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Cationic Polymerization

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14.1

Introduction

Nowadays, polymer synthesis is one of the most fascinating fields in the application of microflow systems. Major advantages of polymerization using microsystems include the control of molecular weights of polymers by modulating the residence time in the reactor [1–3]. It is also noteworthy that continuous microflow systems are suitable for producing libraries of polymers for high-throughput evaluation [4, 5]. There have been a great number of reports on the use of microflow systems for polymerization, including radical polymerization [6–13], coordination polymerization [14], polycondensation reactions [15] and polymerization of amino acids [16–18]. This chapter provides an overview of cationic polymerization in microflow systems.

14.1.1

Basic Principles of Cationic Polymerization

Cationic polymerization is one of the most fundamental methods for synthesizing polymers [19, 20]. Although there are several types of cationic polymerization, the most important one is cationic polymerization of vinyl monomers having a cation stabilizing group (Y) (Scheme 14.1). The initiation usually involves the addition of a cationic species (A^+) to a vinyl monomer to produce a carbocationic intermediate associated with a counter anion (X^-), which is derived from the initiator. In general, proton acids or carbocations generated from their precursors by acid-promoted ionization reactions [21–23] are used as initiators.

The carbocationic intermediate thus obtained adds to another molecule of the monomer to give the next carbocationic intermediate, which adds to another monomer (propagation step). The carbocationic intermediates are usually highly reactive and unstable. They undergo a number of side-reactions such as chain transfer and termination. Chain transfer to monomer is the most problematic from the view point of molecular weight control and molecular weight distribution control.

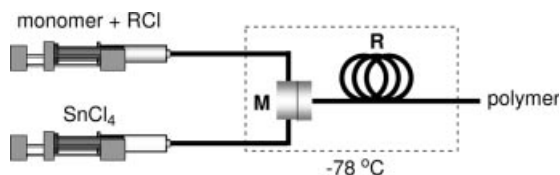


Figure 14.1 Microflow system for controlled/living cationic polymerization.

In both methods, the positive charge of the carbocationic intermediate is reduced and thereby the acidity of the β -proton is reduced to suppress the chain transfer. As a result, good molecular weight control and molecular weight distribution control are attained. On the basis of the principles, a number of initiating systems have been developed for living cationic polymerization [27].

14.2

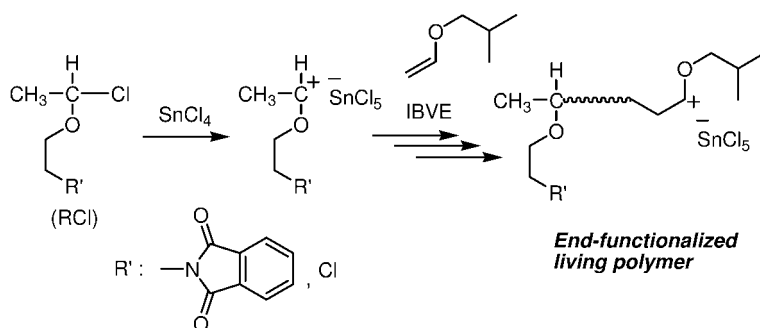
Cationic Polymerization Involving Carbocationic Intermediates Using Microflow Systems

14.2.1

Controlled/Living Cationic Polymerization Based on Cation Stabilization Using Microflow Systems [28]

Living cationic polymerization of vinyl ethers initiated by an SnCl_4/RCl catalytic system can be carried out in a continuous microflow system, which consists of a multilamination micromixer **M** (channel width = 40 μm , IMM) and a microtube reactor **R** (Figure 14.1). A solution of a monomer and RCl is mixed with a solution of SnCl_4 using the micromixer at -78°C and the resulting mixture was allowed to react in the microtube reactor at the same temperature. For example, isobutyl vinyl ether (IBVE) was polymerized using functionalized initiators to obtain end-functionalized polymers of narrow molecular weight distribution ($M_w/M_n < 1.2$) (Scheme 14.4).

