

## Cation Pool-Initiated Controlled/Living Polymerization Using Microsystems

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The discovery of controlled/living polymerization is an epoch-making event in polymer science and technology, and the control of molecular weight and molecular weight distribution is still at the forefront in this field. One of the key issues of controlled/living cationic<sup>1</sup> and radical<sup>2,3</sup> polymerizations is the establishment of a dynamic equilibrium between active (growing) and dormant species to maintain a low concentration of active species. This equilibrium is also helpful in preventing chain-breaking processes, such as termination and transfer reactions.

In the controlled/living cationic polymerization, for example, the growing chain end is represented by the Winstein equilibrium, as shown in Scheme 1. Molecular weight control is possible when the exchange between the active and dormant species is faster than propagation. Therefore, much effort has been devoted to developing efficient systems for this equilibrium. Various counteranions, Lewis acids (catalysts), and noncharged nucleophiles used to form onium ions have been developed to control the exchange process.

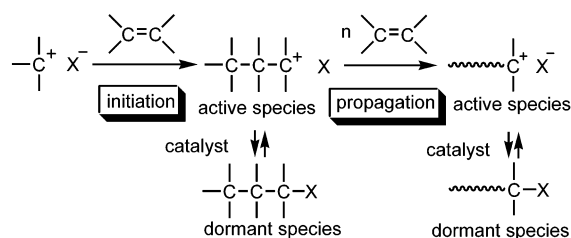
The major drawback of the presence of such an equilibrium is a slow propagation because the concentration of active species is very low. Usually, controlled/living polymerization is 10<sup>7</sup>–10<sup>8</sup> times slower than those without such an equilibrium. Another important feature in controlling molecular weight and its distribution is the initiation. To control the degree of polymerization based on the monomer/initiator ratio, the initiation reaction should be very fast and quantitative. Therefore, in the controlled/living polymerization, the apparent rate of initiation is usually comparable to, or larger than, that of propagation.

We envisioned that the use of the combination of a highly reactive initiator and an extremely fast mixing device would enable the control of molecular weight and its distribution, even in the absence of the dynamic equilibrium that decelerates the propagation. We have recently developed the “cation pool” method,<sup>4</sup> which involves the irreversible generation and accumulation of highly reactive cations in the absence of nucleophiles. We also found that micromixing<sup>5</sup> is quite effective for the reactions of the cation pool.<sup>6</sup> When combined with a microsystem<sup>7</sup> for efficient mixing, this cation pool can serve as an effective initiator for a new controlled/living cationic polymerization. In this paper, we wish to report our results indicating that this concept works.

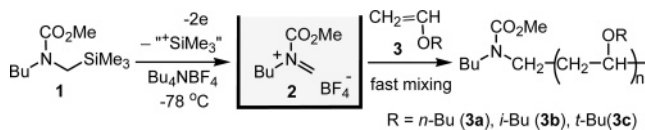
For a cation pool, we chose to study the *N*-acyliminium ion **2**, which is generated from *N*-methoxycarbonyl-*N*-(trimethylsilylmethyl)butylamine **1** by low-temperature electrochemical oxidation and is accumulated in a solution (cation pool) (Scheme 2). The counteranion of **2** seemed to be the tetrafluoroborate anion (BF<sub>4</sub><sup>-</sup>) derived from the supporting electrolyte (Bu<sub>4</sub>NBF<sub>4</sub>) for the electrochemical oxidation.

Before using a microsystem, the reaction using a conventional batch reactor was examined. The addition of a CH<sub>2</sub>Cl<sub>2</sub> solution of butyl vinyl ether (**3a**) (50 equiv, 5 mL/min) to a solution of **2** gave

Scheme 1



Scheme 2



the polymer in quantitative yield after quenching with *i*-Pr<sub>2</sub>NH/CH<sub>2</sub>Cl<sub>2</sub>, but the molecular weight distribution was not narrow ( $M_n = 5700$ ,  $M_w/M_n = 2.56$ ). The reverse addition sequence (**2** to the monomer) gave rise to a similar molecular weight distribution (quantitative yield,  $M_n = 13100$ ,  $M_w/M_n = 2.25$ ). The simultaneous addition of **3a** and **2** did not improve the molecular weight distribution control (quantitative yield,  $M_n = 24500$ ,  $M_w/M_n = 2.43$ ).

