Cyclopolymerization of α,ω-Heterodifunctional Monomers Containing Styrene and Maleimide Moieties

Lei Zou,[1] Jian'an Liu,[2] Ke Zhang,[1] Yongming Chen,[1] Fu Xi[1]

[1]Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, the Chinese Academy of Sciences, Beijing 100190, China
[2]Beijing Mass spectrometry Center, Institute of Chemistry, the Chinese Academy of Sciences, Beijing 100190, China
Correspondence to: Y. Chen (E-mail: ymchen@iccas.ac.cn)

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ABSTRACT: A series of α,ω-heterodifunctional monomers with styrene (St) and maleimide moieties bridged by a varied length of oligo-ethylene glycol (OEG) linkers were synthesized. Cyclopolymerizations of these monomers through reversible addition–fragmentation chain transfer-mediated alternating radical copolymerization between intramolecular St and maleimide moieties were investigated. For the monomers with three or more ethylene glycol (EG) units, their cyclopolymerizations can be realized properly in low monomer feeding concentrations, affording well-defined cyclopolymers with crown ether encircled in their main chains. Importantly, the cyclopolymerizations of monomers with six or seven EG units in the presence of KPF_6 could be enhanced by the supramolecular effects between the OEG linkers and the potassium metal ion. Thus, the monomer feeding concentration could be largely improved, which may benefit preparation of the cyclopolymers with high degrees of copolymerization. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 330–338

KEYWORDS: cyclopolymerization; host-guest systems; reversible addition-fragmentation chain transfer polymerization (RAFT)

INTRODUCTION The polymerization of α,ω-difunctional monomers generally affords branched or even crosslinked structures, resulting from random chain propagation process between intramolecular and intermolecular polymerizable groups. The initial report of Butler and coworkers during the free-radical polymerization of diallyl quaternary ammonium salts which resulted water soluble linear polymers rather than crosslinked quaternary ammonium polymers opened the field of research which is now referred as cyclopolymerization.[1,2] During the process of cyclopolymerization of difunctional monomers, intramolecular and intermolecular chain propagations proceed alternatively, affording well-defined polymers with cyclic moieties along the backbones. Through cyclopolymerization, wide varieties of difunctional monomers have been converted to unique cyclopolymers. Significantly, cyclopolymerization of carefully designed multifunctional monomers has become a very effective method for the synthesis of sequence-regulated polymers.[3–5]

At the very beginning, the majority of researches were confined in the cyclopolymerization of monomers typically proceeded via formation of thermodynamically stable five- or six-membered rings before or during the period of polymerization process.[6–11] Then, cyclopolymerizations proceeded via various mechanisms were discovered. The enhancements of cyclization by bulky substituents were reported by Holmes and coworkers[12,13] and Prata and coworkers.[14] In these systems, two styrene (St) moieties were covalently linked to a directing template possessing a high degree of steric hindrance, which would help keeping the two polymerizable moieties in close proximity and orienting them during propagation. Pasini and coworkers reported the chemically more straightforward scaffolds.[15] They simply covalently linked two 4-styryle substituted moieties to the 1,3-diol moiety of pentaerythritol skeletons and afforded structurally stable cyclopolymers with a high degree of cyclization and good degrees of polymerization (DP). Recently, they reported an easily obtained new styryl difunctional malonate, which was suitably designed for efficient cyclopolymerization.[16] Liu and coworkers designed diacrylate monomers bridged with an 1,2,3-triazole unit. Because the conjugated structure of 1,2,3-triazole fixed two acryloyloxy groups in a plane favorable for ring-closing, the formation of larger rings with high cyclization efficiency was succeeded.[17] Endo and coworkers described the synthesis of polyacryamide containing 10- or 11-membered rings as repeating cyclic units by cyclopolymerization of an optically active bisacrylamide derived from α-pinene, which was benefited from the compulsive conformation arrangement of the two acrylamide groups in the monomeric structure.[18] Recently, they realized

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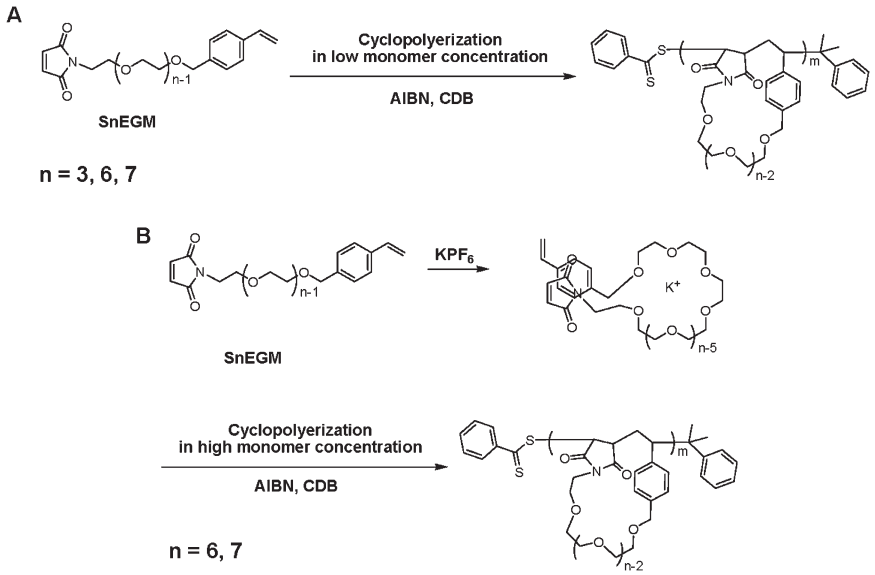


