

Precise analysis and control of polymerization kinetics using a micro flow reactor



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ABSTRACT

Polymerization has a fast, complex reaction kinetics, which is difficult to control with conventional equipment. We employed a micro flow system to design ideal reaction conditions based on a kinetic model. Rate analysis was conducted at a wide range of reaction times, from 10 to 3600 s. The concentration profile of an active intermediate was estimated and utilized for designing advanced reaction schemes, which required rapid concentration and temperature changes. A block copolymer of hexyl norbornene and norbornene carboxylic acid alkyl ester was synthesized by developing a sequential polymerization system. The temperature jump operation, with 0.5 s initiation at 60 °C followed by 30 s propagation at 0 °C, generated a hexyl norbornene polymer with a sharp molecular weight distribution.

1. Introduction

A flow reactor with a small scale diameter, typically tens of microns to a millimeter, enables rapid mass and heat transfer via the short diffusion length, high surface to volume ratio and controlled secondary flows [1,2]. Therefore, a micro flow reactor is an attractive tool for producing fine chemicals and materials that require the strict control of process conditions for product quality [3,4]. For instance, monodispersed quantum dots were synthesized in a silicon carbide micro flow reactor with rapid heating [5]; a synthetic retinoid TAC-101 was synthesized via the Br/Li exchange reaction with rapid mixing [6]; and zeolitic imidazolate framework-8 particles with controlled sizes, shapes and gate adsorption characteristics were produced using a micromixer with 10 sub-streams [7]. Continuous flow synthesis also improves reproducibility [8] and productivity [9]. Therefore, small sized flow reactors, which do not necessarily have a microscale, have been intensively applied for on-demand production, especially of active pharmaceutical ingredients [10–12].

Micro flow reactors have been employed for precision polymerization for decades [13]. First, rapid mixing and heat removal have a significant advantage to make a sharp molecular weight distribution by providing strict control of the concentration and temperature. For example, improvement of molecular weight distributions in the radical polymerization of styrene [14], cationic polymerization of vinyl ether [15], and Grignard metathesis polymerization of 3-hexylthiophene [16]

have been reported. Smaller polymer particles with a tighter size distribution were generated in an ultrasound-assisted, surfactant-free emulsion polymerization in a narrow channel reactor coil [17]. A tiny reaction volume with pressure resistance has advantages that allow us to safely conduct an unconventional reaction scheme that involves hazardous chemicals and high temperature and pressure. End group modification using trimethylsilyl azide at 120 °C and 20 bar, which would have explosion risks and the formation of extremely toxic HN₃ gasses in a batch reactor, was successfully achieved in a commercial microchip [18]. The flow system can be equipped with in-line purification and process automation, which dramatically improve productivity and scalability. A modular flow system with a membrane separator achieved sequence defined polymer synthesis with a 66 g day⁻¹ throughput [19].

Almost all of the above polymerization studies with micro flow reactors have been empirically optimized by changing the temperature, residence time, concentrations and reactors, i.e., without kinetic modeling. One reason is probably the complexity of the polymerization mechanisms. However, optimization based on reaction kinetics would effectively improve the quality and productivity of the process. Kinetic modeling and micro flow reactors would have a strong synergy. Micro flow reactors can acquire reliable data for rate analysis by controlling the reaction time at a surprisingly high-resolution on the order of milliseconds [20]. Furthermore, the complicated behavior of secondary flows and concentration profile in a microreactor can be analyzed and

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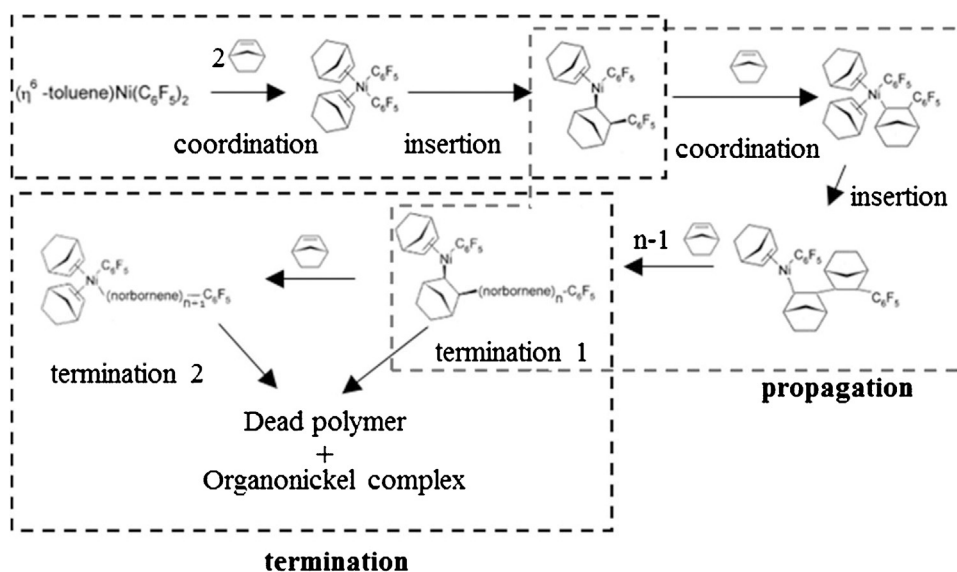


Fig. 1. Proposed reaction mechanism based on Barnes et al. [23].

optimized with the assistance of computational fluid dynamics simulation and 3D printing techniques [21]. An automated experiment that changes numerous variables is also possible with a compact system consisting of a micro flow reactor, pumps, and an analyzer [22]. Rapid heat and mass transfer enable us to realize the ideal conditions derived from the kinetic model, even if they require temperature changes within a second.