Block copolymerization of IBVE and *n*-butyl vinyl ether (NBVE) can also be successfully achieved using a microflow system consisting of two micromixers



Scheme 14.4 An example of controlled/living cation polymerization based on cation stabilization.

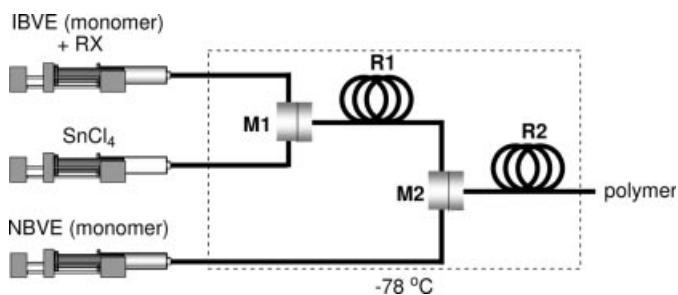


Figure 14.2 Microflow system for block copolymerization.

(M1 and M2) and two microtube reactors (R1 and R2) to obtain the corresponding copolymer of narrow molecular weight distribution ($M_w/M_n < 1.3$) (Figure 14.2).

14.2.2

Controlled/Living Cationic Polymerization Without Stabilization of Carbocationic Intermediates Using Microflow Systems

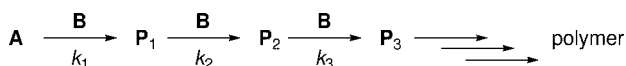
One of the major drawbacks of controlled/living cationic polymerization based on stabilization of the carbocationic intermediates is slow propagation. Because the concentration of the active propagating species is very low by virtue of the equilibrium between active species and dormant species, overall polymerization reactions are much slower than those without the equilibrium. Another important drawback of controlled/living polymerization is the use of additives such as Lewis bases. Such additives should remain in polymer products and it is generally difficult to remove them from the polymer products.

Recently, it has been demonstrated that molecular weight control and molecular weight distribution control can be attained by using microflow systems without stabilizing the carbocationic intermediates. The concept of this new technology (microflow system-controlled polymerization technology) is described in the following section.

14.2.2.1 Concept of Microflow System-controlled Polymerization Technology (MCPT)

Molecular weight and molecular weight distribution control in polymerization can be seen as control of competitive consecutive reactions as shown in Scheme 14.5, where A is an initiator and B is a monomer.

In the first step, A (initiator) reacts with B (monomer) to produce the first carbocationic intermediate P_1 . In the second step, P_1 reacts with another monomer to produce the second carbocationic intermediate P_2 . Further reactions lead to polymer formation. Regulation of the number of monomers incorporated in a single polymer chain allows good molecular weight control and molecular weight



Scheme 14.5 Polymerization as a competitive consecutive reaction.

distribution control. This problem is similar to the problem of competitive consecutive reactions, which often suffer from disguised chemical selectivity. The enhancement of product selectivity of competitive consecutive reactions such as Friedel–Crafts reactions [29, 30], [4 + 2] cycloaddition reactions [31, 32] and aromatic iodination [33] by using microflow systems has been reported. The enhancement of product selectivity in another competitive consecutive reaction, i.e. the reaction of a boron compound with a Grignard reagent, has also been reported [34]. These successful results suggest the possibility of molecular weight and molecular weight distribution control by using microsystems.

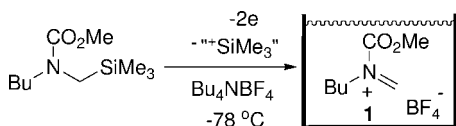
The basic idea of microsystem-controlled polymerization technology (MCPT) stems from the idea of controlling competitive consecutive reactions by taking advantage of characteristic features of microflow systems described above. Extremely fast mixing of an initiator solution and a monomer solution achieved by a micromixer leads to fast initiation, which is advantageous for the control of molecular weight and molecular weight distribution. Fast mixing also diminishes local deviations in concentration. Therefore, the monomer:initiator ratio is controlled exactly as intended. Minimizing local deviations of temperature by fast heat transfer through the wall of a microreactor is also important because polymerization processes are usually highly exothermic. A high surface area-to-volume ratio of microsystem is responsible for fast heat transfer.