SCHEME 1 Cyclopolymerization of styrene-maleimide containing α,ω-heterodifunctional monomers.

the controlled radical cyclopolymerization of bismethacrylate monomer through quantitative 19-membered ring formation.[19] They attributed the monomer conformations favorable for ring-closing to the cyclohexane ring and the urethane groups straining with steric direction and hydrogen bonds. Very recently, Zhu et al. reported ruthenium-catalyzed cascade metathesis cyclopolymerization of bisnorbornenes with flexible linkers.[20] They presumed that intramolecular π–π interactions between the pending aryl groups of the monomer may take place to direct the ring closure process. There were also many reports on the cyclocopolymerization of flexible divinyl ether monomers with maleic anhydride (MAn) based on that vinyl ether and MAn were prone to polymerization following an alternating fashion.[2]

It is well known that radical copolymerizations of MAn and St or their derivatives tend to copolymerize alternatively.[21–23] This group has applied this chemistry to build novel polymeric architectures.[24–29] Very recently, Jia et al. reported the cyclocopolymeriztion of MAn and distyryl flexible monomers in high dilute concentration and the cyclopolymers with crown ether side units were obtained owing to preferential alternating copolymerization effect between St and MAn moieties.[30] However, the concentration was too low and the synthesis of polymers with high DP was difficult.

In this study, we investigated the polymerization of α,ω-heterodifunctional monomers of which St and maleimide moieties were covalently bridged by a series of OEG linkers (Scheme 1). In one aspect, when the monomers have enough length of OEG linkers, which do not hamper the folding of monomer configuration during the polymerization process for the intramolecular interaction of St and maleimide moieties, cyclopolymerization of the monomers underwent smoothly due to the alternating copolymerization tendency between St and maleimide moieties in low concentrations. More interestingly, the cyclopolymerization of monomers with longer OEG linkers was benefited from the pseudo-host–guest interaction between the OEG linkers and metal ion in higher concentrations. The supramolecular effect induced the conformation change of the monomer and thus pushed the St and maleimide moieties close to enhance the intermolecular propagation. Through this strategy, well-defined polymers with crown ether encircled in their main chains could be prepared with convenience. This is of great importance to the researches of crown ether containing polymers which are very useful functional materials or sensors.[31–37] For instance, in early days, Kakuchi and coworkers had developed a series of cyclopolymerization strategies of difunctional monomers bearing an OEG chain to produce polymers with crown cavities for investigating the relevant metal ions binding properties.[38–40] However, they did not employ or design any other effects, which would enhance the cyclopolymerization process and therefore failed to prepare the required well-defined polymers with efficiency and convenience.

EXPERIMENTAL

Materials

Diethylene glycol (99%, J&K), triethylene glycol (99%, Alfa Aesar), 4-vinylbenzyl chloride (90%, Acros), maleimide (98%, J&K), KPF_6 (99%, Acros), and PEG (M_n = 300, Acros) were used as received without further purification. Other reagents were commercialized chemicals and used as received. All solvents were analytical grade and purified through appropriate method. Chain transfer reagent cumyl dithiobenzoate (CDB) was synthesized according to ref. 41. SEG, S2EG, and S3EG were synthesis according to ref. 42.

Measurements and Instruments

^1H and ^{13}C NMR spectra were obtained on a Bruker 400 MHz instrument. High-resolution mass spectrometry (HRMS)

was carried out using a Waters micromass GCT mass spectrometer. Size exclusive chromatography system equipped with a Waters 515 HPLC pump, three Waters Styragel columns (HT2, HT3, and HT4), a Rheodyne 7725i sampler, and a Waters 2414 refractive-index detector was performed to determine the average molecular weights and molar-mass dispersities of all the samples. Polystyrene standards were used to calibrate the SEC system and THF was used as the eluent at a flow rate of 1 mL/min at 35 °C. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry was performed on a Bruker Biflex III spectrometer equipped with a 337 nm nitrogen laser. 4-Hydroxy-cyanocinnamic acid was used as the matrix. The mass spectra were acquired in linear mode or positive reflector mode at an acceleration voltage of +19 kV. External mass calibration was performed using a standard peptide mixture.

Synthesis of FM

Maleimide (2.0 g, 0.02 mol) was suspended in 50 mL of toluene and furan (3.0 mL, 0.044 mol) was added. The mixture was then stirred at 90 °C for 12 h. After cooled to room temperature, the product was obtained by filtration and washed with small mounts of toluene several times as a white powder (3.1 g, yield 95%).

^{1}H NMR (400 MHz, DMSO-d_6, δ (ppm)) 2.83 (s, 2H), 5.10 (s, 2H), 6.51 (s, 2H), 11.13 (bs, H).

Synthesis of SnEGT

A general procedure was given with S3EGT as an example. To a 100-mL round-bottomed flask containing a solution of S3EG (2.66 g, 0.01 mol) and Et_3N (1.51 g, 0.015 mol) in 30 mL of THF, a solution of tosyl chloride (2.85 g, 0.015 mol) in 20 mL of THF was slowly added over 30 min with stirring. The mixture was stirred at room temperature for 24 h. Then, H_2O (1.0 mL) was added and the mixture was stirred for another 4 h. The mixture was diluted with 200 mL of water, and extracted with 100 mL of dichloromethane three times. The dichloromethane extracts were combined and washed with 100 mL of brine for three times, then dried over $MgSO_4$, and concentrated. The product was purified by column chromatography [petrol ether/ethyl acetate, 4/1 (v/v)] as a viscous liquid (3.8 g, yield 91%).

