

Living Copolymerization of EOVE and MOVE: Fast Flow Synthesis and Thermal Responsive Behavior

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 Electronic Supplementary Information

Abstract Random and block copolymers of 2-methoxyethyl vinyl ether (MOVE) and 2-ethoxyethyl vinyl ether (EOVE) were synthesized within 180 s via IBVE-HCl/SnCl₄ initiating system in the presence of THF in a microflow system. The polymers can be produced continuously and efficiently with extremely narrow molecular weight distributions ($M_w/M_n=1.09-1.18$) even at the existence of pendant oxyethylene units. Polymerization rate can be accelerated by reducing THF to very low concentration ([THF]=50 mmol/L), reaching conversions over 60% and 70% in 60 s for EOVE and MOVE, respectively. Random copolymers poly(MOVE_{100x}-*r*-EOVE_{100(1-x)}) ($x=0.25, 0.5, 0.75$) experienced very sensitive phase separation process, of which phase separation temperature (T_{ps}) can be adjusted between 20 and 70 °C by controlling monomer composition. On the other hand, thermally induced phase separation of diblock copolymers poly(MOVE₁₀₀-*b*-EOVE₁₀₀) was not so sensitive as its random copolymer counterpart. Relatively bigger difference between phase separation temperatures of heating and cooling process (ΔT_{ps}) was found for diblock copolymer.

Keywords Living cationic polymerization; Stimuli-responsive; Microflow system

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INTRODUCTION

Stimuli-responsive copolymer has become an active area of research for advanced polymer materials in the past decades.^[1–4] These polymers are able to show sensitive responses to environmental changes like light, pH,^[5] temperature^[6,7] and solvent.^[8] Polymers that can respond to multiple stimuli have also been successfully synthesized.^[3,9,10] These functional polymer materials show potential applications in drug delivery systems,^[11] disease diagnosis^[12] and other high-tech areas.^[13,14]

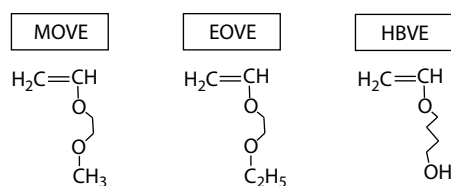
Among all the stimuli responsive polymer materials, thermo responsive polymers are the most well-studied. A typical example of thermo responsive polymer is poly(*N*-isopropylacrylamide) (PNIPAM), which has been widely used as drug and gene delivery system, exhibiting LCST-type phase separation and can transform from soluble to insoluble in water above a certain temperature.^[15] Poly(vinyl ether) with pendant oxyethylene units and ω -alkyl groups is another example of thermo responsive polymer, which was discovered and vastly enriched by Aoshima *et al.* For example, they prepared diblock copolymers of vinyl ethers with oxyethylene pendants and poly(hydroxyethyl vinyl ether) that was able to

experience highly sensitive and reversible thermal-induced micelle formation or physical gelation.^[8] They also prepared various copolymers of vinyl ethers with thermo sensitive segments possessing different phase separation temperature (T_{ps}), such as 2-(2-ethoxy)ethoxyethyl vinyl ether (EOOVE) and 2-methoxyethyl vinyl ether (MOVE), which underwent four different viscoelastic stages while heated.^[6] Critical temperatures of these polymers are closely related to their structure, including sequence of repeat units, composition, molecular weight distribution and side pendant type,^[16–18] thus the precise synthesis of these polymers is key to their sensitive thermo responsive behavior.

For the synthesis of poly(vinyl ether)s, living cationic polymerization is the most widely used method, as it gives polymers with well-defined structures and designed molecular weight. Extremely narrow molecular weight distribution can be obtained by living cationic polymerization, which is essential for a functional polymer.^[19,20] However, the living polymerization of vinyl ethers with polar functional groups like EOVE and MOVE (Scheme 1) needs well-controllable initiation system, because such pendants may severely interfere the stability of propagating carbocations, causing unexpected side reactions.^[21] As a result, although Aoshima's group reported living homopolymerization and copolymerization of EOVE and MOVE using alkyl aluminum chloride as Lewis acid in a batch process long ago,^[21,22] it added extra amount of base, usually 50 times to 250 times of the concentration of ini-

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Scheme 1 Structures of monomers with functional group.

tiator, and required hours to reach sufficient conversion.^[17,18] Since then, it has not any attempt presented to accelerate this copolymerization process or regulate unit sequence in products. It is still lack of flexible and efficient initiation system for the living copolymerization of vinyl ethers with oxyethylene side pendant, which in turn hinders the commercialization of related smart polymer materials.

