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Notes

Improved Control in Nitroxide-Mediated Radical Polymerization Using Supercritical Carbon Dioxide[†]

Fawaz Aldabbagh,*,[‡] Per B. Zetterlund,[§] and Masayoshi Okubo*,[§]

School of Chemistry, National University of Ireland, Galway, Ireland, and Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, Kobe 657-8501, Japan

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Controlled/living radical polymerization (CLRP) has revolutionized the field of radical polymerization in the past 15 years.[1] Synthesis of polymer of narrow molecular weight distribution (MWD), block copolymers, and more complex architectures is now possible by free radical means. The three most widespread CLRP techniques are nitroxide-mediated radical polymerization (NMP),[2] atom transfer radical polymerization (ATRP),[3] and reversible addition−fragmentation chain transfer (RAFT) polymerization.[4] CLRP is based on a dynamic equilibrium between dormant and active chains (propagating radicals), which results in a decrease in the probability of termination events per chain and uniform growth of chains.[5] Extensive research is currently underway aimed at implementing CLRP in heterogeneous systems.[6]

Supercritical carbon dioxide ($scCO_2$) is an environmentally friendly alternative medium for radical and condensation polymerizations, pioneered by DeSimone et al.[7] $ScCO_2$ offers several attractive features; it is cheap and nonflammable, the solubility power is adjustable by varying the temperature and pressure, and the polymer is recovered as a powder after venting of the CO_2. Most polymers are insoluble in $scCO_2$, making it suitable for heterogeneous (precipitation and dispersion) polymerizations. Previous work has shown that CLRP can be successfully implemented in $scCO_2$ as heterogeneous polymerizations (ATRP,[8] NMP,[9–11] and RAFT[12]), but without demonstrating any advantages over the corresponding bulk/solution systems aside from environmental factors and obtaining the polymer directly as a powder and/or particles.

In this Note, we demonstrate how precipitation NMP of styrene in $scCO_2$ can proceed with better control over the MWD than the corresponding solution polymerization. This constitutes, to the best of our knowledge, the first example of a heterogeneous CLRP (in any medium) providing superior control over its homogeneous counterpart and illustrates how benign $scCO_2$ provides new avenues for improved control of radical polymerization.

Precipitation NMP of styrene in $scCO_2$ was performed employing the nitroxides 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy (TIPNO)[13] and *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1)[14] in a 25 mL custom-designed stainless steel reactor at 110 °C and ~30 MPa. The alkoxyamine species were generated in situ using azobis(isobutyronitrile) (AIBN).

The MWD in the TIPNO-mediated precipitation polymerization of styrene (70% (w/v) monomer, $[TIPNO]_0/[AIBN]_0 = 1.99$) shifted to higher MW with increasing conversion with $M_n \approx M_{n,th}$ and $M_w/M_n \approx 1.27$, indicating high control/livingness; i.e., the vast majority of chains contain an alkoxyamine moiety (Figure 1). The corresponding solution polymerizations were carried out using the same recipe replacing $scCO_2$ with toluene (under the present conditions, the number of new chains from chain transfer to toluene is negligible compared to the initial number of chains[15]) in degassed and sealed glass ampules. Precipitation and solution polymerizations were also performed as above replacing TIPNO with SG1. For both nitroxides, the polymerizations in $scCO_2$ resulted in markedly lower M_w/M_n than the solution polymerizations (Figure 2). An overlay of MWDs obtained in $scCO_2$ and toluene reveals how the MWD is much narrower in $scCO_2$ (Figure 3a).