^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)) 2.43 (s, 3H), 3.60–3.70 (m, 10H), 4.15 (t, 2H, J = 4.7 Hz), 4.54 (s, 2H), 5.23 (d, 1H, J = 9 Hz), 5.74 (d, 1H, J = 17.6 Hz), 6.71 (q, 1H, J_1 = 9 Hz, J_2 = 17.6 Hz), 7.28–7.33 (m, 4H), 7.38 (d, 2H, J = 8.5 Hz), 7.79 (d, 2H, J = 8.5 Hz).

Synthesis of SnEGMF

A general procedure was given with S3EGMF as an example. A mixture of the S3EGT (4.2 g, 0.01 mol), FM (1.7 g, 0.01 mol), K_2CO_3 (6.9 g, 0.05 mol), and 5% 2,6-di-tert-butylphenol in 15 mL of DMF was stirred at 50 °C for 12 h. Then, the mixture was diluted with 200 mL of water, and extracted with 100 mL of CH_2Cl_2 for three times. The CH_2Cl_2 extracts were combined, washed with 100 mL of brine for three times, then dried over $MgSO_4$, and concentrated. The product was purified by column chromatography (petrol ether/ethyl acetate, 2/1 (v/v)) as a viscous liquid (3.6 g, yield 87%).

^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)) 2.82 (s, 2H), 3.61–3.70 (m, 12H), 4.54 (s, 2H), 5.23 (d, 1H, J = 9 Hz), 5.24 (s, 2H), 5.74 (d, 1H, J = 17.6 Hz), 6.47 (s, 2H), 6.71 (q, 1H, J_1 = 9 Hz, J_2 = 17.6 Hz), 7.29 (d, 2H, J = 8.5 Hz), 7.38 (d, 2H, J = 8.5 Hz).

Synthesis of SnEGM

A general procedure was given with S3EGM as an example. S3EGMF (4.1 g, 0.01 mol) was dissolved in 100 mL of toluene and 10% 2,6-di-tert-butylphenol was added. The mixture was refluxed at 110 °C for 12 h. Then, toluene was removed under vacuum and the residue was subjected to column chromatography (petrol ether/ethyl acetate, 2/1 (v/v)). The product S3EGM was obtained as a viscous liquid (3.4 g, yield 99%).

^{1}H NMR (400 MHz, $CDCl_3$, δ (ppm)) 3.59–3.74 (m, 12H), 4.54 (s, 2H), 5.23 (s, 1H, J = 10 Hz), 5.74 (d, 1H, J = 17.6 Hz), 6.66 (s, 2H), 6.70 (q, 1H, J_1 = 10 Hz, J_2 = 17.6 Hz), 7.29 (d, 2H, J = 8.5 Hz), 7.38 (d, 2H, J = 8.5 Hz). ^{13}C NMR (400 MHz, $CDCl_3$, δ (ppm)) 37.27, 67.95, 69.58, 70.22, 70.74, 70.81, 73.03, 113.90, 126.35, 128.07, 134.26, 136.71, 137.06, 138.12, 170.77. HRMS (EI) m/z calculated for $C_{19}H_{23}NO_5$ [M^+] 345.1576, found 345.1580.

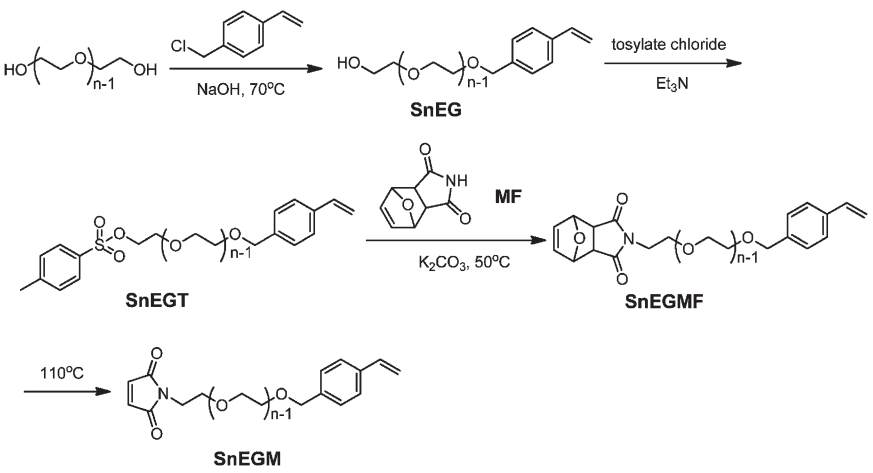
Polymerization

A general procedure was given by taking the polymerization of S6EGM in higher concentration in the presence of KPF_6 as an example. S6EGM (0.24 g, 0.5 mmol), CDB (9.3 mg, 0.034 mmol), AIBN (1.2 mg, 0.007 mmol), CH_3CN (5 mL), and KPF_6 (0.18 g, 1.0 mmol) were charged into a polymerization tube. The tube was sealed after degassed by three freeze-pump-thaw cycles and then was immersed in a 60 °C oil bath for 10 h. After exposing to air, CH_3CN was removed under vacuum and the residue was re-dissolved in 20 mL of CH_2Cl_2. Then, the CH_2Cl_2 solution was wash with water for three times and dried over $MgSO_4$. After concentrated to suitable volume, the solution was precipitated in large amount of diethyl ether for three times. The precipitates were centrifuged and dried under vacuum. The polymer was obtained as pink glass.