Towards thriving demands on stimuli responsive materials, efficient and continuous production of such functional materials is of vital importance. To the best of our knowledge, only few fast living-cationic polymerization process has been realized *via* cautiously selected Lewis acid and added base, and most of them are only used for a homopolymerization process and are applied in batch procedure.^[23,24] Microflow system has been proved to be a very efficient and convenient platform for living ion polymerization. Yoshida and coworkers did great jobs in realizing living polymerization in microreactor.^[25–27] In recent, our group has also studied the feasibility of performing fast living cationic polymerization in microflow system.^[28–30] The intensified mixing and excellent heat transfer capability of microflow system allow the living cationic polymerization to proceed at lower concentration of additives and simplified initiating system, which is benefit for improving repeatability and reducing production cost. Our previous research mainly dealt with monomers with nonpolar functional group like isobutyl vinyl ether (IBVE). To further prove the practicality and versatility of microflow system for the synthesis of monomers with polar functional groups, here we examined the possibility of efficient and continuous production of poly(vinyl ether)s with pendant oxyethylene units, as well as their random and block copolymers. In particular, the fast living cationic polymerization of EOVE and MOVE was successfully achieved in microflow system with commonly used Lewis acid and added base. Copolymers with very narrow molecular weight distribution were also synthesized continuously, which demonstrate adjustable thermo responsive behavior with T_{ps} ranging from 20 °C to 70 °C.

EXPERIMENTAL

Materials

2-Methoxyethyl vinyl ether (MOVE, >95%, Atomax Chemicals), and 2-ethoxyethyl vinyl ether (EOVE, >95%, Atomax Chemicals) were washed with 10 wt% aqueous alkaline solution and then with water. Monomers after washing were dried using excess flake potassium hydroxide for 12 h, and vacuum distilled twice over calcium hydride at 40 and 45 °C, respectively, before use. Toluene, 1,4-dioxane, diethyl ether, ethyl acetate and tetrahydrofuran (A. R. Beijing Lanyi Chemical Products) were refluxed for several hours and distilled over calcium hydride and were stored in the presence of 4Å molecular sieve. Commercially available FeCl_3 (Anhydrous, Acros, 98%) and SnCl_4

(Anhydrous, Acros, 99%) were used without further purification. The adduct of IBVE with HCl (IBVE-HCl) was prepared from the addition reaction of IBVE with HCl.^[31] All chemicals were stored in glovebox under dry argon ($[\text{H}_2\text{O}] < 0.1$ ppm, $[\text{O}_2] < 0.1$ ppm).

Procedures

Homopolymerization and random copolymerization were carried out in a microflow system as shown in Fig. 1, which was composed of two T-shaped micromixers (M1, M2), a microtube reactor R1 (inner diameter of 600 μm) and three precooling coiled tubes (C1, C2, C3, inner diameter of 800 μm). A solution of monomer and IBVE-HCl in toluene and a solution of Lewis acid in toluene were mixed using M1. The resulting solution was introduced to R1, where the polymerization took place. Reaction time can be adjusted easily by changing the flow rate or the length of R1. Termination agent methanol containing a small amount of aqueous ammonia solution (0.1 vol%) was introduced into the reaction system at the end of R1 through M2. Three syringe pumps were used to deliver monomer, Lewis acid, and MeOH solution. For a typical process, flow rates are set at 8.0, 8.0, 9.6 mL/min, respectively.

The quenched mixture was washed with dilute hydrochloric acid, an aqueous NaOH solution, and then washed with water for three times to remove the initiator and co-initiator residues. The volatiles were then removed under reduced pressure at 70 °C, and the residue was vacuum-dried overnight at 30 °C. Monomer conversion was measured by gravimetry of the polymers.

Block copolymerization was carried out in a microflow system as shown in Fig. 2. In this case, M2 was used to introduce

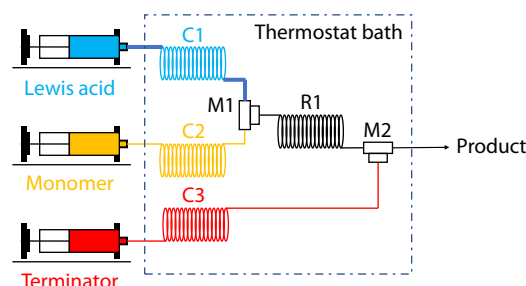


Fig. 1 Schematic diagram of microflow system for homopolymerization/random copolymerization. (M1, M2: T shaped micromixers; C1, C2, C3: curved tubes for precooling; R1: microtube reactor; the part enclosed by dashed line is placed in cooling bath).