In a precipitation polymerization, the mixture is initially homogeneous (transparent). Once the propagating radicals reach a certain (chain length or) critical degree of polymerization (J_{crit}) precipitation occurs, leading to particle formation. In CLRP, all chains ideally reach J_{crit} at the same conversion. J_{crit} was determined by carrying out a TIPNO-mediated precipitation polymerization of styrene in $scCO_2$ (70% (w/v) monomer, $[TIPNO]_0/[AIBN]_0 = 1.89$, 110 °C) in a 90 mL reactor with a sapphire viewing window. J_{crit} was taken as the degree of polymerization at the onset of turbidity, resulting in $J_{crit} \approx 114$ ($M_n = 11\,850$, $M_w/M_n = 1.48$, 26% styrene conversion). The polymerization thus proceeds homogeneously to ~26% conversion, beyond which the particles constitute the main locus of polymerization. This approach illustrates how CLRP can be used to obtain mechanistic information regarding heterogeneous polymerizations (applying equally to nonliving systems).

TIPNO-mediated precipitation polymerizations in $scCO_2$ were also carried out at a lower monomer loading of 40% (w/v), corresponding to $J_{crit} \approx 28$ ($M_n \approx 2900$) at ~8% conversion.[11] The lower the styrene content, the lower the polymer solubility in the CO_2/styrene phase.[16] The resulting MWD was much broader than at 70% monomer, with a very pronounced low-MW shoulder (Figure 3b). It appears that a high J_{crit} is favorable in terms of MWD control in this system. This finding supports the requirement for high nitroxide excess concentrations in heterogeneous polymerizations at low monomer loadings.[10,11] It is speculated that there may be complications with regards to the formation of the initial alkoxyamine species if J_{crit} is too low. If alkoxyamine and particle formation occur simultaneously, reactant partitioning and/or other complications may compromise control/livingness. $J_{crit} \approx 28$ is a number-average, and the MWD contains a significant number fraction of chains of MW < 2900.

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* Corresponding authors. E-mail: fawaz.aldabbagh@nuigalway.ie (F.A.); okubo@kobe-u.ac.jp (M.O.).

[‡] National University of Ireland, Galway.

[§] Kobe University.

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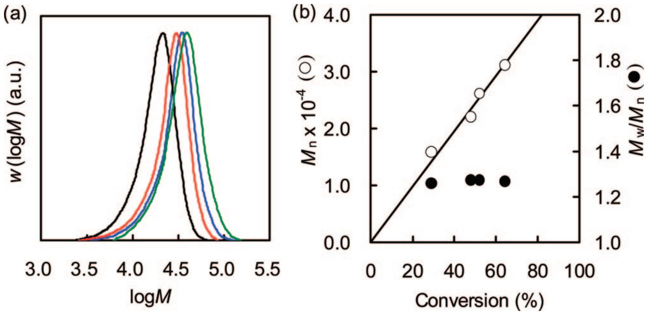

Figure 1. (a) MWDs (normalized to peak height) at 29% (black), 48% (red), 52% (blue), and 64% (green) conversions and (b) M_n and M_w/M_n for precipitation NMP of styrene in $scCO_2$ (70% (w/v) monomer, $[TIPNO]_0/[AIBN]_0 = 1.99$, 110 °C). Line: theoretical M_n ($M_{n,th}$) based on $f = 0.68$.

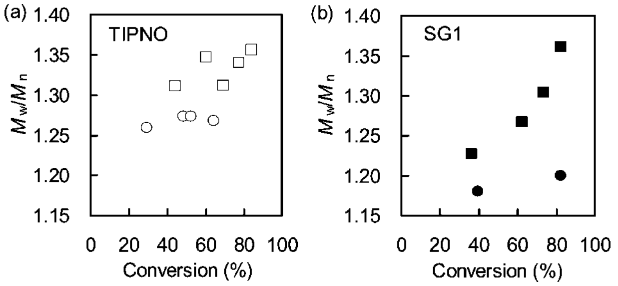

Figure 2. Polydispersities (M_w/M_n) in precipitation ($scCO_2$; ○,●) and solution (toluene; □, ■) NMP of styrene (70% (w/v) monomer, $[nitroxide]_0/[AIBN]_0 = 1.99$, 110 °C). (a) TIPNO; (b) SG1.