14.2.2.2 “Cation Pool”-initiated Polymerization Using a Microflow System

Microsystem-controlled cationic polymerization technology requires extremely reactive initiators and “cation pools” serve as effective initiators for this technology. Usually carbocations are generated by a reversible process from their precursor. Yoshida *et al.* developed the cation pool method [35], in which carbocations are generated irreversibly by low-temperature electrolysis and are accumulated in relatively high concentration in the absence of nucleophiles. *N*-Acyliminium ions, alkoxy-carbenium ions [36–40] and diarylcarbenium ions [41] have been generated by this method. Such cation pools are expected to serve as extremely reactive initiators for cationic polymerization.

A pool of *N*-acyliminium ion **1** can be easily generated from *N*-methoxycarbonyl-*N*-(trimethylsilylmethyl)butylamine by low-temperature electrochemical oxidation (Scheme 14.6). The formation of **1** as a single species is indicated by NMR (¹H NMR, 8.56 and 8.83 ppm due the methylene protons; ¹³C NMR, 177.0 ppm due to the methylene carbon) [42].

Cationic polymerization of vinyl ethers using **1** as an initiator in a conventional batch reactor gives the polymer in quantitative yield after quenching with *i*-Pr₂NH–CH₂Cl₂, but the molecular weight distribution is broad (*M*_n = 5700,



Scheme 14.6 Cationic polymerization of vinyl ethers initiated by *N*-acyliminium ion pool.

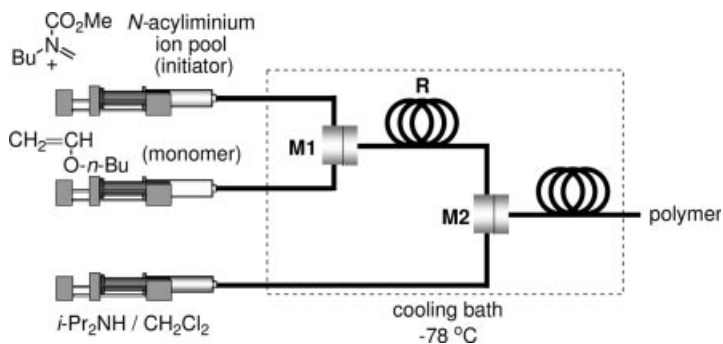


Figure 14.3 Microflow system for polymerization. **M1**, **M2**, micromixer; **R**, microtube reactor.

$M_w/M_n = 2.56$). The reverse addition sequence (**1** to the monomer) gives rise to a similar molecular weight distribution (quantitative yield, $M_n = 13\,100$, $M_w/M_n = 2.25$). The simultaneous addition of a monomer solution and a solution of **1** dose not improve the molecular weight distribution control (quantitative yield, $M_n = 24\,500$, $M_w/M_n = 2.43$). The molecular weight, however, strongly depends upon the method of mixing because the rate of the polymerization is so fast.

