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Reversible Chain Transfer Catalyzed Polymerization (RTCP) of Methyl Methacrylate with Nitrogen Catalyst in an Aqueous Microsuspension System

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Introduction. Controlled/living radical polymerization (CLRP) opens a new era in polymer chemistry. The CLRP enables to synthesize many kinds of vinyl polymers having a narrow molecular weight distribution and to design macromolecular architectures liberally.[1] The CLRP techniques such as nitroxide-mediated living radical polymerization (NMP),[2−6] atom transfer radical polymerization (ATRP),[7−13] reversible addition−fragmentation chain transfer (RAFT),[14−16] and organotellurium-mediated living radical polymerization (TERP)[17−24] have progressed remarkably in the past 15 years.[25−28]

Iodide transfer radical polymerization (ITP) (Scheme 1a),[29,30] which is also a CLRP technique, can be carried out under mild conditions. However, it is difficult to synthesize vinyl polymer with much narrow molecular weight distribution by ITP because the chain transfer constant (k_{ex}, k_{-ex}) of iodide compounds relative to the propagation reaction rate constant is too low to control the polymerization. Recently, Goto et al. discovered reversible chain transfer catalyzed polymerization (RTCP) (Scheme 1),[31] in which a very small quantity of iodide compounds of typically elements such as germanium,[32,33] tin,[32,33] phosphorus,[32−34] or nitrogen[31,35] is added to the ITP system, enables to synthesize vinyl polymers having a narrow molecular weight distribution. These compounds caused a reversible chain transfer (RT) (Scheme 1b) reaction with radical species. Because RT is much faster than degenerative chain transfer (DT) (Scheme 1a), RT is a dominant mechanism in RTCP.[36]

CLRP has another attraction for the application to aqueous dispersed systems.[6,28,37−40] The most applicable technique for CLRP is microsuspension and miniemulsion polymerizations because the ideally monomer droplets works as an isolated bulk system. In our previous works,[41,42] several CLRP techniques, which are NMP, ATRP, and TERP, were successfully applied to aqueous dispersed systems.

In this Communication, we will attempt to apply RTCP with nitrogen compounds to the microsuspension system for the first time.

Experimental Part. *Materials.* Methyl methacrylate (MMA) (Tokyo Kasei Kogyo Co. Ltd., Tokyo, Japan, >99.8%) and styrene (Mitsubishi Chemical Co. Ltd., Tokyo, Japan, >99.6%) were purified by distillation under reduced pressure in a nitrogen atmosphere. Water used in all experiments was obtained using an Elix UV (Millipore Japan) purification system and had a resistivity of 18.2 MΩ·cm. Reagent grade 2,2′-azobis(isobutyronitrile) (AIBN) (Nacalai Tesque, Kyoto, Japan) was purified by recrystallization. *N*-Iodosuccinimide (NIS) (Aldrich Chem Co. Ltd., 95%) and *n*-tetradecyltrimethylammonium bromide (TTAB) (Tokyo Kasei Kogyo Co. Ltd., Tokyo, Japan) were used as received. 2-Cyanopropyl iodide (CP-I) (97%) was supplied from Tokyo Kasei Kogyo Co. Ltd.

RTCP in Microsuspension System (*Microsuspension RTCP*). A monomer solution (AIBN 20 mg, 0.13 mmol; CP-I 0.195 g, 1.0 mmol; NIS 3.0 mg, 13 μmol; MMA 10 g, 0.10 mol) was mixed with an aqueous (90 g) solution of TTAB (0.45 g) and stirred vigorously at 5000 rpm using a homogenizer for 2 min. The emulsion was subsequently transferred to glass ampules and degassed using several vacuum/N_2 cycles, and then the ampules were sealed off under vacuum. The microsuspension RTCP of MMA was carried out at 80 °C with shaking of the ampules horizontally at 80 cycles min^{-1}. All of these processes were performed under a safe light because iodo compounds are light-sensitive.

ITP in Microsuspension System (*Microsuspension ITP*). The microsuspension ITP of MMA was carried out in the same way as the microsuspension RTCP, except for without NIS.