RESULTS AND DISCUSSION

Synthesis of the Monomers

In order to investigate intramolecular cyclopolymerization of monomers bearing α,ω-terminated St and maleimide, we synthesized a series of α,ω-heterofunctional monomers bridged with different number of EG units. For the monomers with n = 1, 2, 3, they were synthesized straight forward as shown in Scheme 2. 4-Vinylbenzyl chloride reacted with one terminal of ethylene glycol, diethylene glycol, and triethylene glycol, respectively by Williams etherification reaction and the obtained SnEG (n = 1, 2, 3) reacted with tosyl chloride to activate another terminal. Then furan-protected maleimide (FM) was introduced by substitution reaction to SnEGT in



SCHEME 2 Synthetic route of α,ω-heterodifunctional monomers of styrene and maleimide bridged with different number of ethylene oxide units.

high yield. The final products were obtained by refluxing to remove the furan unit quantitatively. For the monomers of $n = 6$ and 7, they were prepared by the same procedure from commercially available PEG ($M_n = 300$) which contains six to nine ethylene glycol units. The samples were fractionated by column chromatography at SnEGT step to give the S6EGT and S7EGT. The structures of these monomers were identified by ^{1}H NMR, ^{13}C NMR and HRMS as given in Experimental section.

Cyclopolymerization of Monomers with Short OEG Linkers

Reversible addition–fragmentation chain-transfer (RAFT)-mediated radical polymerizations of the monomers with relatively short OEG linkers were first conducted to investigate whether their cyclopolymerizations could be realized by intramolecular interaction of St and maleimide moieties. It is expected that the concentration of monomers is the most critical factor to give the intramolecular cyclopolymer [Chart 1(A)]. In a higher concentration, intermolecular copolymerization should be easily to occur and the products would have branches [Chart 1(B)] and pendent unreacted vinyl units [Chart 1(C)] and thus they would be ill-controlled.

With this consideration, the feed ratio of monomer/CDB/AIBN was kept at 15/1/0.2 and the monomer feeding concentration was varied to optimize the condition (Table 1). The polymerizations were conducted at 60 °C in 1,4-dioxane and all entries gave soluble polymers.

For the polymerizations of S3EGM, the feeding concentrations were 0.0125, 0.025, 0.061, and 0.10 M. As shown in Table 1 (Entries 1–4), the M_w/M_n increased with increase of feeding concentration and the M_w/M_ns from the lower concentrations, 0.0125 and 0.025 M, were 1.25 and 1.31, implying that polymerizations could be controlled. By size exclusive chromatography (SEC) traces as shown in Figure 1(A), the eluent peaks of the Entries 1 and 2 in Table 1, were relatively narrow and symmetric. As contrast, the traces at higher concentration were very broad (Entries 3 and 4 in Table 1), demonstrating that the polymerization in high concentration lost control.

The polymer obtained in 0.025 M (Entry 2 in Table 1) was further characterized by NMR spectrometry. In Figure 2(A), the proton resonances appeared as very broad peaks. The signal between 6.5–7.8 ppm was attributed to aromatic rings, the signal at 4.5 ppm to benzylic CH_2, the signal at 3.7 ppm to the OEG linker and signal at 8 ppm to the moieties of RAFT reagent. The integration ratio of b/c was 1/2, consistent with the polymer structure from S3EGM. The broadening of the resonance signals implied some extent of conformation rigidity of the polymer chain. Importantly, there were hardly any resonances between 5 and 6.5 ppm, which were assigned to double bonds, demonstrating that the vinyl groups were most likely consumed. This precluded the liner structure in Chart 1(C). In the ^{13}C NMR spectrum [Fig. 2(B)], the signal of the aromatic "next to polymer chain" carbon appeared at 136–139 ppm. This was perfectly consistent with an alternative sequence of St-maleimide copolymer.[18]

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum of the polymer obtained in 0.025 M (Entry 2 in Table 1) was also obtained for further characterization of the product structure. As demonstrated in Figure 3(A), two series of peaks were observed. The interval of both series was about 345, which was the mass of monomer S3EGM. The peak series with higher mass (marked with *) can be assigned to be $m_{S3EGM} \times DP + m_{CDB} + m_{Na+} = 345.2 \times DP + 272 + 23$ that was consistent with the macromolecules with S3EGM repeating units being capped with one *Ph(C=S)S* and one cumyl moieties. Another series (marked with ▼) can be assigned to be $m_{S3EGM} \times DP + 119 + m_{Na+} = 345.2 \times DP + 119 + 23$. The mass was about 153 smaller than the former, which was the mass of the CDB moiety of *Ph(C=S)S*. These peaks could be the chains generated in the ionization process of the former series by the

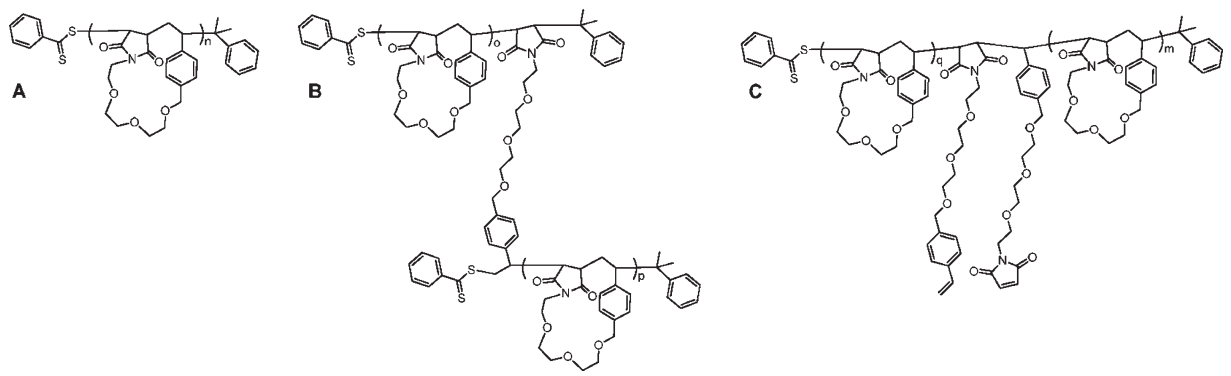


CHART 1 Three of possible structures of the polymerization of S3EGM: (A) linear structure, (B) branched structure, and (C) structure with unconsumed double bonds.

fraction of *Ph(C=S)S* terminals. Therefore, both peak series detected from the MALDI-TOF mass spectrum were attributed to the linear cyclopolymers [Chart 1(A)].