The use of a microflow system shown in Figure 14.3, however, leads to excellent control of molecular weight and its distribution [43]. A microsystem consisting of two micromixers (**M1** and **M2**) (IMM micromixer or YM-1) and a microtube reactor (**R**). A multi-lamination-type micromixer (channel width: $40\ \mu\text{m}$) is used as **M1**, where the cation pool and the monomer are mixed. Thus, solutions of **1** (0.05 M: concentration of the precursor of **1**) (because the yield of **1** from precursor is estimated as ca. 80% based on the reactions with various nucleophiles, hereafter 1.2 equiv of precursor is used when 1.0 equiv of **1** is needed for polymerization) and NBVE (0.5–2.5 M) are introduced to **M1** by the syringe pumping technique (flow rate: $5.0\ \text{mL}\ \text{min}^{-1}$) at $-78\ ^\circ\text{C}$. Then, the reaction mixture is introduced into a microtube reactor (**R**) ($\phi = 1.0\ \text{mm}$, 10 cm), in which the polymerization takes place. In the final stage, $i\text{-Pr}_2\text{NH}-\text{CH}_2\text{Cl}_2$ (0.83 M, $3\ \text{mL}\ \text{min}^{-1}$) is introduced through **M2** to quench the polymerization. A splitting and recombination-type micromixer, Yamatake YM-1, is used as **M2**.

The polymerization takes place fairly effectively and is complete within a residence time of 0.5 s. Even if the residence time is much smaller (0.05 s), the polymer can be obtained quantitatively. The molecular weight can be controlled by changing the molar ratio of the initiator to the monomer. The molecular weight (M_n) increases linearly with the amount of NBVE, indicating that transfer reactions does not play significant roles in this system (Figure 14.4).

The effect of the flow rate on molecular weight distribution (Table 14.1, runs 4–6) indicates the importance of mixing, because it is known that mixing efficiency decreases with decrease in flow rate in the IMM micromixer [44]. Reaction temperature is also important for controlling molecular weight distribution. M_w/M_n increases with increase in the temperature (runs 4, 7, 8 and 9). Anyway, a high level of

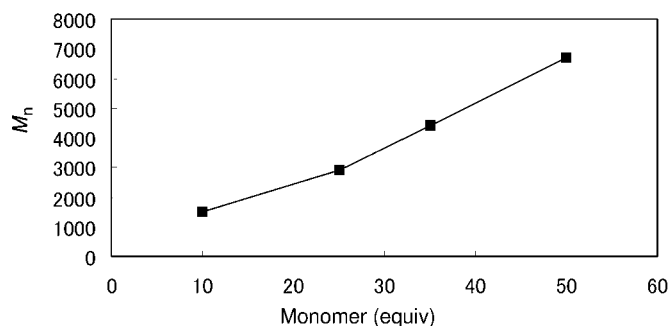


Figure 14.4 Plots of molecular weight against the amount of the monomer used for polymerization at $-78\text{ }^\circ\text{C}$.

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

The polymer end is really living during the propagation, because it can be effectively trapped by allyltrimethylsilane. For example, the polymerization of NBVE (10 equiv.) was carried out with **1** and was quenched with the addition of allyltrimethylsilane using the flow system. The polymer thus obtained was analyzed by ^1H NMR spectroscopy (Figure 14.5). The ester methoxy group from **1** 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; 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 the 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

Table 14.1 Cationic polymerization of NBVE initiated by a pool of *N*-acyliminium ion **1** using a microflow system^a

Run	Monomer equiv.	Flow rate (mL min^{-1})	Temperature ($^\circ\text{C}$)	M_n^b	M_w/M_n^b
1	10	5.0	-78	1500	1.40
2	25	5.0	-78	2900	1.26
3	35	5.0	-78	4400	1.17
4	50	5.0	-78	6700	1.14
5	50	3.0	-78	5600	1.35
6	50	1.0	-78	6200	2.84
7	50	5.0	-48	8200	1.30
8	50	5.0	-27	5500	1.34
9	50	5.0	0	6500	1.61

^a The polymerization was carried out in CH_2Cl_2 at $-78\text{ }^\circ\text{C}$ and was almost quantitative in all cases.

^b 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.