Conversion Measurement. Conversion was determined by gas chromatography (GC-18A, Shimadzu Co., Kyoto, Japan) employing helium as carrier gas, *N*,*N*-dimethylformamide as solvent, and *p*-xylene as internal standard.

Molecular Weight Measurement. Number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution (MWD) were measured by gel permeation chromatography (GPC) with two S/divinylbenzene gel columns (TOSOH Corp., TSKgel GMH_{HR}-H, 7.8 mm i.d. × 30 cm; bead size = 5 μm) using tetrahydrofuran (THF) as eluent at 40 °C at a flow rate of 1.0 mL/min employing refractive index (RI) (TOSOH RI-8020/21) and ultraviolet (UV) detectors (TOSOH UV-8II). The columns were calibrated with six standard PS samples (1.05×10^3−5.48×10^6, M_w/M_n = 1.01−1.15). Theoretical molecular weight ($M_{n,th}$) was obtained using $M_{n,th} = \alpha M_M[M]_0/[R-I]_0$, where α is the fractional conversion of monomer, M_M is the molecular weight of monomer, and $[M]_0$ and $[R-I]_0$ are the initial concentrations of monomer and transfer agent (alkyl iodide), respectively.

Particle Observation. Dried particles were observed with a transmission electron microscope (TEM, JEM-1230, JEOL Co. Ltd., Tokyo, Japan) at a voltage of 100 kV and a scanning electron microscope (SEM, JSM-6510, JEOL Co. Ltd.).

Results and Discussion. Figure 1 shows conversion−time and first-order plots of microsuspension RTCP of MMA with NIS as catalyst and CP-I as control agent. The polymerization smoothly proceeded without induction period and reached 93% within 2 h. The rate of the microsuspension RTCP was almost the same as that of RTCP in a bulk system (bulk RTCP) conducted under the same conditions except for TTAB and water.[31] The first-order plot ($-\ln(1-x)$ vs time) (where x stands for conversion) did not increase linearly above 50% conversion. This tendency was also observed in the bulk system.[31] The reason is unclear.

Figure S1 shows TEM and SEM photographs of PMMA particles prepared by the microsuspension RTCP with NIS and CP-I. The obtained particles were micrometer-size:

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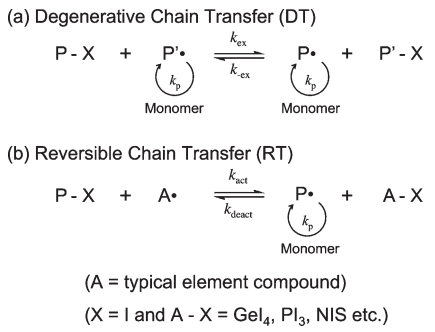
Scheme 1. Reversible Chain Transfer Catalyzed Polymerization (RTCP) (NIS = *N*-Iodosuccinimide)



number-average diameter (D_n), 5.54 μm; coefficient of variation, 30%. The obtained particle size distribution was almost the same as the original droplet size distribution according to optical microscope observation. Byproduct particles were not almost observed in the TEM and SEM observations, indicating that emulsion polymerization was negligible.

Figure 2 shows MWD (with RI detector), M_n, and M_w/M_n at different conversions of the microsuspension RTCP of MMA with NIS and CP-I. The MWD shifted to higher molecular weight side maintaining a narrow molecular weight distribution with conversion. The M_n value increased linearly with conversion and agreed with the $M_{n,th}$. In addition, the M_w/M_n values were relatively low (~1.54), which indicates that good control was maintained throughout the polymerization. The M_w/M_n of bulk RTCP of MMA was ~1.4 at 90% conversion.[35] These results indicate that NIS worked efficiently even in the aqueous dispersed system and was successfully applied to microsuspension RTCP.

