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Anionic polymerization of alkyl methacrylates using flow microreactor systems

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ABSTRACT

Living anionic polymerization of alkyl methacrylates initiated by 1,1-diphenylhexyllithium was conducted in a flow microreactor system. A high level of molecular-weight distribution control was achieved under easily accessible conditions, such as at −28 °C (MMA: Mw/Mn = 1.16), 0 °C (BuMA: Mw/Mn = 1.24) and 24 °C (Bu^tMA: Mw/Mn = 1.12). The molecular weight (Mn) increased with an increase in the monomer/initiator ratio. The subsequent reaction of a reactive polymer chain end with a second alkyl methacrylate in integrated flow micoreactor systems led to the formation of a block copolymer having narrow molecular-weight distribution.

1. Introduction

Chemical synthesis in flow microreactor systems has received significant research interests from both academia and industry [1–16]. Recent investigations revealed significant features of flow microreactor systems involving fast mixing stemming from short diffusion path and fast heat transfer by virtue of high surface-to-volume ratio, which are advantageous to increase the selectivity of chemical reactions [17–19]. Short residence time in a microchannel is beneficial for controlling highly reactive intermediates [20–27]. By taking advantages of such features of flow microreactor systems, various chemical reactions for organic synthesis have been developed so far. Polymerization that converts small molecules into macro molecules by repeating chemical reactions is also a fascinating field in the applications of flow microreactor systems [28,29]. Nowadays extensive studies on radical polymerization of vinyl monomers [30–34], coordination polymerization [35], polycondensation [36], and ring-opening polymerization [37,38] using flow microreactor systems have been reported. Major advantages of polymerization using flow microreactor systems include the control of molecular weights of polymers by modulating the monomer/initiator ratio with the change of the relative flow rates. It is also noteworthy that the continuous microreactor systems are suitable for producing libraries of polymers for high-throughput evaluation. Recently we have reported that cationic polymerization in a flow microreactor system led to high degree of molecular-weight distribution control without the deceleration inherent in the dynamic equilibrium between active and dormant species in classical living polymerization [39–41]. The characteristic features of flow microreactor systems, including fast mixing, fast heat transfer, and short residence time, seem to be responsible for the excellent molecular-weight distribution control.

Among various methods of polymerization, anionic polymerization of vinyl monomers serves as an excellent method for the synthesis of polymers with well-defined end-structures, because the anionic polymer ends are living even in the absence of a capping agent [42] and can be utilized for end-functionalization reactions with various electrophiles, and block copolymerization [43]. Especially, synthesis of poly(alkyl methacrylate)s via anionic polymerization of alkyl methacrylate has received significant research interests because poly(alkyl methacrylate)s are utilized as versatile materials such as plastics, adhesives and elastomers containing a number of different reactive functions [44]. However, using a conventional macrobatch reactor, living anionic polymerization of alkyl methacrylates should be carried out at low temperatures such as −78 °C to obtain polymers of narrow molecular-weight distribution [45,46]. The requirement of such low temperatures causes several limitations in the use of this highly useful polymerization technology in industry. Therefore, these commercially available methacrylate polymers are prepared by radical polymerization processes. Recent development in living radical polymerization method offers great promise [47], and a number of methods using a capping agent have been developed such as degeneration or exchange chain transfer, atom transfer radical polymerization, nitroxide-mediated radical polymerization, and reversible addition-fragmentation chain transfer polymerization [48,49]. However, if the problem on the requirement of such low temperatures in anionic polymerization is solved [50–52], living anionic polymerization of alkyl methacrylate will become a powerful method in poly(alkyl methacrylate)s synthesis. In a preliminary communication, we reported that the use of flow microreactor systems enabled living anionic polymerization of alkyl methacrylates

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initiated by 1,1-diphenylhexyllithium under easily accessible conditions compared with conventional macrobatch polymerization. Herein, we report the full details of this study.

2. Experimental

2.1. General

GC analysis was performed on a SHIMADZU GC-2014 gas chromatograph equipped with a flame ionization detector using a fused silica capillary column. ^{1}H NMR spectra were recorded in $CDCl_3$ on Varian MERCURY plus-400 (^{1}H 400 MHz) spectrometer with Me_4Si as an internal standard unless otherwise noted. THF was purchased from Kanto as a dry solvent and used as obtained. All monomers were distilled twice over CaH_2 before use. 1,1-Diphenylethylene was purchased from Aldrich and distilled before use. *n*-BuLi in hexane (2.6 M) was purchased from Kanto and used as obtained. Stainless steel (SUS304) T-shaped micromixers having inner diameter of 250 and 500 μm were manufactured by Sanko Seiki Co., Inc. Stainless steel (SUS316) microtube reactors having inner diameter of 1000 μm were purchased from GL Sciences. Micromixers and microtube reactors were connected with Stainless Type Fittings (GL Sciences, 1/16 OUW). The flow microreactor system was dipped in a cooling bath to control the temperature. Solutions were introduced to a flow microreactor system using syringe pumps, Harvard Model 11 Plus or Harvard PHD 2000, equipped with gastight syringes purchased from SGE.

The molecular weight (Mn) and molecular-weight distribution (Mw/Mn) were determined in THF at 40 °C with a Shodex GPC-101 equipped with two LF-804L columns (Shodex) and a RI detector using a polystyrene standard sample for calibration.

2.2. Preparation of a solution of 1,1-diphenylhexyllithium (DPHLi)

To a solution of a little excess of 1,1-diphenylethylene in THF (1.1 equiv.) was added a solution of *n*-BuLi in hexane at 0 °C, and the solution was allowed to gradually attain room temperature.