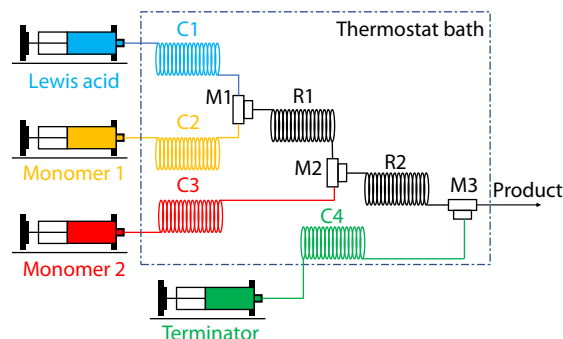


Fig. 2 Schematic diagram of microflow system for block copolymerization. (M1, M2, M3: T shaped micromixers; C1, C2, C3, C4: curved tubes for precooling; R1, R2: microtube reactor).

the second monomer, while M3 was used for the injection of termination agent. Another microtube reactor R2 was connected to M2 for the second stage polymerization. Other procedures were similar to the synthesis of homopolymers.

Characterizations

Number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution (MWD, M_w/M_n) of polymers were measured by gel permeation chromatography (GPC). GPC was carried out using a Waters 1515 isocratic HPLC pump connected to three Waters Styragel HT2, HT3, and HT4 columns and a Waters 2414 Refractive Index Detector at 30 °C [Waters; styragel HT2 (THF), styragel HT3 (THF), and styragel HT4 (THF); molecular weight range=100–10k, 500–30k, 5–600k; particle size=10 μ m; column size=7.8 mm (internal diameter) $\times$ 300 mm; flow rate=1.0 mL/min]. The instrument was calibrated with polystyrene standards.

The T_{ps} s of copolymers were measured on a Shimadzu 2450 UV-Vis spectrophotometer equipped with a thermostatic cell holder TCC-240A. Aqueous poly(MOVE-*r/b*-EOVE) solutions (1.0 wt%) were heated or cooled between 10 °C and 80 °C, while the transmittance was recorded at 500 nm (1 cm of quartz sample cell), and each point was stabilized for 2 min.

RESULTS AND DISCUSSION

Feasibility of Living Cationic Polymerization of MOVE and EOVE

Since the first example of living cationic polymerization of vinyl ether was demonstrated by Higashimura and coworkers,^[32] various initiating systems have been reported for a living polymerization process. However, most of the initiating systems reported are designed for a batch process and extended time is required to obtain quantitative conversion. Therefore, we first set out to find a propiate initiating system that can induce fast cationic polymerization and tolerant the existence of pendant oxyethylene units at the same time. The acidity of Lewis acid and the basicity of added base are two main factors that have strong effect on the living cationic polymerization rate. A strong Lewis acid and a weak added base are usually preferred combination for fast polymerization. Proper combination of Lewis acid and added base is very important for a living cationic polymerization, especially for monomers with polar side groups.

Improper combination will result in uncontrolled reaction process and unexpected products. Herein, two Lewis acids (FeCl_3 , SnCl_4) and three added bases (1,4-dioxane, ethyl acetate, tetrahydrofuran) commonly used for the living cationic polymerization of vinyl ether were chosen.^[23,24,33,34] The results of polymerization *via* different Lewis acid and added base combinations are presented in Table 1.

Cationic polymerization of EOVE *via* FeCl_3/DO (1,4-dioxane) system proceeded in a very fast fashion and conversion over 87% could be achieved in just 2.12 s. But the M_n s measured by GPC were much smaller than the calculated values and the MWDs were relatively broad ($M_w/M_n \sim 1.2$), which means considerable chain transfer may exist under this condition. These results indicate that the acidity of FeCl_3 is too strong for the living cationic polymerization of EOVE and a weaker Lewis acid may be expected for better controllability. Therefore, SnCl_4 was used in the following experiments as it was reported to have a weaker acidity than FeCl_3 .^[35] In this case, polymerization was much slower compared with FeCl_3 , and the added base showed a significant effect on polymerization results. When SnCl_4 was combined with EA, only 13.6% monomer was transformed in 11.31 s. Though M_n was close to the calculated value, the MWDs were still not narrow enough ($M_w/M_n > 1.25$) for a precise synthesis. Narrower MWDs were obtained when DO and THF were used as added base. In the case of DO, $M_w/M_n < 1.20$ can be achieved with relatively fast polymerization rate. But the M_n still deviated severely from the calculated values, which may be attributed to the weak interaction between DO and active propagating species. Extremely narrow MWDs (Table 1, entry 11, $M_w/M_n < 1.10$) were obtained when THF was used as added base and the M_n were all very close to calculated values.