In the MALDI-TOF mass spectrum of the polymer obtained in 0.1 M [Entry 4 in Table 1, Fig. 3(B)], the major peaks were still consistent with the linear structure capped with one Ph(C=S)S and one cumyl moieties. However, minor peaks (marked with ◆) could be found at higher mass region. They can be figured out as $m_{S3EGM} \times DP + m_{CDB} \times 2 + m_{Na+} = 345.2 \times DP + 272 \times 2 + 23$. Namely, these peaks indicated the structure capped with two CDB moieties, a branched structure as shown in Chart 1(B).

By the evidences from ^{1}H NMR, ^{13}C NMR spectrum, and MALDI-TOF mass spectrum, we came to the conclusion that the polymers obtained in low concentration should be a strictly alternate linear cyclopolymer [Chart 1(A)]. Other kinds of structures would be not consistent with either a structure without double bonds as demonstrated by ^{1}H NMR, a strictly alternate structure as demonstrated by ^{13}C NMR or a linear structure as demonstrated by MALDI-TOF mass spectrum.

Subsequently, polymerizations of the monomers with two and one ethylene glycol linkers, S2EGM and SEGM, were conducted. From the SEC curves of the resultant polymers [Fig. 1(B)] in different concentrations, we can see that the cyclopolymerization behavior of S2EGM was similar to that of S3EGM except it needs a lower concentration to give a well-controlled cyclopolymerization. In similar feed concentration, the polymerization of S3EGM (0.025 M, Entry 2 in Table 1) was under control while that of S2EG (0.02 M, Entry 6 in Table 1) gave much higher M_w/M_n of 1.80. With decrease of the feeding concentrating to 0.01 M, the polymerization of S2EG seemed to be controlled as shown by SEC traces [Fig. 1(B)] and gave the M_w/M_n of 1.34. However, minor branched structure could be found from the MALDI-TOF mass spectrum of resultant polymer from the concentration of 0.01 M, which was different from that of S3EGM (Supporting Information Fig. S1). For the monomer with only one ethylene glycol unit (SEGM), the cyclopolymerization at both concentrations, 0.01 and 0.02 M, gave very broad and multimodel polydispersed SEC traces [Fig. 1(C)]. It demonstrated that well-controlled cyclopolymerization of SEGM could not be realized by simply reducing the feeding concentration.

The phenomenon in polymerizations of these monomers can be attributed to the influence of both feeding concentration and length of linkers. In lower concentrations, there was mainly intramolecular interaction of St and maleimide

TABLE 1 Results of the Polymerization of S3EGM, S2EGM, and SEGM in 1,4-Dioxane

Entries	Monomer	Monomer Concentration (M)	Feed Ratio (Monomer/CDB/AIBN)	Conversion (Weight) (%)	M_n[a]	M_w/M_n(SEC)[a]
1	S3EGM	0.0125	15/1/0.2	81	3,300	1.25
2	S3EGM	0.025	15/1/0.2	56	4,000	1.31
3	S3EGM	0.061	15/1/0.2	67	4,300	1.78
4	S3EGM	0.1	15/1/0.2	43	8,700	>3
5	S2EGM	0.01	15/1/0.2	63	2,600	1.34
6	S2EGM	0.02	15/1/0.2	63	7,600	1.80
7	SEGM	0.01	15/1/0.2	~60[b]	–	–
8	SEGM	0.02	15/1/0.2	~60[b]	–	–

[a] Determined by SEC.
[b] There may be deviations in the data, because of difficulties in precipitations of polymers.

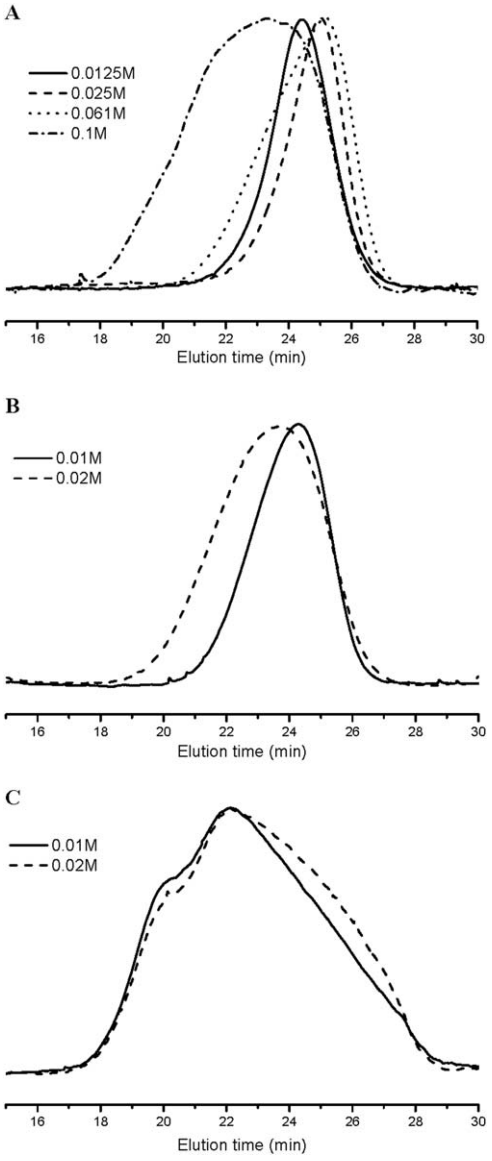


FIGURE 1 SEC elution curves of the resultant polymers given by RAFT-mediated radical copolymerization of (A) S3EGM, (B) S2EGM, and (C) SEGM in different concentrations.