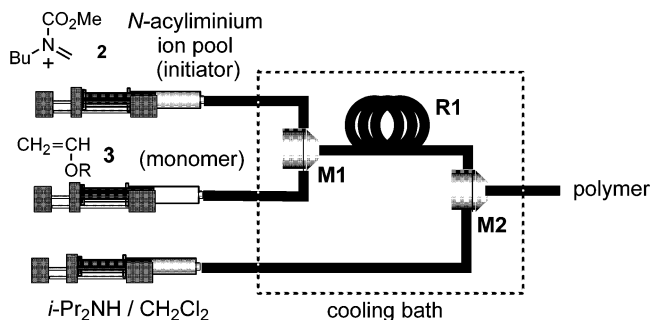
To effect an efficient and extremely fast mixing for controlled polymerization, we then employed a microsystem consisting of two micromixers (M1 and M2) and a microtube reactor (R1), as shown in Figure 1. At M1, where the cation pool and the monomer are mixed, a multilamination-type micromixer (40 μm channel width) manufactured by IMM (Institut für Mikrotechnik Mainz GmbH) was used. Thus, solutions of **2** (0.05 M) and **3a** (0.5–2.5 M) were introduced to M1 by the syringe pumping technique (5.0 mL/min flow rate) at  $-78$  °C. Then, the reaction mixture was introduced to a microtube reactor (R1) ( $\phi = 1.0$  mm, 10 cm), in which the polymerization took place. In the final stage, *i*-Pr<sub>2</sub>NH/CH<sub>2</sub>Cl<sub>2</sub> (0.83 M, 3 mL/min) was introduced through M2 to quench the polymerization. At M2, a splitting and recombination-type micromixer (Yamatate YM-1) was used.

We found that the polymerization took place quite effectively. The polymerization was complete within the residence time of 0.5 s. The molecular weight ( $M_n$ ) increased linearly with an increase in the amount of **3a** (Table 1, runs 1–4), indicating that transfer reactions did not play significant roles in this system.

More outstanding is the significant improvement of the control of molecular weight distribution by micromixing (run 4,  $M_w/M_n = 1.14$ ). The effect of the flow rate on molecular weight distribution (runs 4–6) indicates the importance of mixing because it is known that mixing efficiency decreases with a decrease in flow rate in the IMM micromixer.<sup>5a</sup> Reaction temperature was also important for controlling molecular weight distribution.  $M_w/M_n$  values increased with increasing temperature (runs 4 and 7–9). The present results demonstrate that a high level of molecular weight control

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**Figure 1.** Microsystem for polymerization. M1 and M2: micromixers. R1: microtube reactor.

**Table 1.** Cationic Polymerization of Vinyl Ethers (**3a–3c**) Initiated by the *N*-Acyliminium Ion Pool (**2**) Using a Microsystem<sup>a</sup>