Though living cationic polymerization of EOVE can be realized *via* SnCl_4/THF system, the polymerization rate is still not fast enough for a continuous synthesis of block copolymer, since close to full conversion of the first monomer is required for the synthesis of block copolymer by sequential monomer addition method. In our previous work, we have proved that decreasing concentration of added base together with the use of microflow system is an efficient way to accelerate living cationic polymerization of isobutyl vinyl ether,^[28] thus the concentration of THF was examined to accelerate this reaction. Results from Table 2 show that when concentration of

Table 1 Cationic polymerization of EOVE initiated by FeCl_3/DO or SnCl_4/DO (or EA or THF) system.^a

Entry	Monomer	Lewis acid	Added base	<i>t</i> (s)	Conv. ^b (%)	$M_{n,\text{cal.}}$ ^c ($\text{g}\cdot\text{mol}^{-1}$)	M_n ^d ($\text{g}\cdot\text{mol}^{-1}$)	M_w/M_n ^d
1	EOVE	FeCl_3	DO	0.53	59.5	13800	6100	1.24
2				1.06	73.6	17100	8500	1.21
3				2.12	87.8	20400	9600	1.20
4			EA	3.77	4.2	1000	1500	1.36
5				7.54	6.7	1500	1700	1.28
6				11.31	13.6	3200	1900	1.27
7		SnCl_4	DO	3.39	45.1	10500	5700	1.18
8				8.48	75.0	17400	8800	1.17
9				13.57	85.6	19900	9100	1.19
10			THF	15.07	13.2	3100	2400	1.12
11				24.12	19.2	4500	3800	1.08
12				36.17	23.2	5400	4600	1.10

^a $[\text{IBVE-HCl}]_0 = 4 \text{ mmol/L}$, $T = 0 \text{ }^\circ\text{C}$, $[\text{monomer}]_0 = 0.8 \text{ mol/L}$; $[\text{FeCl}_3]_0 = 5 \text{ mmol/L}$, for dissolving FeCl_3 : $[\text{Et}_2\text{O}]_0 = 250 \text{ mmol/L}$, or $[\text{SnCl}_4]_0 = 5 \text{ mmol/L}$; added base: $[\text{DO/EA}]_0 = 1.0 \text{ mol/L}$; $[\text{THF}]_0 = 0.1 \text{ mol/L}$; ^b Gravimetric conversion; ^c $M_{n,\text{cal.}} = [\text{EOVE}] \times 116.16 \times \text{Conv.}/[\text{IBVE-HCl}]$; ^d M_n : number-average molecular weight, M_w/M_n : dispersity.

THF was reduced to 50 mmol/L, polymerization rate of EOVE increased obviously while maintaining a narrow MWDs ($M_w/M_n < 1.15$). The value of M_n increased proportionally to monomer conversion and was in good agreement with the calculated value (Fig. 3b).

Cationic polymerization of MOVE was then carried out with SnCl_4/THF initiating system to verify whether these two monomers can be polymerized under the same condition. As the results from Table 3 shown, M_n of poly(MOVE) was very close to the calculated value and was directly proportional to monomer conversion (Fig. 3d). The MWDs were also very narrow for each conversion and the polydispersity index maintains below 1.15. We also noticed that polymerization rate of MOVE was slightly higher than EOVE under the same condi-

tion. The apparent constants of propagation rate for EOVE and MOVE polymerization are calculated to be 0.0164 and 0.0216 s^{-1} , respectively. The slight rate difference may be attributed to the relatively bigger steric hindrance and stronger electron donating capacity of ethyl group compared to methyl group, which may affect the stabilization of carbocation during polymerization.

In general, the microflow system proved to be a very convenient platform for the selection of proper initiating system and control of polymerization rate. The SnCl_4/THF was proved to be a highly efficient system for the living cationic polymerization of both EOVE and MOVE. Therefore, the synthesis of copolymer of EOVE and MOVE was affordable by using $\text{IBVE-HCl}/\text{SnCl}_4/\text{THF}$ as initiating system.

Table 2 Living cationic polymerization of EOVE initiated by SnCl_4/THF system.^a

Entry	Concentration of THF (mmol/L)	<i>t</i> (s)	Conv. (%)	$M_{n,\text{cal}}$ ($\text{g}\cdot\text{mol}^{-1}$)	M_n ($\text{g}\cdot\text{mol}^{-1}$)	M_w/M_n
13	50	6.03	9.7	2300	1800	1.14
14		15.07	25.6	6000	5100	1.09
15		24.12	33.7	7800	6700	1.11
16		36.17	43.5	10100	8000	1.10
17		48.23	55.4	12900	10500	1.14
18		60.29	62.3	14500	11200	1.14

^a $[\text{IBVE-HCl}]_0 = 4 \text{ mmol/L}$, $T = 0^\circ\text{C}$, $[\text{EOVE}]_0 = 0.8 \text{ mol/L}$; $[\text{SnCl}_4]_0 = 5 \text{ mmol/L}$; added base: $[\text{THF}] = 50 \text{ mmol/L}$.