2.3. Anionic polymerization of methyl methacrylate using a macro batch reactor

To a solution of 1,1-diphenylethylene in THF (19.8 mg, 0.110 mmol, 1.9 mL) was added a solution of *n*-BuLi in hexane (2.77 M, 0.036 mL) in a 20 mL flask. To the resulting solution was added a solution of methyl methacrylate (0.50 M, 6.0 mL) in THF within 3 s at T °C (T = 0, −28, −48, −78 °C). After 1 min (T = 0, −28, −48 °C) or 5 min (T = −78 °C), the reaction mixture was quenched by a solution of methanol in THF (0.33 M, 3.0 mL) at T °C. The conversion of the methyl methacrylate was determined by GC. The solvent was removed under reduced pressure to obtain the polymer product and the polymer sample was analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (see the Supplementary Information for details, Figs.S-1–S-4).

2.4. Anionic polymerization of alkyl methacrylates using flow microreactor systems

2.4.1. Typical procedure for anionic polymerization of alkyl methacrylates using flow microreactor systems

A flow microreactor system composed of two T-shaped micromixers (M1 and M2) and two microtube reactors (R1 and R2) was used. Microtube pre-cooling units (ϕ = 1000 μm, length = 100 cm) were connected to each inlets of M1 and M2. The whole flow microreactor system was dipped in a cooling bath. A solution of alkyl methacrylate in THF (0.50 M) and a solution of 1,1-diphenylhexyllithium in THF/hexane (99/1, v/v) (0.050 M) were introduced to M1 by syringe pumps. The resulting solution was passed through R1 (ϕ = 1000 μm) and was quenched with a solution of methanol in THF (0.33 M) (flow rate: 3.0 mL/min) in M2 (ϕ = 500 μm). The resulting solution was passed through R2 (ϕ = 1000 μm, length = 50 cm). After a steady state was reached, the product solution was taken (30 s). The flow microreactor system was dipped in a cooling bath to control the temperature. Residence time in R1 (t^R) was controlled by changing the length of R1 with the fixed flow rate. The polymerization was carried out with varying temperature, residence time in R1, flow rate of a solution of alkyl methacrylate and 1,1-diphenylhexyllithium, and inner diameter of M1. The conversion of alkyl methacrylate was determined by GC. The solvent was removed under reduced pressure to obtain the polymer product and the polymer sample was analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (see the Supplementary Information for details, Figs. S-5–S-51).

2.4.2. Typical procedure: livingness of the reactive carbanionic polymer chain end in anionic polymerizations of alkyl methacrylates using flow microreactor systems

A flow microreactor system composed of two T-shaped micromixers (M1 and M2) and two microtube reactors (R1 and R2) was used. Microtube pre-cooling units (ϕ = 1000 μm, length = 100 cm) were connected to each inlets of micromixers M1 and M2. A solution of monomer-1 in THF (0.50 M) (flow rate: 3.0 mL/min) and a solution of 1,1-diphenylhexyllithium in THF/hexane (99/1, v/v) (0.050 M) (flow rate: 1.0 mL/min) were introduced to M1 (ϕ = 250 μm) by syringe pumps. The resulting solution was passed through R1 (ϕ = 1000 μm) and was mixed with monomer-2 in THF (0.50 M) (flow rate: 3.0 mL/min) in M2 (ϕ = 250 μm). The resulting solution was passed through R2 (ϕ = 1000 μm, length = 200 cm). After a steady state was reached, the product solution was introduced (30 s) to methanol to quench the polymerization. The flow microreactor system was dipped in a cooling bath to control the appropriate temperature (−28 °C (MMA), 0 °C (BuMA)). Residence time in R1 (t^R) was controlled by changing the length of R1. The polymerization was carried out with varying residence time in R1. MMA or BuMA monomers were used. The conversions of the alkyl methacrylates were determined by GC. The solvent was removed under reduced pressure to obtain the polymer product and the polymer sample was analyzed with size exclusion chromatography with the calibration using standard polystyrene samples (see the Supplementary Information for details, Figs. S-52–S-59). Results are summarized in Table S-1 (see the Supplementary Information for details).

2.4.3. Typical procedure for anionic block copolymerizations of alkyl methacrylates using flow microreactor systems

A flow microreactor system composed of two T-shaped micromixers (M1 and M2) and two microtube reactors (R1 and R2) was used. Microtube pre-cooling units (ϕ = 1000 μm, length = 100 cm) were connected to each inlets of micromixers M1 and M2. A solution of monomer-1 in THF (0.50 M) (flow rate: 3.0 mL/min) and a solution of 1,1-diphenylhexyllithium in THF/hexane (99/1, v/v) (0.050 M) (flow rate: 1.0 mL/min) were introduced to M1 (ϕ = 250 μm) by syringe pumps. The resulting solution was passed through R1 (Bu^{t}MA: ϕ = 1000 μm, length = 100 cm (11.8 s); BuMA: ϕ = 1000 μm, length = 7 cm (0.825 s)) and was mixed with monomer-2 in THF (0.50 M) (flow rate: 3.0 mL/min) in M2 (ϕ = 250 μm). The resulting solution was passed through R2 (ϕ = 1000 μm, length = 50 cm (monomer-1: Bu^{t}MA) or 200 cm (monomer-1: BuMA)). After a steady state was reached, the product solution was introduced (30 s) to methanol