To confirm chain extension (livingness) of the PMMA-I prepared by the microsuspension RTCP, bulk RTCP of styrene with the PMMA-I was carried out at 80 °C for various times in degassed and sealed glass ampules: PMMA-I (90% conversion sample; 1.0 g) in styrene (2.0 g, 19 mmol) with AIBN (11 mg, 6.6 μmol) and NIS (3.0 mg, 13 μmol). Figure 3 shows MWD (with RI detector), M_n, and M_w/M_n for PMMA-*b*-PS at the different conversions of the bulk RTCP of styrene. The polymerization smoothly proceeded and the conversion almost reached 90% within 5 h. The MWD shifted to higher molecular weight side with increasing conversion. The M_n value increased linearly and agreed well with the $M_{n,th}$. These results indicate that the PMMA-I maintained the livingness.

Figure S2 shows MWD obtained using UV detector with an incident wavelength of 254 nm, which enables to detect only polymer containing styrene units for the PMMA-*b*-PS. A large number of the low molecular weight polymer chains (log M = 3.5) observed with RI detector in Figure 3 were not detected with a UV detector in Figure S2. This result indicates that a small amount of nonactive PMMA was formed with PMMA-I prepared by the microsuspension RTCP. The livingness of the PMMA-I macro-transfer agent was calculated by transforming the MWD data of the bulk RTCP obtained from GPC with UV and RI detectors to number of polymer chains.

Figure S3 shows the number of polymer chains as a function of molecular weight of product at 6% conversion of the bulk RTCP of styrene at 80 °C with the PMMA-I. The distributions were subsequently normalized for conditions such that the high molecular weight segments were exactly superimposed. The fraction of nonextended macro-transfer agent relative to the total number of chains was then simply obtained as the integral of the UV-derived number distribution. RTCP needs additional radicals derived from initiator,

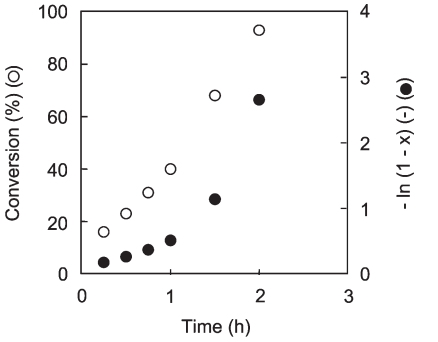


Figure 1. Conversion-time (open circles) and first-order plots (where x stands for conversion) (closed circles) for the microsuspension reversible chain transfer catalyzed polymerization of methyl methacrylate with *N*-iodosuccinimide (NIS) and 2-cyanopropyl iodide (CP-I) at 80 °C. $[CP\text{-}I]_0/[2,2'\text{-azobis(isobutyronitrile)}]_0/[NIS] = 80/10/1$.

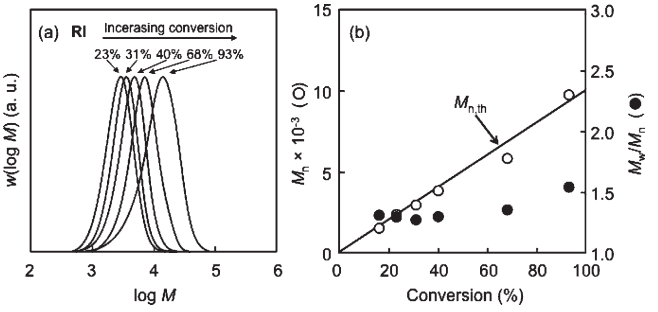


Figure 2. Molecular weight distribution (with RI detector) at various conversions (a) and number-average molecular weight (M_n) (open circles) and polydispersity index (M_w/M_n) (closed circles) vs conversion plots (b) for microsuspension reversible chain transfer catalyzed polymerization of methyl methacrylate with *N*-iodosuccinimide (NIS) and 2-cyanopropyl iodide (CP-I) at 80 °C. $[CP\text{-}I]_0/[2,2'\text{-azobis(isobutyronitrile)}]_0/[NIS] = 80/10/1$.

