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Microsystem controlled cationic polymerization of vinyl ethers initiated by CF_3SO_3H†

Takeshi Iwasaki,[a] Aiichiro Nagaki[b] and Jun-ichi Yoshida*[b]

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Practical cationic polymerization and block-copolymerization of vinyl ethers have been achieved at −25 °C by using CF_3SO_3H initiator in microsystems with high level of molecular weight distribution control.

Chemical synthesis in microsystems has received significant research interests from both academia and industry.[1,2] Recent investigations revealed significant features of microsystems involving fast mixing stemming from short diffusion time and fast heat transfer by virtue of high surface-to-volume ratio, which are advantageous to increase the selectivity of chemical reactions.[3] Short residence time in the micro channel is beneficial for controlling highly reactive intermediates.[4] By taking advantages of such features of microsystems, various chemical reactions for organic synthesis have been developed so far.[5] Polymer synthesis is also a fascinating field in the applications of microsystems.[6] Recently, we found that cationic polymerization in a microsystem 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.[7] However, the needs of low temperature electrochemical generation of a "cation pool"[8] initiator might be the major drawback from a view-point of polymer synthesis. Thus, we initiated our project on proton-initiated polymerization in microsystems, because various Brønsted acids are commercially available.

We focused on the polymerization of vinyl ethers.[9] Because some poly(vinyl ethers) of low molecular weight are known to be lubricating oil for compression refrigerators and is expected to serve as an environmentally benign substitute of freon,[10] the polymerization was conducted at a low monomer/initiator ratio to obtain a polymer of relatively low molecular weight. As a Brønsted acid initiator, we chose to study trifluoromethane-sulfonic acid (TfOH) after several trials with other acids.[11] Before using a microsystem, the reaction using conventional batch reactor was examined. The polymerization of isobutyl vinyl ether (IBVE) in 1,2-dichloroethane (20 mL scale) was complete within 10 s at −25 °C (100% conversion). The molecular weight distribution was, however, rather broad and Mw/Mn ranged from 2.73 to 4.71, indicating that the polymerization is too fast to control in a macro-scale batch system.[12]

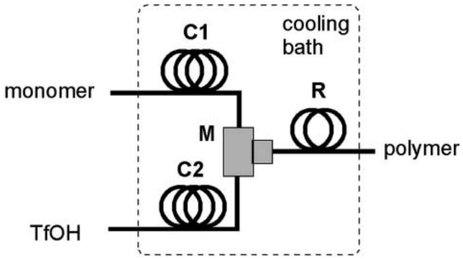

Fig. 1 Schematic diagram of the microsystem for polymerization (C1, C2: pre-cooling unit; M: T-shaped micromixer; R: microtube reactor).

Thus, the polymerization in a microsystem was examined. A microsystem consisting of a T-shaped micromixer (inner diameter: 250 μm) and a microtube reactor (inner diameter: 500 μm, length: 50 cm) with pre-cooling units (inner diameter = 1.0 mm, length: 2 m) was used (Fig. 1). As shown in Table 1 the microsystem was quite effective for the polymerization. The polymerization was complete within the residence time of 0.37–1.5 s (almost quantitative yield).

High level of molecular distribution control was attained even at −25 °C, although the Mw/Mn increased with the decrease of the flow rate (<5 ml min^{-1}). It is important to note that very low temperatures such as −78 °C, which might be an obstacle to industrial-scale applications,[13] is not required in the present system. Slightly lower reactivity of TfOH compared with "cation pools"[14] as well as fast mixing and efficient heat transfer in the microsystem seems to be responsible for the observed high degree of molecular weight distribution control.

As shown in Fig. 2 the molecular weight (Mn) increased with an increase in the monomer/initiator ratio. The result indicates that transfer reactions did not play significant roles in the present

Table 1 TfOH initiated polymerization of isobutyl vinyl ether (IBVE) in microsystem[a]

monomer flow rate/mL min^{-1}	initiator flow rate/mL min^{-1}	residence time/sec	Mn	Mw/Mn
2	2	1.5	2880	2.30
3	3	0.98	2350	2.34
4	4	0.74	1630	1.61
5	5	0.59	1490	1.22
6	6	0.49	1470	1.22
7	7	0.42	1450	1.19
8	8	0.37	1530	1.22

[a] A solution of IBVE (0.2 M) in 1,2-dichloroethane and a solution of TfOH (0.02 M) in 1,2-dichloroethane were allowed to react in the microsystem at −25 °C.