moieties of the monomers and, thus, intramolecular chain propagation was dominant during the period of polymerization process, providing that the OEG linkers were long and soft enough for the intramonomeric folding to achieve linear chain propagation. The shorter the linker was, more difficulty for monomer folded for intramolecular propagation. Therefore, lower concentration was necessarily for intramolecular chain propagation against intermolecular chain propagation. This was the reason for that S3EGM was likely to intramolecular cyclcopolymerize than that of S2EG in the similar concentration. However, when the linker was so short, such as in SEGM, that the molecule cannot fold to facilitate the intramolecular interaction of St and maleimide moieties, cyclopolymerization became difficult even at highly diluted concentrations. With increase of concentration, the opportunity of the intermolecular interaction between St and maleimide units from different monomers increases, thus the branched structure resulted.

Cyclopolymerization of Monomers with Longer OEG Linkers

From the polymerizations of S3EGM, we can see that well-defined cyclopolymers could be obtained by intramolecular interaction of St and maleimide moieties of the monomers. However, a well-controlled cyclopolymerization still occurred at low monomer concentration, and it is not convenient for preparation of the cyclopolymers with high DP. To improve the monomer feeding concentration with controlled cyclopolymerization, there should be additional effects to enhance the cyclopolymerization. Those monomers with relatively longer OEG linkers such as six EG units (S6EGM) and seven EG units (S7EGM) could be regarded as pseudocrown ethers. If host–guest interactions between crown ethers and metal ion could also occur between such open chain structures and metal ions, the configuration change of these monomers

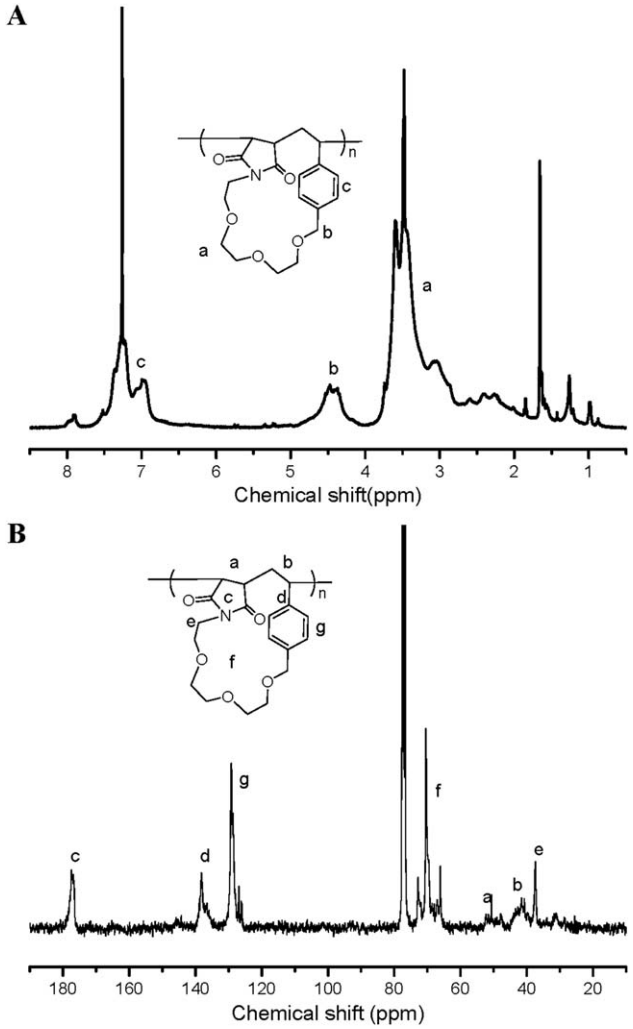


FIGURE 2 (A) ^{1}H NMR (B) ^{13}C NMR spectra in $CDCl_3$ of resultant polymers of S3EGM in low concentration (0.025 M) (Entry 2 in Table 1).

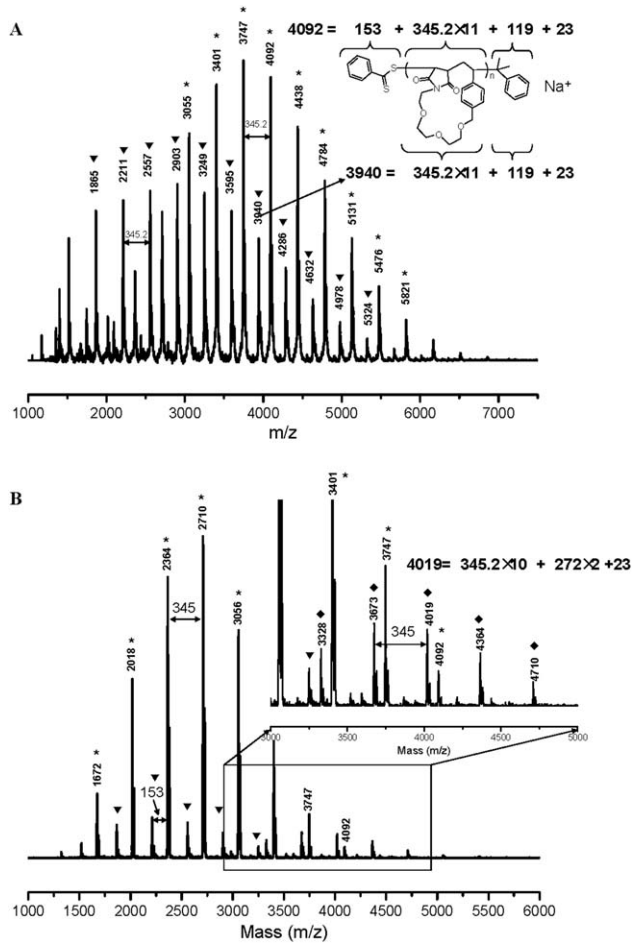


FIGURE 3 (A) MALDI-TOF mass spectra of resultant polymer of polymerization of S3EGM in low concentration (0.025 M) and (B) in high concentration (0.1 M).