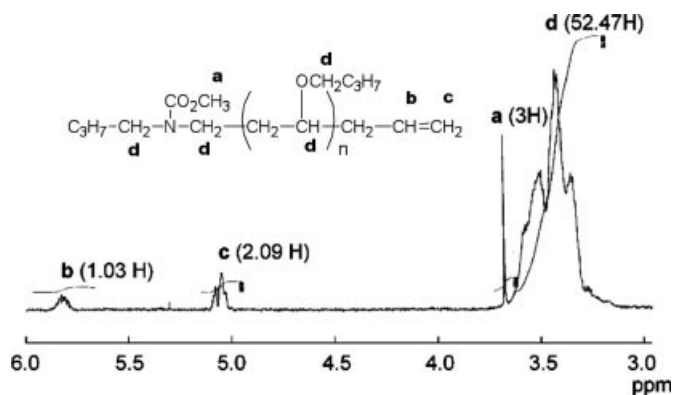


Figure 14.5 ¹H NMR spectrum (600 MHz, in CDCl₃) of the polymer obtained by the micromixing-controlled polymerization of NBVE, which was initiated by **1** and terminated by allyltrimethylsilane.

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 of **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 the precursor to **1** is 70–80%.





Therefore, as shown in the above example, the polymer end is really living within a residence time of 0.5 s at -78°C in the cation pool-initiated polymerization using MCPT.

The present cation pool-initiated polymerization using a microflow system can be applied to other vinyl ethers such as isobutyl vinyl ether (IBVE) and *tert*-butyl vinyl ether (TBVE) (Table 14.2). The corresponding macroscale batch polymerization results in much poorer molecular weight distribution control.

14.2.2.3 Proton Acid-initiated Polymerization Using Microflow Systems

Proton addition is one of the most simple and straightforward methods for the initiation of cationic polymerization. Brønsted acids are effective for this purpose. However, if we use a weak Brønsted acid, i.e. a conjugate acid of a strong nucleophilic anion, the addition of a Lewis acid is necessary to establish a reversible activation of a covalent end group for effective propagation. On the other hand, if we use a strong

Table 14.2 Cationic polymerization of vinyl ethers initiated by a pool of *N*-acyliminium ion **1** using a microflow system.

Monomer	[M]/[I]	Mixing method	Temperature (°C)	M_n	M_w/M_n
 <i>iso</i> -Bu	50	Batch	-78	6900	4.31
 <i>tert</i> -Bu	50	Micro flow system	-78	7900	1.12
 <i>iso</i> -Bu	50	Batch	-78	7100	2.29
 <i>tert</i> -Bu	50	Micro flow system	-78	7600	1.50

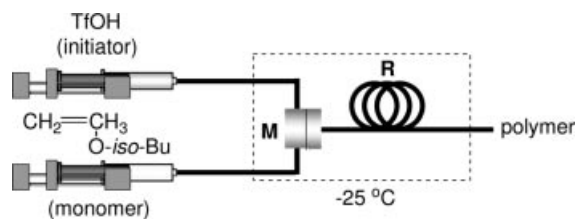


Figure 14.6 Microflow system for polymerization (M, T-shaped micromixer; R, microtube reactor).

Brønsted acid, i.e. a conjugate acid of an extremely weak nucleophilic anion, the addition of a Lewis base is required to stabilize the carbocationic propagating polymer ends [45]. In the absence of a Lewis base, highly ionic polymer ends are too reactive and participate in transfer reactions by loss of β -protons, leading to a very broad molecular weight distribution.

Trifluoromethanesulfonic acid (TfOH) is an effective initiator for cationic polymerization. For example, TfOH-initiated polymerization of isobutyl vinyl ether (IBVE) in 1,2-dichloroethane using a macroscale batch system (20 mL scale) [46] is complete within 10 s at $-25\text{ }^{\circ}\text{C}$. The molecular weight distribution is, however, rather broad and M_w/M_n ranges from 2.73 to 4.71, presumably because of chain transfer reactions due to the high reactivity of the polymer ends.

By employing microflow systems, however, cationic polymerization using a strong proton acid such as TfOH can be accomplished in a highly controlled manner without adding a Lewis base (Figure 14.6) [47].