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[a] *Central Research Laboratories, Idemitsu Kosan Co. Ltd., 1280 Kami-izumi, Sodegaura, Chiba 299-0293, Japan*
[b] *Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan. E-mail: yoshida@sbchem.kyoto-u.ac.jp; Fax: +81-75-383-2727; Tel: +81-75-383-2726*

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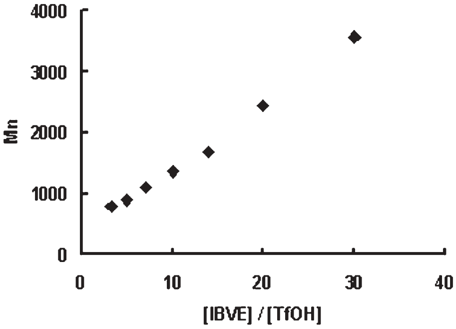

Fig. 2 Plots of the molecular weight against the monomer/initiator ratio in the polymerization of IBVE in 1,2-dichloroethane (residence time: 0.49 s).

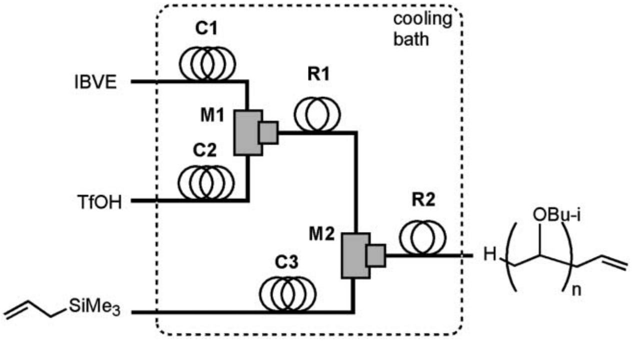

Fig. 3 A schematic diagram of the microsystem for polymerization and termination with allyltrimethylsilane (C1, C2, C3: pre-cooling unit; M1, M2: T-shaped micromixer; R1, R2: microtube reactor).

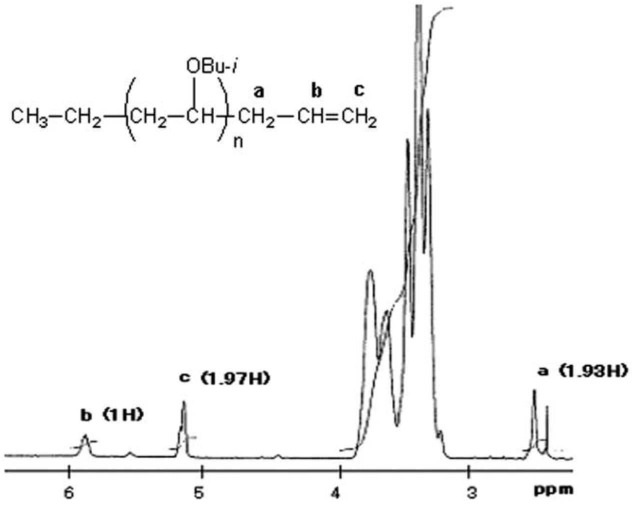

Fig. 4 600 MHz ^{1}H NMR spectrum of the polymer obtained by quenching with allyltrimethylsilane.

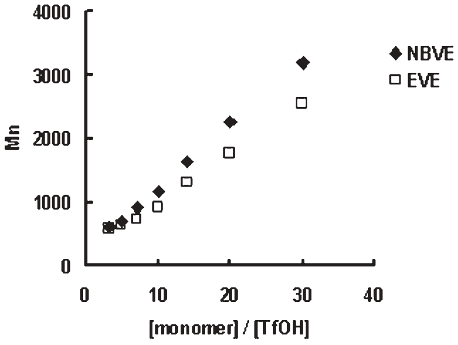

Fig. 5 Plots of the molecular weight against the monomer/initiator ratio for the polymerization of NBVE and EVE.

system, which is consistent with observed high level of molecular weight distribution control.