would take place and two polymerizable terminals would become close to each other to facilitate the supramolecular effects, which may no doubtless benefit the cyclopolymerization.

The ^{1}H NMR spectra of S6EGM with and without potassium ions (Fig. 4) were recorded to check the supramolecular structure. The host–guest interactions would be observed by an up- or downfield shift of the corresponding signals, which is a common phenomenon in host–guest chemistry. From the ^{1}H NMR spectra of S6EGM before and after the addition of KPF_6 (1 equiv), we can see the signals belong to oxyethylene protons obviously divided from multiply peaks at 3.46–3.62 ppm to the signals at 3.40, 3.49, 3.53, and 3.60 ppm. This clearly indicated the occurrence of host–guest interaction between the monomer and the metal ion. Furthermore, the signal shifts of the protons of terminal groups could also be found. The protons of styryl moiety appeared at 5.24, 5.79, 7.30, 7.43, and 4.49 ppm and shifted to 5.25 (0.01 ppm downfield shift), 5.80 (0.01 ppm downfield shift), 7.31 (0.01 ppm downfield shift), 7.45 (0.02 ppm downfield shift), and 4.52 ppm (0.03 ppm downfield shift) after the addition of K^+. And that of the maleimide moiety appeared at 6.75 ppm and shifted to 6.77 ppm (0.02 ppm downfield shift). This result indicated the relevant configuration change of the two polymerizable functional groups of the monomer motivated by the host–guest interaction between the pseudocrown ether and the metal ion. The host–guest interaction between the monomer and the metal ion seemed to be a 1/1 (monomer/metal ion) stoichiometry since the chemical shifts remained unchanged on adding more metal ion up to 2 equiv (Supporting Information Fig. S2).

We then carried out the RAFT copolymerization of S6EGM (Table 2). There was no difference between the polymerizations of S6EGM to S3EGM in the absence of the metal ions. In the lower concentrations such as 0.02 M, the polymerizations seem to be controlled (Entry 1 in Table 2, Fig. 5). In the ^{1}H NMR spectrum (Supporting Information Fig. S3) of the resultant polymers, every signal appeared very broad. Nearly no resonances between 5 and 6.5 ppm that were contributed from the double bonds could be found. The signal at 136–139 ppm in the ^{13}C NMR spectrum indicated the alternative sequence of the resultant polymer (Supporting Information Fig. S4). In the MALDI-TOF mass spectrum (Supporting Information Fig. S5), the distribution of the molecular ions was very symmetrical with the interval of 477.5, which was consistent with the mass of monomer S6EGM. The mass of every peak (marked with *) could be figured

TABLE 2 Results of the Polymerization of S6EGM in CH_3CN under Different Conditions

Entries	Monomer Concentration (M)	Feed Ratio (Monomer/CDB/AIBN)	Conversion (NMR)[a] (%)	M_n[b]	M_w/M_n[b]
1	0.02	15/1/0.2	50	2,300	1.26
2	0.05	15/1/0.2	~80[c]	4,200	>2
3	0.05+K^+	15/1/0.2	85	2,800	1.25
4	0.1+K^+	15/1/0.2	81	2,500	1.27
5	0.16+K^+	15/1/0.2	~70[c]	3,100	1.62

[a] Calculated according to the integral areas of resonance of —CH_2O— attached to the styrene moieties in NMR spectrum.
[b] Determined by SEC.
[c] There may be deviations in the conversion of monomer calculated by NMR because of signals of unconsumed terminals in branched structure.

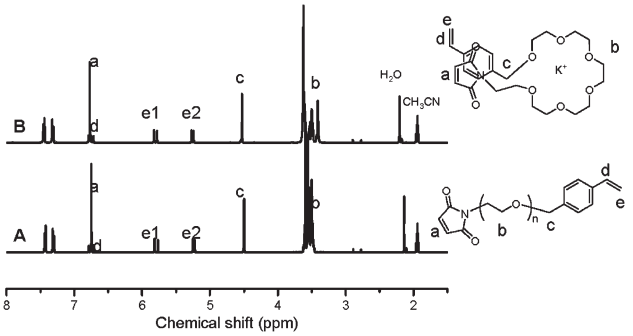


FIGURE 4 ^{1}H NMR spectra of (A) S6EGM and (B) S6EGM with 1 equiv KPF_6.

out as $m_{S6EGM} \times DP + m_{CDB} + m_{Na+} = 477.5 \times DP + 272 + 23$. This was consistent with the polymer being capped with one *Ph(C=S)S* and one cumyl moieties, a linear structure from the cyclopolymerization of S6EGM. However, when increasing the concentration to 0.05 M, the copolymers with $M_w/M_n > 2$ were obtained (Entry 2 in Table 2, Fig. 5), indicating that the polymerization lost control.