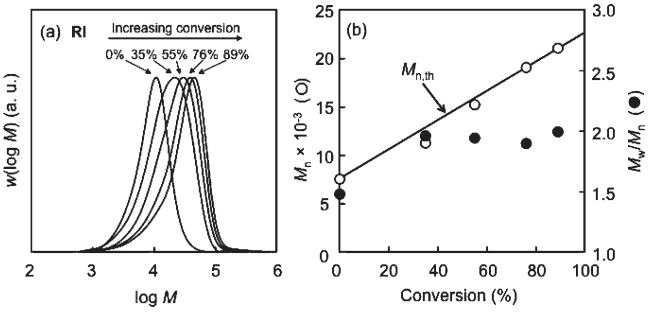


Figure 3. Molecular weight distribution (with RI detector) at various conversions (a) and number-average molecular weight (M_n) (open circles) and polydispersity index (M_w/M_n) (closed circles) vs conversion plots (b) for bulk reversible chain transfer catalyzed polymerization (RTCP) of styrene with *N*-iodosuccinimide (NIS) using PMMA-I prepared by the microsuspension RTCP at 80 °C.

which results in inevitable formation of PS homopolymer. The blocking efficiency (i.e., PMMA-I livingness) at 6% conversion was 70%, which is a relatively high value.

To understand the utility of the nitrogen catalyst (NIS), microsuspension ITP (i.e., without NIS) of MMA was carried out with CP-I at 80 °C. The polymerization proceeded smoothly without an induction period and almost finished within 1.5 h. However, the MWD did not shift to higher molecular weight side with increasing conversion, and the M_n values were high molecular weight even in the early stage of the polymerization like a conventional radical

polymerization. These results indicate that the microsuspension ITP of MMA did not proceed with living nature, and in other words, NIS is very important for the RTCP of MMA to proceed with living nature. On the other hand, bulk ITP under the same recipe except for without the TTAB aqueous solution proceeded with living nature. At present, the reason why microsuspension ITP did not proceed with living nature is unclear.

Conclusions. RTCP of MMA with nitrogen catalyst at 80 °C was successfully applied to an aqueous microsuspension system for the first time. The polymerization proceeded smoothly to 93% conversion in 2 h, and prepared PMMA particles had 5.54 μm diameter. The M_n value increased linearly with conversion and agreed well with the $M_{n,th}$. The MWD was narrow ($M_w/M_n \sim 1.5$), and bulk RTCP of styrene for chain extension test of PMMA-I indicated relatively high degrees of livingness (blocking efficiency = 70%).

