. Sci.* **280**, 183–187 (2002).
- Canelas, D. A. & DeSimone, J. M. Dispersion polymerizations of styrene in carbon dioxide stabilized with poly(styrene-*b*-dimethylsiloxane). *Macromolecules* **30**, 5673–5682 (1997).
- Canelas, D. A., Betts, D. E. & DeSimone, J. M. Dispersion polymerization of styrene in supercritical carbon dioxide: importance of effective surfactants. *Macromolecules* **29**, 2818–2821 (1996).
- Okubo, M., Fujii, S., Maenaka, H. & Minami, H. Production of polyacrylonitrile particles by precipitation polymerization in supercritical carbon dioxide. *Colloid Polym. Sci.* **281**, 964–972 (2003).

- 7 Georges, M. K., Veregin, R. P. N., Kazmaier, P. M. & Hamer, G. K. Narrow molecular weight resins by a free-radical polymerization process. *Macromolecules* **26**, 2987–2988 (1993).
- 8 Hawker, C. J., Bosman, A. W. & Harth, E. New polymer synthesis by nitroxide mediated living radical polymerizations. *Chem. Rev.* **101**, 3661–3688 (2001).
- 9 Solomon, D. H. Genesis of the CSIRO polymer group and the discovery and significance of nitroxide-mediated living radical polymerization. *J. Polym. Sci. Part A: Polym. Chem.* **43**, 5748–5764 (2005).
- 10 Matyjaszewski, K. & Xia, J. Atom transfer radical polymerization. *Chem. Rev.* **101**, 2921–2990 (2001).
- 11 Kamigaito, K., Ando, T. & Sawamoto, M. Metal-catalyzed living radical polymerization. *Chem. Rev.* **101**, 3689–3745 (2001).
- 12 Barner-Kowollik, C., Buback, M., Charleux, B., Coote, M. L., Drache, M., Fukuda, T., Goto, A., Klumperman, B., Lowe, A. B., McLeary, J. B., Moad, G., Monteiro, M. J., Sanderson, R. D., Tonge, M. P. & Vana, P. Mechanism and kinetics of dithiobenzoate-mediated RAFT polymerization. I. The current situation. *J. Polym. Sci.; Part A: Polym. Chem.* **44**, 5809–5831 (2006).
- 13 Moad, G., Rizzardo, E. & Thang, S. H. Living radical polymerization by the RAFT process - A first update. *Aust. J. Chem.* **59**, 669–692 (2006).
- 14 Goto, A., Kwak, Y., Fukuda, T., Yamago, S., Iida, K., Nakajima, M. & Yoshida, J. Mechanism-based invention of high-speed living radical polymerization using organotellurium compounds and azo-initiators. *J. Am. Chem. Soc.* **125**, 8720–8721 (2003).
- 15 Yamago, S., Iida, K. & Yoshida, J. Organotellurium compounds as novel initiators for controlled/living radical polymerizations. synthesis of functionalized polystyrenes and end-group modifications. *J. Am. Chem. Soc.* **124**, 2874–2875 (2002).
- 16 Yamago, S., Ray, B., Iida, K., Yoshida, J., Tada, T., Yoshizawa, K., Kwak, Y., Goto, A. & Fukuda, T. Highly versatile organostibine mediators for living radical polymerization. *J. Am. Chem. Soc.* **126**, 13908–13909 (2004).
- 17 Yamago, S. Development of organotellurium-mediated and organostibine-mediated living radical polymerization reactions. *J. Polym. Sci. Part A: Polym. Chem.* **44**, 1–12 (2006).
- 18 Kwak, Y., Tezuka, M., Goto, A., Fukuda, T. & Yamago, S. Kinetic study on role of ditelluride in organotellurium-mediated living radical polymerization (TERP). *Macromolecules* **40**, 1881–1885 (2007).
- 19 Sugihara, Y., Kagawa, Y., Yamago, S. & Okubo, M. Organotellurium-mediated living radical polymerization in miniemulsion. *Macromolecules* **40**, 9208–9211 (2007).
- 20 Okubo, M., Sugihara, Y., Kitayama, Y., Kagawa, Y. & Minami, H. Emulsifier-free, organotellurium-mediated living radical emulsion polymerization of butyl acrylate. *Macromolecules* **42**, 1979–1984 (2009).
- 21 Kitayama, Y., Chaiyasat, A. & Okubo, M. Emulsifier-free, organotellurium-mediated living radical emulsion polymerization of styrene. *Macromol. Symp.* **288**, 25–32 (2010).
- 22 Matyjaszewski, K., Gaynor, S. & Wang, J. S. Controlled radical polymerizations: the use of alkyl iodides in degenerative transfer. *Macromolecules* **28**, 2093–2095 (1995).
- 23 David, G., Boyer, C., Tonnar, J., Ameduri, B., Lacroix-Desmazes, P. & Boutevin, B. Use of iodo compounds in radical polymerization. *Chem. Rev.* **106**, 3936–3962 (2006).
- 24 Goto, A., Tsujii, Y. & Fukuda, T. Reversible chain transfer catalyzed polymerization (RTCP): a new class of living radical polymerization. *Polymer* **49**, 5177–5185 (2008).
- 25 Goto, A., Zushi, H., Hirai, N., Wakada, T., Kwak, Y. & Fukuda, T. *Macromol. Symp.* **248**, 126–131 (2006).