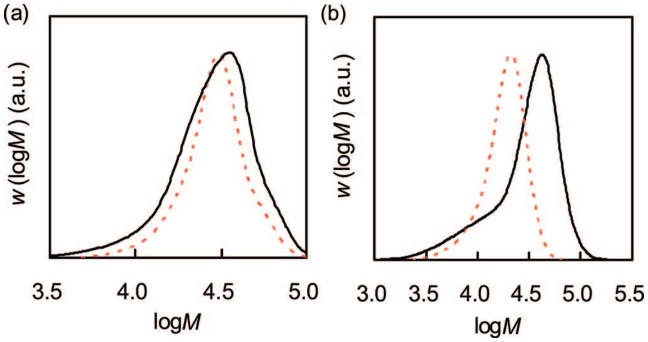

Figure 3. MWDs (normalized to peak height) for (a) SG1-mediated polymerizations of styrene in $scCO_2$ (dotted red line; conversion = 82%, M_n = 26 100, M_w/M_n = 1.20) and toluene (full black line; conversion = 82%, M_n = 23 800, M_w/M_n = 1.36) with 70% (w/v) monomer and (b) TIPNO-mediated polymerizations of styrene in $scCO_2$ with 70% (w/v) monomer (dotted red line; conversion = 29%, M_n = 15 950, M_w/M_n = 1.26) and 40% (w/v) monomer (full black line; conversion = 33%, M_n = 19 550, M_w/M_n = 1.85). $[Nitroxide]_0/[AIBN]_0$ = 1.99 and 110 °C in all cases.

In general, M_w/M_n is governed by the extent of termination (and side reactions) and the number of activation−deactivation cycles a chain experiences during its growth.[5] The greater the nitroxide concentration in the vicinity of the propagating radical chain end or the higher the rate coefficient of deactivation (k_{deact}), the higher is the number of cycles and the lower is the termination rate.[5] Thus, the most likely explanation for improved MWD control in $scCO_2$ relative to toluene at 70% monomer (w/v) is that the nitroxide concentration at the polymerization locus is higher and/or k_{deact} is higher in the precipitation system. This is consistent with the polymerization rate being lower in $scCO_2$ (Supporting Information).

At lower polymer content, the termination rate coefficient (k_t) increases significantly in $scCO_2$ due to poor solvent quality.[16] A tightly coiled polymer radical reacts more rapidly than a less tightly coiled polymer radical[16,17] —this is expected to also affect the deactivation rate. This would lead to improved MWD control if the effect on k_{deact} outweighs that on k_t, which is plausible because termination does not have a significant effect on the MWD if the livingness is high. Narrowing of the living segment of the MWD in $scCO_2$ relative to toluene has previously been observed in homogeneous RAFT polymerization of styrene and attributed to an increase in activation−deactivation rate.[18] At high conversions, $scCO_2$ has a strong plasticizing effect, enhancing molecular mobility[19] and leading to an increase in the rate of diffusion-controlled termination[16] and deactivation. The diffusivity of small molecules in $scCO_2$ is one or two orders of magnitude higher than in liquids.[20] Deactivation in ATRP becomes diffusion-controlled in cross-linking polymerizations,[21] and this may also occur in linear NMP when the polymer weight fraction is high. Again, if the effect on k_{deact} exceeds that on k_t, this would lead to a narrower MWD.

In summary, superior control indicated by narrower MWD in precipitation NMP of styrene in $scCO_2$ is obtained relative to the analogous homogeneous solution polymerization. This has significant implications for optimization of CLRP, especially in view of the fact that implementation of CLRP in heterogeneous systems is crucial from a commercial/industrial perspective.

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Supporting Information Available: Detailed experimental polymerization procedures, SEM photographs, conversion−time data, and MWDs corresponding to Figure 2. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93–146.

(2) (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987–2988. (b) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661–3688.

(3) (a) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921–2990. (b) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689–3745.

(4) (a) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2006**, *59*, 669–692. (b) Villarroya, S.; Thurecht, K. J.; Heiseb, A.; Howdle, S. M. *Chem. Commun.* **2007**, 3805–3813.

(5) Goto, A.; Fukuda, T. *Prog. Polym. Sci.* **2004**, *29*, 329–385.