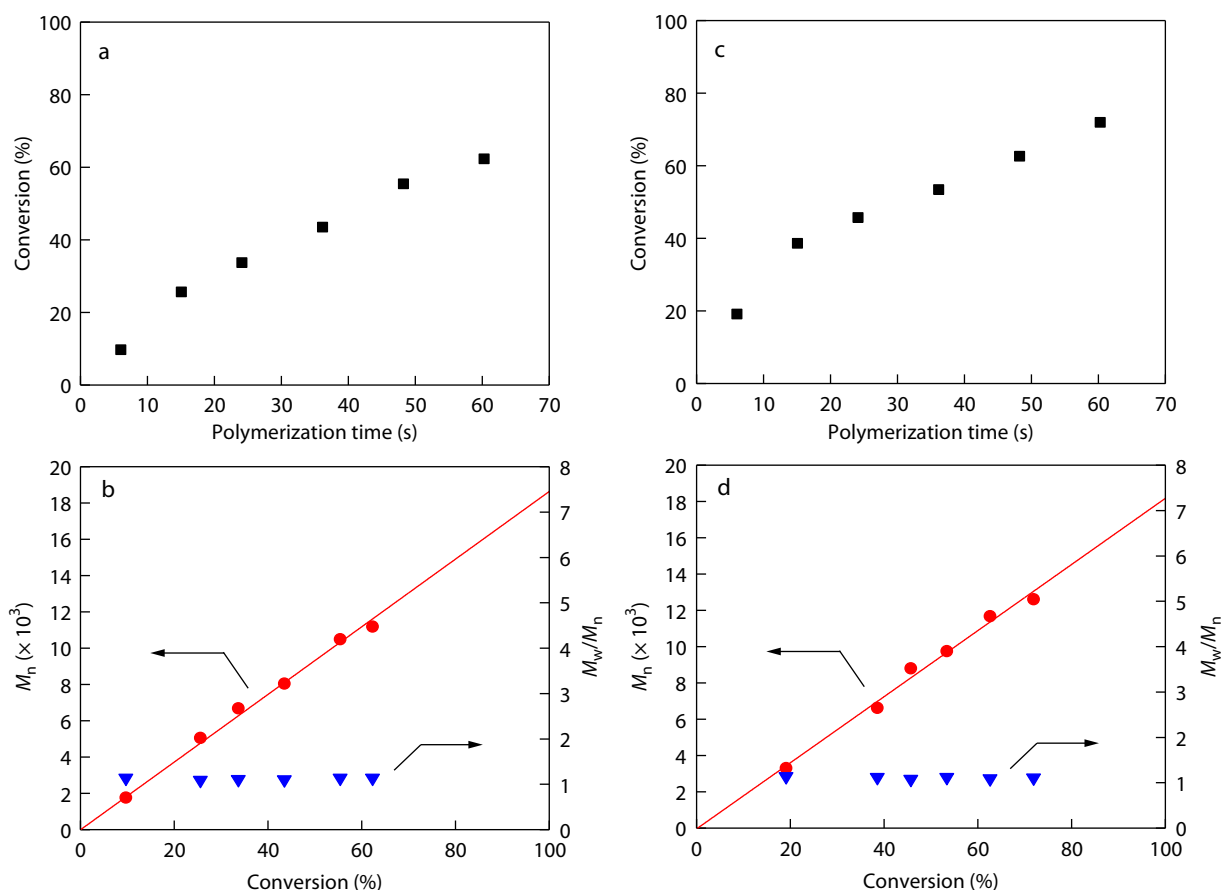


Fig. 3 (a) Time-conversion curves of EOVE; (b) M_n and M_w/M_n for the polymerization of EOVE; (c) Time-conversion curves of MOVE; (d) M_n and M_w/M_n for the polymerization of MOVE. (Polymerization conditions: $[\text{monomer}]_0 = 0.8 \text{ mol/L}$, $[\text{IBVE-HCl}]_0 = 4.0 \text{ mmol/L}$, $[\text{SnCl}_4]_0 = 5.0 \text{ mmol/L}$, $[\text{THF}] = 50 \text{ mmol/L}$, in toluene at 0°C).