A microflow system consisting of a T-shaped micromixer and a microtube reactor is effective for the polymerization (Figure 14.6). The polymerization is complete within a residence time of 0.37–1.5 s at $-25\text{ }^{\circ}\text{C}$ (almost quantitative yield). The degree of molecular weight distribution control depends strongly on the inner diameter of the mixer and the flow rate, as depicted in Table 14.3. M_w/M_n decreased with decrease in the mixer inner diameter, presumably because faster mixing is achieved by a mixer

Table 14.3 TfOH-initiated polymerization of isobutyl vinyl ether (IBVE) in a microflow system.

T-mixer i.d. (μm)	Monomer flow (rate mL min^{-1})	Initiator flow (rate mL min^{-1})	Residence time (sec)	M_n	M_w/M_n
250	2	2	1.50	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
	500	5	5	0.59	2030
6		6	0.49	1470	1.82
7		7	0.42	1420	1.67
800	6	6	0.49	2450	2.27

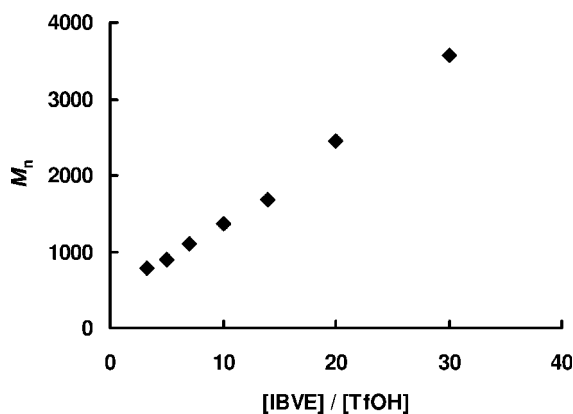


Figure 14.7 Plots of molecular weight against monomer:initiator ratio in the polymerization of IBVE in 1,2-dichloroethane (residence time: 0.49 s).

of smaller diameter. M_w/M_n also decreases with increase in the flow rate, probably because this enhanced the mixing efficiency.

A high level of molecular distribution control can be attained even at $-25\text{ }^\circ\text{C}$ with a mixer of $250\text{ }\mu\text{m}$ diameter and a flow rate higher than 5 mL min^{-1} . It is important to note that very low temperatures such as $-78\text{ }^\circ\text{C}$, which might be an obstacle to industrial-scale applications [48, 49] is not required.

As shown in Figure 14.7, the molecular weight (M_n) increases with increase in monomer:initiator ratio. The results indicate that transfer reactions do not play a significant role in the present system, which is consistent with the observed high level of molecular weight distribution control ($M_w/M_n = 1.06\text{--}1.23$).

The propagating polymer end can be trapped by allyltrimethylsilane using the second micromixer, suggesting that the living nature of the polymer ends during the propagation step (Figure 14.8). As shown in Figure 14.9, ^1H NMR analysis of the polymer ($M_n = 1240$, $M_w/M_n = 1.36$) revealed that an allyl group was introduced as

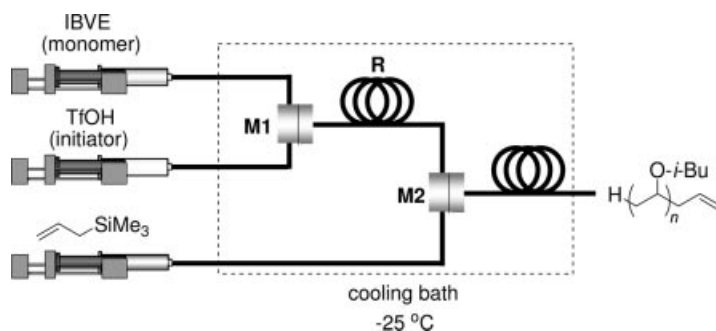


Figure 14.8 Microsystem for polymerization and termination with allyltrimethylsilane (M1, M2, T-shaped micromixer; R1, R2, microtube reactor).