(6) (a) Cunningham, M. F. *Prog. Polym. Sci.* **2002**, *27*, 1039–1067. (b) Qiu, J.; Charleux, B.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 2083–2134. (c) Save, M.; Guillaneuf, Y.; Gilbert, R. G. *Aust. J. Chem.* **2006**, *59*, 693–711. (d) Delaittre, G.; Nicolas, J.; Lefay, C.; Save, M.; Charleux, B. *Chem. Commun.* **2005**, *5*, 614–616. (e) Min, K.; Gao, H. F.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2006**, *128*, 10521–10526. (f) Zetterlund, P. B.; Okubo, M. *Macromolecules* **2006**, *39*, 8959–8967. (g) Kagawa, Y.; Zetterlund, P. B.; Minami, H.; Okubo, M. *Macromolecules* **2007**, *40*, 3062–3069.

(7) (a) DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. R.; Combes, J. R. *Science* **1994**, *265*, 356–359. (b) Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M. *Chem. Rev.* **1999**, *99*, 543–563.

(8) (a) Xia, J.; Johnson, T.; Gaynor, S. G.; Matyjaszewski, K.; DeSimone, J. M. *Macromolecules* **1999**, *32*, 4802–4805. (b) Minami, H.; Kagawa, Y.; Kuwahara, S.; Shigematsu, J.; Fujii, S.; Okubo, M. *Des. Monomers Polym.* **2004**, *7*, 553–562.

(9) (a) Odell, P. G.; Hamer, G. K. *Polym. Mater. Sci. Eng.* **1996**, *74*, 404–405. (b) Ryan, J.; Aldabbagh, F.; Zetterlund, P. B.; Okubo, M. *Polymer* **2005**, *46*, 9769–9777. (c) McHale, R.; Aldabbagh, F.;

Zetterlund, P. B.; Okubo, M. *Macromol. Rapid Commun.* **2006**, *27*, 1465–1471.

(10) McHale, R.; Aldabbagh, F.; Zetterlund, P. B.; Okubo, M. *Macromol. Chem. Phys.* **2007**, *208*, 1813–1822.

(11) McHale, R.; Aldabbagh, F.; Zetterlund, P. B.; Minami, H.; Okubo, M. *Macromolecules* **2006**, *39*, 6853–6860.

(12) Thurecht, K. J.; Gregory, A. M.; Wang, W.; Howdle, S. M. *Macromolecules* **2007**, *40*, 2965–2967.

(13) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904–3920.

(14) Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J.-P.; Tordo, P.; Gnanou, Y. *J. Am. Chem. Soc.* **2000**, *122*, 5929–5939.

(15) Ueda, A.; Nagai, S. In *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; John Wiley & Sons: New York, 1999; p II/97.

(16) Beuermann, S.; Buback, M.; Isemer, C.; Wahl, A. *Macromol. Rapid Commun.* **1999**, *20*, 26–32.

(17) (a) Dionisio, J.; Mahabadi, H. K.; O'Driscoll, K. F.; Abuin, E.; Lissi, E. A. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1891. (b) Keskinel, M.; Okay, O. *Polym. Bull.* **1998**, *40*, 491.

(18) Arita, T.; Beuermann, S.; Buback, M.; Vana, P. *e-Polym.* **2004**, *003*, 1–14.

(19) (a) Gupta, R. R.; Lavery, K. A.; Francis, T. J.; Webster, J. R. P.; Smith, G. S.; Russell, T. P.; Watkins, J. J. *Macromolecules* **2003**, *36*, 346–352. (b) Yang, Y.; Cheng, M. M. C.; Hu, X.; Liu, D.; Goyette, R. J.; Lee, L. J.; Ferrari, M. *Macromolecules* **2007**, *40*, 1108–1111.

(20) McHugh, M.; Krukonis, V. *Supercritical Fluid Extraction*, 2nd ed.; Butterworth-Heinemann: Newton, 1994.

(21) Wang, A. R.; Zhu, S. *Macromolecules* **2002**, *35*, 9926–9933.

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