Table 3 Living cationic polymerization of MOVE initiated by SnCl_4/THF system.^a

Entry	Concentration of THF (mmol/L)	<i>t</i> (s)	Conv. (%)	$M_{n,\text{cal}}$ ($\text{g}\cdot\text{mol}^{-1}$)	M_n ($\text{g}\cdot\text{mol}^{-1}$)	M_w/M_n
19	50	6.03	19.1	3900	3300	1.14
20		15.07	38.6	7900	6600	1.12
21		24.12	45.7	9300	8800	1.08
22		36.17	53.4	10900	9800	1.12
23		48.23	62.6	12800	11700	1.09
24		60.29	71.9	14700	12600	1.11

^a $[\text{IBVE-HCl}]_0=4$ mmol/L, $T=0^\circ\text{C}$, $[\text{MOVE}]_0=0.8$ mol/L; $[\text{SnCl}_4]_0=5$ mmol/L; added base: $[\text{THF}]=50$ mmol/L.

Living Copolymerization of MOVE and EOVE

Based on the results discussed above, living copolymerization of MOVE and EOVE was carried out in a microflow system via SnCl_4/THF system. Random copolymers and block copolymers of different composition were successfully obtained in this section.

The results of living cationic random copolymerization of MOVE and EOVE are listed in Table 4. Total monomer concentration here was set at 0.8 mol/L, and the ratio of $[\text{MOVE}]/$

$[\text{EOVE}]$ were set as 1:1, 1:3, 3:1. Quantitative conversions were achieved in all cases with a very narrow MWDs ($M_w/M_n \leq 1.10$, Fig. 4a), which means well defined random copolymers of EOVE and MOVE can be synthesized within 2 min.

The results of living cationic block copolymerization of MOVE and EOVE are summarized in Table 5. In this process, MOVE was first polymerized in reaction tube R1. Then EOVE was directly added into the system by micromixer M2 and was polymerized in the following reaction tube R2. The

Table 4 Living cationic random copolymerization of MOVE and EOVE initiated by SnCl_4/THF system.

Entry	F_{monomer} ($\text{mL}\cdot\text{min}^{-1}$)	$F_{\text{Lewis acid}}$ ($\text{mL}\cdot\text{min}^{-1}$)	F_{MeOH} ($\text{mL}\cdot\text{min}^{-1}$)	<i>t</i> (s)	Conv. (%)	M_n ($\text{g}\cdot\text{mol}^{-1}$)	M_w/M_n
25 ^a	5	5	6	60.32	56	11600	1.09
26 ^a	5	5	6	90.48	75	13100	1.09
27 ^a	3	3	3.6	100.53	84	14100	1.09
28 ^b	3	3	3.6	110.58	91	11600	1.10
29 ^c	3	3	3.6	100.53	95	13400	1.10

All experiments: $[\text{Monomer}]=0.8$ mol/L, $[\text{IBVE-HCl}]_0=4$ mmol/L, $[\text{SnCl}_4]_0=5$ mmol/L; added base: $[\text{THF}]=50$ mmol/L. ^a $[\text{MOVE}]_0=0.4$ mol/L, $[\text{EOVE}]_0=0.4$ mol/L; ^b $[\text{MOVE}]_0=0.2$ mol/L, $[\text{EOVE}]_0=0.6$ mol/L; ^c $[\text{MOVE}]_0=0.6$ mol/L, $[\text{EOVE}]_0=0.2$ mol/L; in toluene at 0°C .