In order to get an insight into the nature of the polymer end, the polymerization of IBVE was carried out with 0.1 equiv. of CF_3SO_3H, and was quenched by the addition of allyltrimethylsilane using the second micromixer (Fig. 3) (R1: 20 cm, R2: 50 cm). The ^{1}H NMR analysis of the resulting polymer (Mn = 1240, Mw/Mn = 1.36) revealed that an allyl group was introduced as the end group (olefinic protons, 5.0–5.1 and 5.7–5.9 ppm) (Fig. 4). The present observation indicates that the carbocationic polymer end was effectively trapped by the added allyltrimethylsilane, suggesting the living nature of the polymer end during the propagation step.[12]

The polymerization of other vinyl ether monomers such as *n*-butyl vinyl ether (NBVE) and ethyl vinyl ether (EVE) also took place in highly controlled manners. The molecular weight increased with an increase with the monomer/initiator ratio as shown in Fig. 5.

One of the advantages of living polymerization is that the method allows flexible synthesis of structurally defined block copolymers composed of different monomers, which would offer greater opportunities for the synthesis of organic materials with interesting properties. Thus, we next examined block copolymerization using the microsystem (Fig. 6) (R1: 20 cm, R2: 50 cm). The polymerization of IBVE (10 equiv. based on TfOH initiator) followed by MeOH quenching at the second micromixer (M2) gave the homopolymer (Table 2). The introduction of the second monomer (NBVE or EVE) at the second micromixer (M2) resulted in the formation of the polymer of higher molecular weight with narrow molecular weight distribution (Fig. 7). Block copolymerization can be carried out with any combination and with either order of monomer addition as shown in Table 2, demonstrating that the present method serves as an effective method for the synthesis of block copolymers.

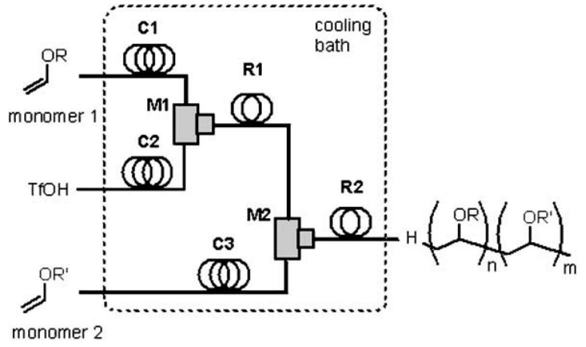

Fig. 6 A schematic diagram of the microsystem for block copolymerization (C1, C2, C3: pre-cooling unit; M1, M2: T-shaped micromixer; R1, R2: microtube reactor).

Table 2 Block polymerization using the microsystem[a]

Monomer 1	Monomer 2	Mn	Mw/Mn
IBVE	—	1360	1.18
IBVE	NBVE	2260	1.43
IBVE	EVE	1780	1.54
NBVE	—	1010	1.24
NBVE	IBVE	1670	1.45
NBVE	EVE	1940	1.55
EVE	—	860	1.16
EVE	IBVE	2100	1.54
EVE	NBVE	2100	1.41

[a] Polymerization was carried out with 10 equiv. of monomer 1 and 10 equiv. of monomer 2 based on TfOH initiator in dichloroethane at −25 °C.

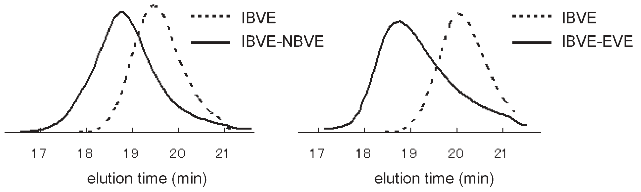

Fig. 7 GPC traces of copolymerization with different monomers.

In summary, the cationic polymerization of vinyl ethers was conducted by using a simple and readily-available trifluromethanesulfonic acid (TfOH) as an initiator at −25 °C in the microsystem. A high level of molecular weight distribution control was achieved under easily accessible conditions. The observations illustrated here open the possibility of microsystem-controlled polymerization in the synthesis of structurally well-defined polymers and copolymers in both academia and industry. It is also important to note that the present polymerization using commercially available initiator has high potential of industrial production by numbering-up, which has already been shown for radical polymerization.[13c]

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