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Supporting Information Available: TEM and SEM photographs of PMMA particles prepared by microsuspension RTCP at 80 °C; MWD (with UV detector) at various conversions for the bulk RTCP of styrene at 80 °C with PMMA-I macrotransfer agent prepared by microsuspension RTCP; number of polymer chains as a function of molecular weight of product at 6% conversion of the bulk RTCP of styrene at 80 °C with the PMMA-I macro-transfer agent prepared by the microsuspension RTCP calculated GPC data obtained using RI and UV detectors. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317–350.
(2) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987–2988.
(3) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661–3688.
(4) Nakamura, T.; Zetterlund, P. B.; Okubo, M. *Macromol. Rapid Commun.* **2006**, *27*, 2014–2018.
(5) Zetterlund, P. B.; Okubo, M. *Macromolecules* **2006**, *39*, 8959–8967.
(6) Charleux, B. Nitroxide-mediated polymerization in miniemulsion: A direct way from bulk to aqueous dispersed systems. In *Advances in Controlled/Living Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series 854; American Chemical Society: Washington, DC, 2003; pp 438−451.
(7) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614–5615.
(8) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721–1723.
(9) Kamigaito, K.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689–3745.
(10) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921–2990.
(11) Kagawa, Y.; Zetterlund, P. B.; Minami, H.; Okubo, M. *Macromol. Theory Simul.* **2006**, *15* (8), 608–613.
(12) Kagawa, Y.; Zetterlund, P. B.; Minami, H.; Okubo, M. *Macromolecules* **2007**, *40* (9), 3062–3069.
(13) Kitayama, Y.; Yorizane, M.; Kagawa, Y.; Minami, H.; Zetterlund, P. B.; Okubo, M. *Polymer* **2009**, *50*, 3182–3187.
(14) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559–5562.
(15) Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polymer* **2005**, *46*, 8458–8468.
(16) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2006**, *59*, 669–692.
(17) Goto, A.; Kwak, Y.; Fukuda, T.; Yamago, S.; Iida, K.; Nakajima, M.; Yoshida, J. *J. Am. Chem. Soc.* **2003**, *125*, 8720–8721.
(18) Yamago, S.; Iida, K.; Yoshoda, J. *J. Am. Chem. Soc.* **2002**, *124*, 13666–13667.
(19) Yamago, S.; Ray, B.; Iida, K.; Yoshida, J.; Tada, T.; Yoshizawa, K.; Kwak, Y.; Goto, A.; Fukuda, T. *J. Am. Chem. Soc.* **2004**, *126*, 13908–13909.
(20) Yamago, S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44* (1), 1–12.
(21) Kwak, Y.; Tezuka, M.; Goto, A.; Fukuda, T.; Yamago, S. *Macromolecules* **2007**, *40*, 1881–1885.
(22) Sugihara, Y.; Kagawa, Y.; Yamago, S.; Okubo, M. *Macromolecules* **2007**, *40*, 9208–9211.
(23) Okubo, M.; Sugihara, Y.; Kitayama, Y.; Kagawa, Y.; Minami, H. *Macromolecules* **2009**, *42*, 1979–1984.
(24) Kitayama, Y.; Chaiyasat, A.; Okubo, M. *Macromol. Symp.* **2010**, *288*, 25–32.
(25) Matyjaszewski, K. *Controlled/Living Radical Polymerization: Progress in ATRP, NMP, and RAFT*; American Chemical Society: Washington, DC, 2000.
(26) Matyjaszewski, K. *Advances in Controlled/Living Radical Polymerization*; American Chemical Society: Washington, DC, 2003.
(27) Braunecker, W.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93–146.
(28) Zetterlund, P. B.; Kagawa, Y.; Okubo, M. *Chem. Rev.* **2008**, *108*, 3747–3794.
(29) Matyjaszewski, K.; Gaynor, S.; Wang, J. S. *Macromolecules* **1995**, *28*, 2093–2095.
(30) Gaynor, S. G.; Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 8051–8056.
(31) Goto, A.; Tsujii, Y.; Fukuda, T. *Polymer* **2008**, *49*, 5177–5185.
(32) Goto, A.; Zushi, H.; Hirai, N.; Wakada, T.; Kwak, Y.; Fukuda, T. *Macromol. Symp.* **2006**, *248*, 126–131.
(33) Goto, A.; Zushi, H.; Hirai, N.; Wakada, T.; Tsujii, Y.; Fukuda, T. *J. Am. Chem. Soc.* **2007**, *129*, 13347–13354.
(34) Goto, A.; Hirai, N.; Tsujii, Y.; Fukuda, T. *Macromol. Symp.* **2008**, *261*, 18–22.
(35) Goto, A.; Hirai, N.; Wakada, T.; Nagasawa, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2008**, *41*, 6261–6264.
(36) Goto, A.; Wakada, T.; Fukuda, T.; Tsujii, Y. *Macromol. Chem. Phys.* **2010**, *211*, 594–600.
(37) Cunningham, M. F. *Prog. Polym. Sci.* **2008**, *33* (4), 365–398.
(38) Lansalot, M.; Farcet, C.; Charleux, B.; Vairon, J. P.; Pirri, R.; Tordo, P. Nitroxide-mediated controlled free-radical emulsion and miniemulsion polymerizations of styrene. In *Controlled/Living Radical Polymerization: Progress in ATRP, NMP and RAFT*; Matyjaszewski, K., Ed.; ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000; pp 138−151.
(39) Cunningham, M. F. *Prog. Polym. Sci.* **2002**, *27* (6), 1039–1067.
(40) Pham, B. T. T.; Nguyen, D.; Ferguson, C. J.; Hawkett, B. S.; Serelis, A. K.; Such, C. H. *Macromolecules* **2003**, *36*, 8907–8909.
(41) Kagawa, Y.; Minami, H.; Okubo, M.; Zhou, J. *Polymer* **2005**, *46*, 1045–1049.
(42) Zetterlund, P. B.; Alam, M. N.; Minami, H.; Okubo, M. *Macromol. Rapid Commun.* **2005**, *26*, 955–960.