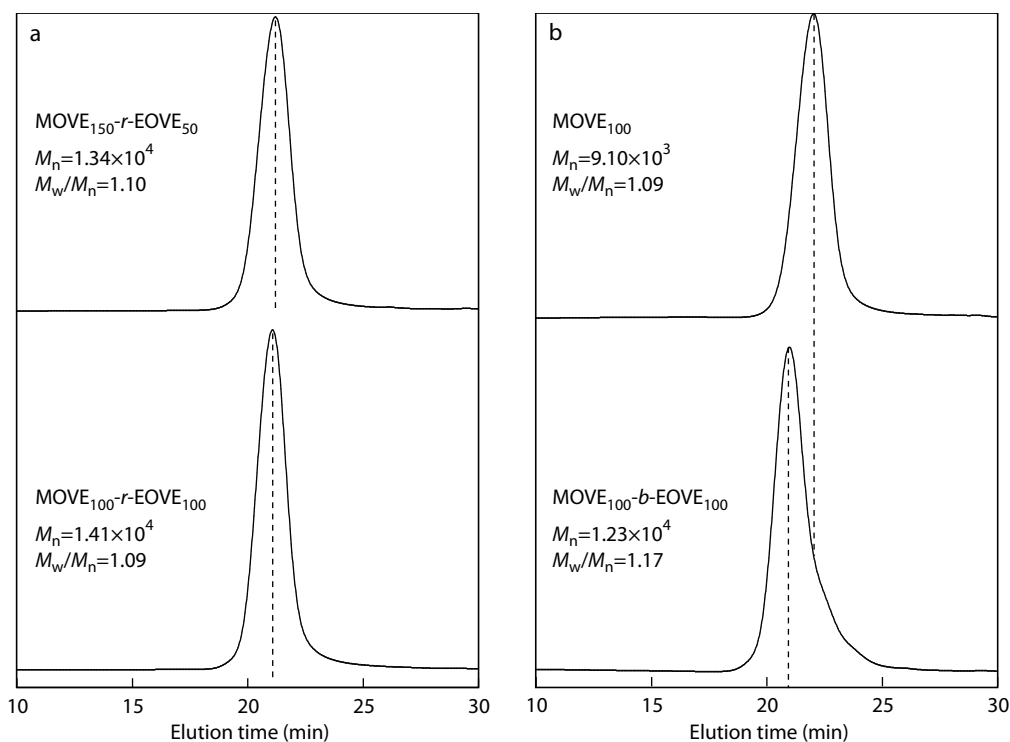


Fig. 4 (a) MWD curves of random copolymers: poly(MOVE₁₅₀-*r*-EOVE₅₀) and poly(MOVE₁₀₀-*r*-EOVE₁₀₀); (b) MWD curves of diblock copolymers poly(MOVE₁₀₀-*b*-EOVE₁₀₀).

Table 5 Living cationic block copolymerization of MOVE and EOVE initiated by SnCl_4/THF system.

Entry	$F_{\text{MOVE}}^{\text{I}} (\text{mL} \cdot \text{min}^{-1})$	$F_{\text{Lewis acid}}^{\text{I}} (\text{mL} \cdot \text{min}^{-1})$	$F_{\text{EOVE}}^{\text{I}} (\text{mL} \cdot \text{min}^{-1})$	$F_{\text{MeOH}}^{\text{I}} (\text{mL} \cdot \text{min}^{-1})$	t (s)	Conv. (%)	$M_n (\text{g} \cdot \text{mol}^{-1})$	M_w/M_n
30 ^a	5	5	0	6	24.13	75	7600	1.09
31 ^a	3	3	0	3.6	40.21	88	8100	1.10
32 ^a	2.5	2.5	0	3	48.25	91	9100	1.09
33 ^b	2.5	2.5	5	6	48.25+120.64	93	12200	1.18
34 ^b	2.5	2.5	5	6	54.29+120.64	98	12300	1.17

^a $[\text{MOVE}]_0 = 0.8 \text{ mol/L}$, $[\text{IBVE-HCl}]_0 = 8 \text{ mmol/L}$, $[\text{SnCl}_4]_0 = 10 \text{ mmol/L}$, added base: $[\text{THF}] = 0.1 \text{ mol/L}$; ^b $[\text{MOVE}]_0 = 0.4 \text{ mol/L}$, $[\text{EOVE}]_0 = 0.4 \text{ mol/L}$, $[\text{IBVE-HCl}]_0 = 4 \text{ mmol/L}$, $[\text{SnCl}_4]_0 = 5 \text{ mmol/L}$, added base: $[\text{THF}] = 50 \text{ mmol/L}$; in toluene at 0°C .

second monomer was added when the first monomer was close to quantitative conversion in order to guarantee the transition process. Close to full conversions can be realized for block copolymerization of EOVE and MOVE with a narrow MWDs. GPC spectra in Fig. 4(b) shift towards higher molecular weight, indicating that all $\text{poly}(\text{MOVE})_{100}$ chains were successfully extended by EOVE, without formation of any homopolymers.

Phase Separation Behavior of Copolymers

Aqueous solutions of $\text{poly}(\text{MOVE})$ and $\text{poly}(\text{EOVE})$ were reported to have very sensitive thermal responsive behaviors, with T_{ps} at 70 and 20°C , respectively.^[21] The thermoresponsive property of MOVE and EOVE copolymers was also studied previously and was reported to have different phase separation behavior depend on their structures.^[22] Thus, UV-Vis spectrophotometer was applied to verify the thermally-induced phase separation behavior of copolymers obtained in our study.

Fig. 5(a) shows the relationships between transmittance and temperature for $1.0 \text{ wt\%}$ aqueous solutions of random copolymers $\text{poly}(\text{MOVE}_{100x-r}\text{-EOVE}_{100(1-x)})$. As we expected, sharp and reversible phase separation phenomena were observed for random copolymers with three different compositions. And T_{ps} s were found to locate between the cloudy point of homopolymers of EOVE (20°C) and MOVE (70°C), and increased with the content of MOVE, which is consistent with polymers obtained from batch process. These results demonstrate that random copolymers with designed T_{ps} may be controllably and continuously produced in our microflow system.