- 26 Goto, A., Zushi, H., Hirai, N., Wakada, T., Tsujii, Y. & Fukuda, T. Living radical polymerizations with germanium, tin, and phosphorous catalysts - reversible chain transfer catalyzed polymerizations (RTCPs). *J. Am. Chem. Soc.* **129**, 13347–13354 (2007).
- 27 Goto, A., Hirai, N., Tsujii, Y. & Fukuda, T. Reversible chain transfer catalyzed polymerizations (RTCPs) of styrene and methyl methacrylate with phosphorous catalysts. *Macromol. Symp.* **261**, 18–22 (2008).
- 28 Goto, A., Hirai, N., Wakada, T., Nagasawa, K., Tsujii, Y. & Fukuda, T. Living radical polymerization with nitrogen catalyst: reversible chain transfer catalyzed polymerization with N-iodosuccinimide. *Macromolecules* **41**, 6261–6264 (2008).
- 29 Goto, A., Wakada, T., Fukuda, T. & Tsujii, Y. A systematic kinetic study in reversible chain transfer catalyzed polymerizations (RTCPs) with germanium, tin, phosphorous, and nitrogen catalysts. *Macromol. Chem. Phys.* **211**, 594–600 (2010).
- 30 Charleux, B. Nitroxide-mediated polymerization in miniemulsion: a direct way from bulk to aqueous dispersed systems. *ACS Symposium Series* **854**, 438–451 (2003).
- 31 Zetterlund, P. B., Kagawa, Y. & Okubo, M. Controlled/living radical polymerization in dispersed systems. *Chem. Rev.* **108**, 3747–3794 (2008).
- 32 Zetterlund, P. B., Aldabbagh, F. & Okubo, M. Controlled/living heterogeneous radical polymerization in supercritical carbon dioxide. *J. Polym. Sci. Part A: Polym. Chem.* **47**, 3711–3728 (2009).
- 33 Kagawa, Y., Minami, H., Okubo, M. & Zhou, J. Preparation of block copolymers by two-step atom transfer radical polymerization in aqueous media and its unique morphology. *Polymer* **46**, 1045–1050 (2005).
- 34 Zetterlund, P. B., Alam, M. N., Minami, H. & Okubo, M. Nitroxide-mediated controlled/living free radical copolymerization of styrene and divinylbenzene in aqueous miniemulsion. *Macromol. Rapid Commun.* **26**, 955–960 (2005).
- 35 Minami, H., Kagawa, Y., Kuwahara, S., Shigematsu, J., Fujii, S. & Okubo, M. Dispersion atom transfer radical polymerization of methyl methacrylate with bromo-terminated poly(dimethylsiloxane) in supercritical carbon dioxide. *Des. Monom. Polym.* **7**, 553–562 (2004).
- 36 Ryan, J., Aldabbagh, F., Zetterlund, P. B. & Okubo, M. First nitroxide-mediated free radical dispersion polymerizations of styrene in supercritical carbon dioxide. *Polymer* **46**, 9769–9777 (2005).
- 37 McHale, R., Aldabbagh, F., Zetterlund, P. B. & Okubo, M. Nitroxide-mediated radical dispersion polymerization of styrene in supercritical carbon dioxide using a poly(dimethylsiloxane-*b*-styrene) alkoxyamine as initiator and stabilizer. *Macromol. Rapid Commun.* **27**, 1465–1471 (2006).
- 38 McHale, R., Aldabbagh, F., Zetterlund, P. B. & Okubo, M. Nitroxide-mediated radical precipitation polymerization of styrene in supercritical carbon dioxide. *Macromol. Chem. Phys.* **208**, 1813–1822 (2007).
- 39 McHale, R., Aldabbagh, F., Zetterlund, P. B., Minami, H. & Okubo, M. Nitroxide-mediated radical dispersion polymerization of styrene in supercritical carbon dioxide using a poly(dimethylsiloxane-*b*-methyl methacrylate) stabilizer. *Macromolecules* **39**, 6853–6860 (2006).
- 40 Aldabbagh, F., Zetterlund, P. B. & Okubo, M. Improved control in nitroxide-mediated radical polymerization using supercritical carbon dioxide. *Macromolecules* **41**, 2732–2734 (2008).
- 41 Aldabbagh, F., Zetterlund, P. B. & Okubo, M. Nitroxide-mediated precipitation polymerization of styrene in supercritical carbon dioxide: effects of monomer loading and nitroxide partitioning on control. *Eur. Polym. J.* **44**, 4037–4046 (2008).
- 42 Kuroda, T., Tanaka, A., Taniyama, T., Minami, H., Goto, A., Fukuda, T. & Okubo, M. Iodine transfer dispersion polymerization (dispersion ITP) with  $\text{CHI}_3$  and reversible chain transfer catalyzed dispersion polymerization (dispersion RTCP) with  $\text{Gel}_4$  of styrene in supercritical carbon dioxide. *Polymer* **53**, 1212–1218 (2012).
- 43 Guan, Z., Combes, J. R., Menciloglu, Y. Z. & DeSimone, J. M. Homogeneous free radical polymerizations in supercritical carbon dioxide: 2. Thermal decomposition of 2,2'-azobis(isobutyronitrile). *Macromolecules* **26**, 2663–2669 (1993).
- 44 Brandrup, J., Immergut, E. H., Grulke, E. A., Abe, A. & Bloch, D. R. *Polymer Handbook* (Wiley Interscience, NY, USA, 1999).