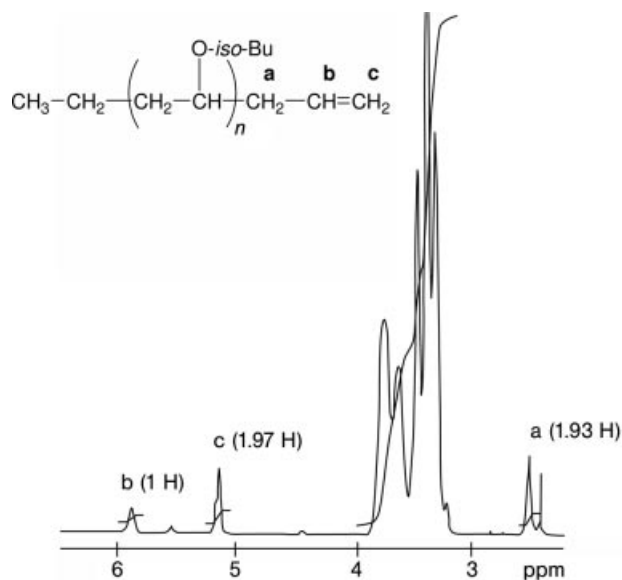


Figure 14.9 600 MHz ^1H NMR spectrum of the polymer obtained by quenching with allyltrimethylsilane.

the end group (olefinic protons, 5.0–5.10 and 5.7–5.9 ppm). The observed relative numbers of protons indicated that the carbocationic polymer end was effectively trapped by the added allyltrimethylsilane.

The polymerization of other vinyl ether monomers such as *n*-butyl vinyl ether (NBVE) ($M_w/M_n = 1.06\text{--}1.16$) and ethyl vinyl ether (EVE) ($M_w/M_n = 1.05\text{--}1.15$) also takes place in a highly controlled manner. The molecular weight increases with increase in the monomer:initiator ratio, as shown in Figure 14.10.

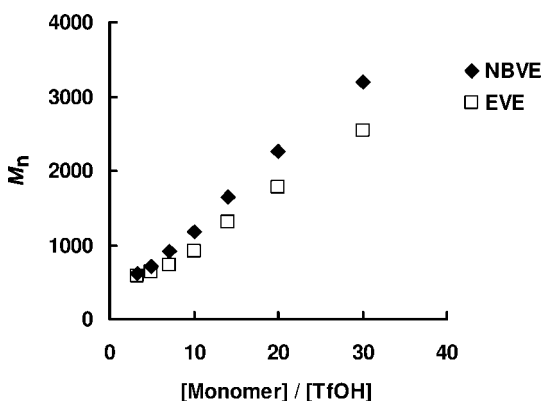


Figure 14.10 Plots of molecular weight against monomer:initiator ratio for the polymerization of NBVE and EVE.

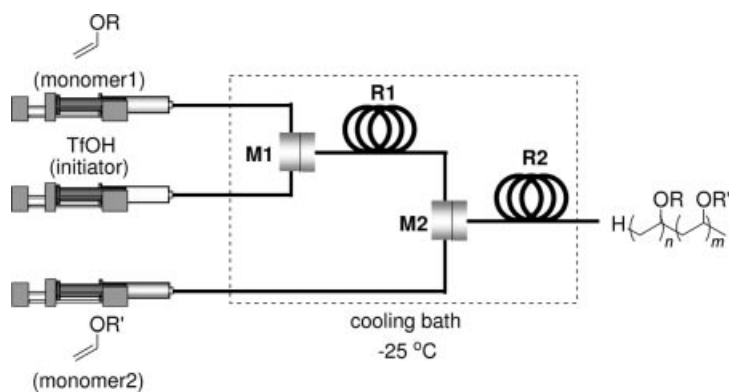


Figure 14.11 Schematic diagram of the microsystem for block copolymerization (M1, M2, T-shaped micromixer; R1, R2, microtube reactor).