From the SEC traces of the resultant polymers in the presence of KPF_6 (Entries 3 and 4 in Table 2, Fig. 5), we could see that the polymerization of S6EGM in the higher concentrations up to 0.1 M in the presence of KPF_6 resulted well-controlled polymers compared to those resulted in the absence of the salt. Also, the result of MALDI-TOF mass spectrum was similar to that obtained from the polymers at low concentration (Supporting Information Fig. S6). Thus, the linear structure was obtained at higher concentration in the presence of metal ion.

We believed that the polymerization behavior of S6EGM in higher concentration could be explained by the host–guest interaction of metal ion and monomer as we can see from the ^{1}H NMR spectra (Fig. 4). The interaction induced the preorganization of the monomer conformation. When the monomer adopted this structure, the two polymerizable

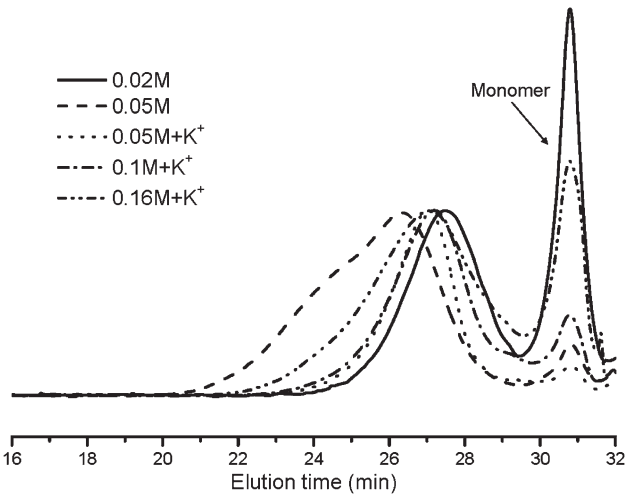


FIGURE 5 SEC profiles of polymerization of S6EGM under different conditions.

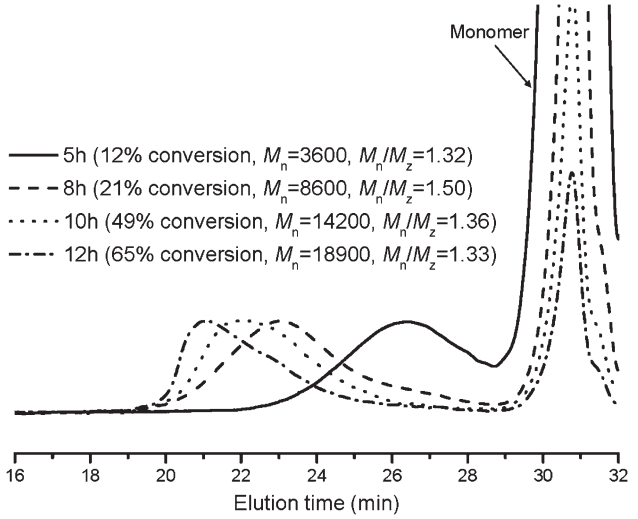


FIGURE 6 SEC profiles at different conversions in the cyclopolymerization of S6EGM. Feed ratio: S6EGM/CDB/AIBN/KPF_6 = 100/1/0.2/200.

groups of the same monomer got close to each other. This kind of effects had been reported previously by others in the selective ion sensing with squaraine tethered bichromophoric pseudocrown ether systems.[43] Therefore, the intramolecular interactions of St and maleimide moieties from the same diheterofunctional monomer were enhanced and the intermolecular interactions were suppressed even at a higher concentration. Thus, intramolecular propagation can proceed alternatively, affording well-defined cyclocopolymers.

When the OEG linker was further elongated to seven EG units (S7EGM), the cyclopolymerization could also be assisted by supramolecular effects between the OEG linker and K^+ ion (Supporting Information Table S1). As we could see from SEC profiles of polymerization of S7EGM under different conditions (Supporting Information Fig. S7), the polymerization in higher concentration (0.05 M) in the presence of KPF_6 could result well-controlled polymers compared to those resulted in the absence of the salt. However, the supramolecular effect no longer affected so much at the concentration of 0.1 M, which was not so effective than that in the polymerization of S6EGM at the same concentration. It could be explained by weaker interaction between the monomer with seven EGs and K^+ ion. The up- or downfield shifts of the corresponding signals from ^{1}H NMR of the monomer after the addition of KPF_6 (Supporting Information Fig. S8) were not so obvious, compared to that of S6EGM. The situation may be improved by the use of more suitable metal ion.

With aid of K^+ templating, we easily obtained the cyclopolymers with M_n up to 18,900 g/mol (dash dot line of Fig. 6), which had not been achieved in the reports of other kinds of cyclopolymerization. From the polymerization profiles of experiment with a large feed ratio of RAFT polymerization of S6EGM in 0.1 M (S6EGM/CDB/AIBN/KPF_6 = 100/1/0.2/200) (Fig. 6), we can see that the cyclopolymerization proceeded smoothly. Molecular weights increased gradually with

increase of the monomer conversion while distributions remained narrow.

CONCLUSIONS

We have synthesized a series of difunctional monomers with St and maleimide moieties covalently linked by varied length of OEG linkers. The cyclopolymerizations of these monomers under different conditions were carried out. In low concentrations, the cyclopolymerizations of those monomers with three or more EG units could be realized properly, affording well-defined polymers with crown ether encircled in their main chain. In high concentrations, the polymerizations of these monomers resulted branched polymers as indicated by above spectroscopic methods. However, with aid of supramolecular interaction, the cyclopolymerizations of monomers with six or seven EG units in the presence of KPF_6 in high concentrations underwent smoothly. These findings will be helpful to the synthesis of functional materials through cyclopolymerization with convenience by elevating the feeding concentration.

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