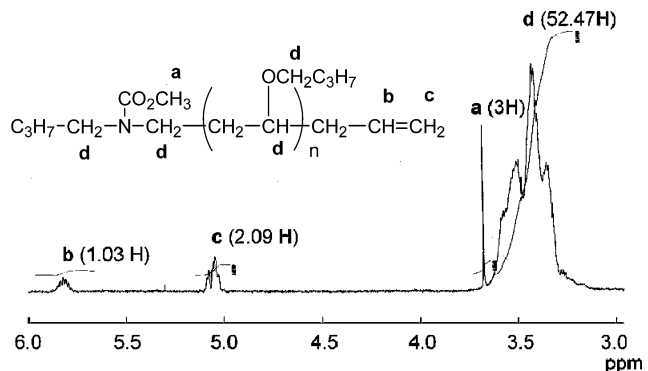
runs	monomer (equiv)	flow rate (mL/min)	<i>T</i> (°C)	<i>M<sub>n</sub></i> <sup>b</sup>	<i>M<sub>w</sub>/M<sub>n</sub></i> <sup>b</sup>
1	<b>3a</b> (10)	5.0	−78	1500	1.40
2	<b>3a</b> (25)	5.0	−78	2900	1.26
3	<b>3a</b> (35)	5.0	−78	4400	1.17
4	<b>3a</b> (50)	5.0	−78	6700	1.14
5	<b>3a</b> (50)	3.0	−78	5600	1.35
6	<b>3a</b> (50)	1.0	−78	6200	2.84
7	<b>3a</b> (50)	5.0	−48	8200	1.30
8	<b>3a</b> (50)	5.0	−27	5500	1.34
9	<b>3a</b> (50)	5.0	0	6500	1.61
10	<b>3b</b> (50)	5.0	−78	7900	1.12
11	<b>3c</b> (50)	5.0	−78	7600	1.50

<sup>a</sup> Polymerization was carried out in CH<sub>2</sub>Cl<sub>2</sub> at −78 °C and was almost quantitative in all cases. <sup>b</sup> Polymer samples were filtered through a short silica gel column to remove the supporting electrolyte and analyzed by size exclusion chromatography with a polystyrene calibration.

can be achieved by controlling the initiation process, which is effected by micromixing. Precise control of polymerization temperature in the microsystem by virtue of effective heat transfer also seems to be responsible for the remarkable control.

The present cation pool/micromixer method can be applied to other vinyl ethers, such as isobutyl vinyl ether (**3b**, run 10) and *tert*-butyl vinyl ether (**3c**, run 11). The corresponding macroscale batch reactions for these monomers resulted in much poorer molecular weight distribution control (**3b**, *M<sub>w</sub>/M<sub>n</sub>* = 4.31; **3c**, *M<sub>w</sub>/M<sub>n</sub>* = 2.29).

It is important to know whether the *N*-acyliminium ion initiating group was really incorporated into the polymer chain. It is also important to know the nature of the polymer end. To examine these factors, the polymerization of **3a** (10 equiv) was carried out with **2** and was quenched with the addition of allyltrimethylsilane. The resulting polymer was analyzed by <sup>1</sup>H NMR. As shown in Figure 2, the ester methoxy group from **2** was clearly observed at 3.68 ppm. It is also worth noting that an allyl group was observed as the end group (olefinic protons, 5.02–5.10 and 5.76–5.88 ppm, with the relative number of protons based on the methoxy group, 2.09 and 1.03, respectively), indicating that the carbocationic polymer end was trapped by the added allyltrimethylsilane. It is also noteworthy that a relative number of protons adjacent to oxygen in the main chain (3.3–3.7 ppm) was 48.47 (four protons adjacent to nitrogen overlapped), indicating that 16.16 of the monomer units were incorporated in a single polymer chain, on average. Because 10 equiv of the monomer based on precursor **1** was used for the polymerization, this number is slightly large but cannot be unreasonable if we consider that the efficiency of the conversion of **1** to **2** is 70–80%. The present observations indicate that the polymer end was really living within the residence time of 0.5 s at −78 °C.



**Figure 2.** <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of the polymer obtained by the micromixing controlled polymerization of **3a**, which was initiated by **2** and terminated by allyltrimethylsilane.

In summary, the present observations illustrate the potential of microsystems, in conjunction with our cation pool, to effect cationic polymerization in a highly controlled manner without the deceleration inherent in the dynamic equilibrium between active and dormant species. The molecular weight distribution can be controlled by extremely fast micromixing, and the polymer end can be used as the living reactive species for the follow-up reaction. Further applications of the present concept based on the inherent advantages of microsystems will hopefully appear in the field of polymer science and technology in the future.

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**Supporting Information Available:** Experimental procedures and characterization of polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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