One of the advantages of controlled/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. This is also true for microflow system controlled polymerization technology (MCPT).

An example of microflow systems for block copolymerization is shown in Figure 14.11. The first monomer IBVE is mixed with TfOH in the first micromixer (M1). Introduction of the second monomer (NBVE or EVE) at the second micromixer M2 results in the formation of a polymer of higher molecular weight with a narrow molecular weight distribution. Block copolymerization can be carried out with any combination and with either order of monomer addition, as shown in Table 14.4, demonstrating that the present method serves as an effective technique for the synthesis of block copolymers. The observations illustrate the possibility of using MCPT in the synthesis of structurally well-defined polymers and copolymers both in the laboratory and industry.

Table 14.4 Block polymerization using the microsystem.

Monomer 1	Monomer 2	M_n	M_w/M_n
IBVE	–	1470	1.22
IBVE	NBVE	2260	1.42
IBVE	EVE	2400	1.46
NBVE	–	1780	1.54
NBVE	IBVE	1750	1.55
NBVE	IBVE	1750	1.55
EVE	–	1470	1.22
EVE	IBVE	2260	1.42
EVE	NBVE	2400	1.46

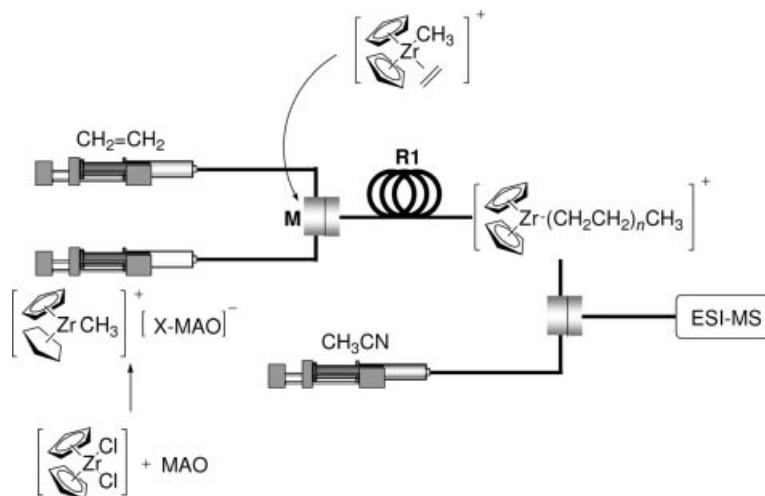


Figure 14.12 Ziegler–Natta polymerization using a microflow system.

14.3

Ziegler–Natta Polymerization

Usually Ziegler–Natta polymerization has not been classified as a cationic polymerization. However, here we briefly touch on Ziegler–Natta polymerization using a microflow system because the polymerization involves cationic metal complex intermediates.

As reported by Santos and Metzger [50], Ziegler–Natta polymerization can be carried out in a microflow system coupled directly to the ESI source of a Q-TOF mass spectrometer (Figure 14.12). In the first micromixer, catalyst (Cp_2ZrCl_2 –MAO) and monomer solutions are mixed continuously to initiate the polymerization. The polymerization occurs in the microtube reactor. The solution thus obtained is introduced into the second micromixer M2, where the polymerization is quenched by acetonitrile. The quenched solution is fed directly into the ESI source. The transient cationic species can be characterized by mass spectrometry. This is the first case where an alkyl zirconium cation intermediate in the homogeneous Ziegler–Natta polymerization of ethylene is detected directly.

14.4

Conclusion

Cationic polymerization without stabilization of a carbocationic intermediate can be carried out in a microflow system. Good molecular weight control and molecular weight distribution control are attained by virtue of characteristic features of microflow systems (microflow-system-controlled polymerization technology, MCPT). Conventional controlled/living cationic polymerization based on cation stabilization can be also carried out in a microflow system.

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