Fig. 5(b) shows relationships between transmittance and

temperature for $1.0 \text{ wt\%}$ aqueous solutions of random/block copolymers $\text{poly}(\text{MOVE}_{100-r}\text{-}b\text{-EOVE}_{100})$. Different phase separation phenomena were found for these two copolymers. Block copolymers has a higher T_{ps} than random copolymers with the same composition and retardation existed between heating and cooling. The relatively broad difference between phase separation temperature observed from heating and cooling process (ΔT_{ps}) of block copolymer may be explained by different responsive order while heating and cooling. When the solution was heated from low temperature to high temperature, the blocks with lower T_{ps} (i.e., EOVE unit) aggregate first, and the aggregation is strong enough to affect the hydration effect of another block. While the solution was cooled, the blocks with higher T_{ps} (i.e., MOVE unit) disaggregate first, and the hydration of it can also affect the aggregation of nearby EOVE units. This different responsive order finally resulted in the broadening of T_{ps} for block copolymers. In addition, the thermoresponsive behavior of block copolymers obtained in our study was also different from the literature. The block copolymer is supposed to exhibit a multistage phase separation according to previous research.^[22] But in our study, the block copolymer of EOVE and MOVE only experienced a single stage phase separation. This different phenomenon was quite interesting and further investigation was required to explain or take advantage of it.

Generally, copolymers of MOVE and EOVE obtained here all show a thermo responsive behavior with random copolymers behaving in a more sensitive way. And all these results proved the efficiency and feasibility of microflow system to synthesize thermal responsive polymer materials.

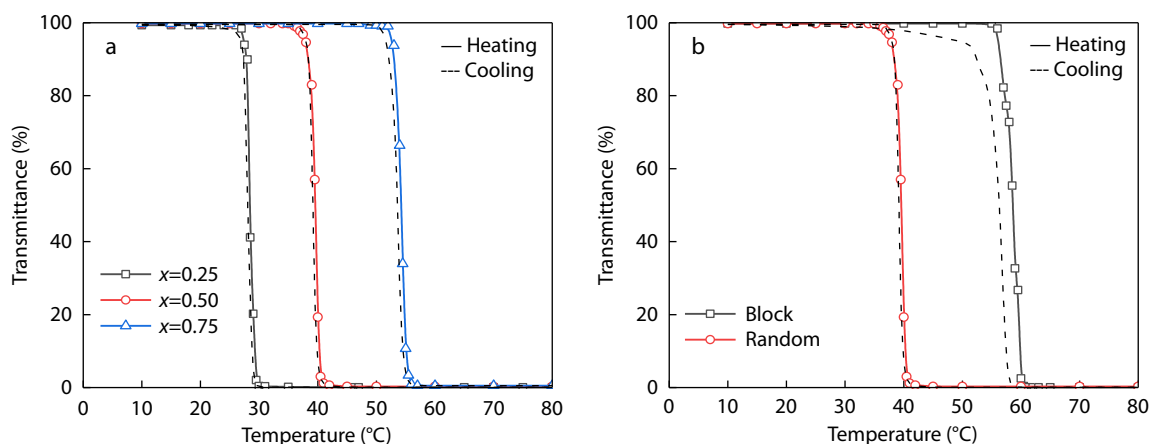


Fig. 5 UV curves obtained by transmittance at 500 nm for $1.0 \text{ wt\%}$ aqueous solutions of (a) random copolymers $\text{poly}(\text{MOVE}_{100x-r}\text{-EOVE}_{100(1-x)})$; (b) diblock copolymers $\text{poly}(\text{MOVE}_{100-r}\text{-}b\text{-EOVE}_{100})$.

CONCLUSIONS

In conclusion, thermal responsive copolymers of 2-methoxyethyl vinyl ether and 2-ethoxyethyl vinyl ether were successfully synthesized in microflow system using IBVE-HCl/SnCl₄ initiating system in toluene in the presence of THF at 0 °C. Among all the combination of Lewis acid and added base, SnCl₄/THF appeared to have the best controllability over the polymerization of both monomers. Polymerization rate can be significantly accelerated by decreasing the concentration of THF to 50 mmol/L while keeping a low dispersity. Close to full conversions can be realized for the synthesis of both random and block copolymers in 3 min without further broadening the MWDs. UV studies showed that random copolymers poly(MOVE_{100x-r}-EOVE_{100(1-x)}) of different composition experience sharp and reversible phase separation. *T*_{ps} of such random copolymers can be conveniently adjusted by changing the relative content of these two monomers. Retardation of phase separation was found for block copolymer poly(MOVE₁₀₀-*b*-EOVE₁₀₀), which may arise from different responsive order for each block during heating and cooling process.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2739-8>.

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