This study intended to invent a precision polymerization procedure based on polymerization kinetics. We chose the non-living coordination polymerization of norbornene derivatives as a model. Fig. 1 illustrates a proposed reaction mechanism for this system based on Barnes et al. [23]. Polymerization proceeds via insertion and coordination of a monomer to the nickel complex. There are two types of termination via proton transfer to an end group norbornene, where one is in the state of one monomer coordination (termination 1) and the other one is in the state of two monomer coordination (termination 2). This study attempted to acquire the kinetic parameter for each step and design a procedure to synthesize a block copolymer and a polymer with a monodispersed molecular weight distribution. These are challenging objectives in a non-living system in which an undesirable termination reaction exists. However, it would be a promising approach to intensify the versatility of polymer processing by expanding the scope of precision polymerization.

2. Methods

2.1. Materials

Monomer materials of hexyl norbornene (monomer A) and norbornene carboxylic acid alkyl ester (monomer B) and an initiator of $(\eta^6\text{-toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$ were supplied from SUMITOMO BAKELITE (Tokyo, Japan). Toluene, tetrahydrofuran (THF), ethyl acetate, 30 wt% hydrogen peroxide, and acetic acid were purchased from Wako Pure Chemical Industries (Osaka, Japan). The monomer was diluted with a mixture of toluene and ethyl acetate at a weight ratio of 3:7. The prepared monomer solution was dried by bubbling with nitrogen gas for 30 min before usage. The initiator solution was prepared by diluting $(\eta^6\text{-toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$ with toluene. The aqueous peracetic acid solution for termination was prepared as THF = 27 wt%, H_2O = 53 wt%, H_2O_2 = 8 wt%, and CH_3COOH = 12 wt%.

2.2. Constant temperature polymerization for kinetic analysis

Fig. 2(a) illustrates the reactor system. The reactor was constructed

using SUS tubing and tees. Tubing with an outer diameter (o.d.) of 1/16" and an inner diameter (i.d.) of 1.0 mm was connected to union tees (Swagelok, USA) with an i.d. of 1.3 mm. All tubing was coiled to enhance the heat and mass transfer and to reduce the residence time distribution [24,25]. The first tee mixes the monomer and initiator solution, and the other tee injects the peracetic acid solution to terminate the reaction. All were placed in a water bath to keep the temperature constant. The reaction time was controlled by changing the flow rate and length of tubing between tees. Two meters of tubing was used for reaction times from 10 to 20 s, 5 m of tubing was used for 30 to 60 s, and 10 m of tubing was used for 150 to 3600 s. Four concentration sets were examined. The monomer A ($[\text{M}]$) and initiator ($[\text{I}]$) concentrations after the first tee for each set are listed as follows:

set 1 (monomer 5 wt%): $[\text{M}] = 0.25 \text{ M}$, $[\text{I}] = 0.0049 \text{ M}$

set 2 (monomer 10 wt%): $[\text{M}] = 0.49 \text{ M}$, $[\text{I}] = 0.0049 \text{ M}$

set 3 (monomer 15 wt%): $[\text{M}] = 0.74 \text{ M}$, $[\text{I}] = 0.0049 \text{ M}$

set 4 (monomer 14 wt%): $[\text{M}] = 0.68 \text{ M}$, $[\text{I}] = 0.0048 \text{ M}$.

The ratios of the flow rates of the monomer solution, 5 kg m^{-3} initiator solution, and terminator solution were 0.86: 1: 1 for set 4 and 1.3: 1: 1 for the other sets. The flow rate was controlled using PHD Ultra syringe pumps (Harvard Apparatus, Massachusetts, USA).

To confirm that the kinetic parameters were not contaminated by heat and mass transfer issue, which originates from the enhanced viscosity with molecular weight build up, we measured the viscosity of a polymer solution. The sample polymer solution was obtained by polymerization in a batch reactor. Set 4 concentration was employed. A conical flask placed in a water bath at 25 °C was used as a batch reactor. Air was purged with nitrogen gas before the injection of initiator solution. After 1 h reaction, kinematic viscosity of the solution was measured by an Ostwald viscometer with an inner diameter of 1.75 mm (As One, Osaka, Japan). Terminator solution was not added for measuring the viscosity before the dilution. The density of the solution was also obtained by weighing the 1 mL solution to convert kinematic viscosity to absolute viscosity.

2.3. Block copolymer synthesis

Fig. 2(b) illustrates the reactor system. Union tees with an i.d. of 0.33 mm were used. The first tee mixes the monomer A and initiator solutions. The second tee mixes the reacting stream and the monomer B solution. The third tee injects the terminator. Two water baths were used to change the temperature from 40 °C to 25 °C. The lengths of tubing were 2 m for both the first and second steps. The concentrations after the first tee were $[\text{M}] = 0.61 \text{ M}$ and $[\text{I}] = 0.0043 \text{ M}$. The

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