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Crown Ether Cavity-Containing Copolymers via Controlled Alternating Cyclocopolymerization

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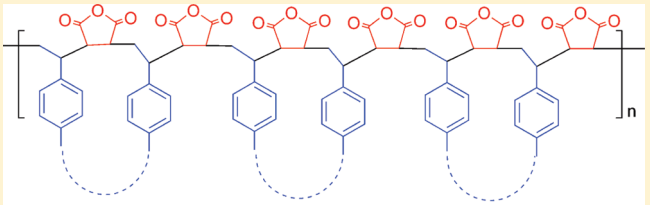
Supporting Information

ABSTRACT: The cyclocopolymerization of difunctional styrenic flexible monomers with maleic anhydride via reversible addition−fragmentation chain transfer (RAFT) has been investigated. The reaction proceeded to yield gel-free copolymers soluble in organic solvents. The kinetic study indicated that the cyclocopolymerization of difunctional styrenic flexible monomer with maleic anhydride proceeded in a controlled manner. The structures of resulting crown ether cavity-containing copolymers were characterized by the use of NMR spectroscopy and MALDI-TOF mass spectrometry. The crown ether cavities in copolymers exhibited a selective recognition for certain dialkylammonium ions.



The dashed flexible spacers contain tri- or tetra(ethylene glycol) moieties

INTRODUCTION

Butler and co-workers demonstrated the formation of water-soluble linear polymers via cyclopolymerization as compared to the formation of highly cross-linked quaternary ammonium polymers during the conventional free-radical polymerization of diallylquaternaryammonium salts.[1,2] The cyclo(co)polymerization has been considered as one of the most convenient method for the preparation of a polymer with a cyclic structure in the main chain because it provides the unique way to generate cyclic structures in the polymer backbone while making the polymers efficiently.[3,4] Cyclo(co)polymerization generally produces thermodynamically stable five- or six-membered rings as the repeating units along the backbone.[5−9] These very compact rings provide rigidity to the resulting polymers but are too small for the inclusion of other molecules, making them difficult to be used, for example, as stationary phases for chromatographic separation and metal scavengers.[10−12] Larger rings may be incorporated by the polymerization of properly designed difunctional monomers[3,4,13−20] which contain bulky or orienting groups joining the two polymerizable groups in such a way to favor intramolecular cyclization of the growing species in a chain-addition polymerization process rather than cross-linking. For instance, Endo's group[16,17] attained selective ring-closure using the monomer's constrained conformation and the directing groups; Kakuchi's group[18−20] developed the cyclopolymerization of difunctional monomers derived from a large series of optically active diol tethers elaborated as 4-vinyl benzoate esters. More recently, Pasini's group[3,4] achieved the cyclopolymerization of difunctional styrenic monomers through the introduction of pentaerythritol. To date, most examples of cyclo(co)polymerization are realized through the help of metal catalysts forming five- or six-membered rings or based on monomers possessing constrained conformation capable of selective ring closure. It is difficult to construct a cyclo(co)polymerization system forming larger rings with flexible monomers because of large ring distortion and longer distances for ring closure.

In Butler's early studies, the cyclocopolymerization of flexible divinyl ether monomer with maleic anhydride (MAn) was achieved via radical initiation, resulting in large ring-containing copolymers,[21−24] but most reports on cyclocopolymerization all focused on the system of divinyl ether monomers and MAn.[25,26] These studies prompted us to study the cyclocopolymerization of more flexible difunctional styrenic monomers with MAn since an alternating copolymer is preferentially obtained when styrene is copolymerized with MAn.[27,28] To the best of our knowledge, difunctional styrenic monomer cyclocopolymerization with MAn has never been reported. With the development of controlled radical polymerization techniques, reports on the successful application of these methods to cyclo(co)polymerizable systems have appeared in the literature.[16,17,29−32] The major objective of this study is to develop a new controlled cyclocopolymerization system for the common flexible monomers. We attempted to copolymerize MAn with difunctional styrenic monomers in which the styrene moieties are covalently linked to a tri- or tetra(ethylene glycol) (Scheme 1). The copolymerization was achieved with slower propagation via the reversible addition−fragmentation transfer (RAFT) polymerization technique that would take a thermodynamically favorable process in

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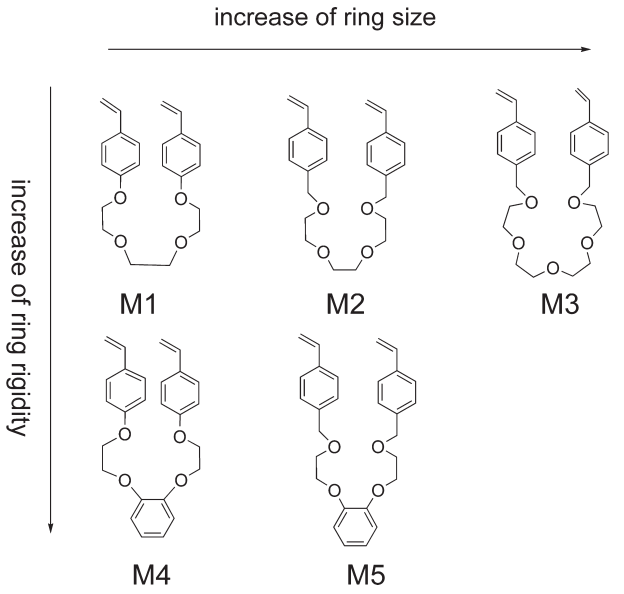
Scheme 1. Difunctional Styrenic Monomers with Different Spacers and Rigidities



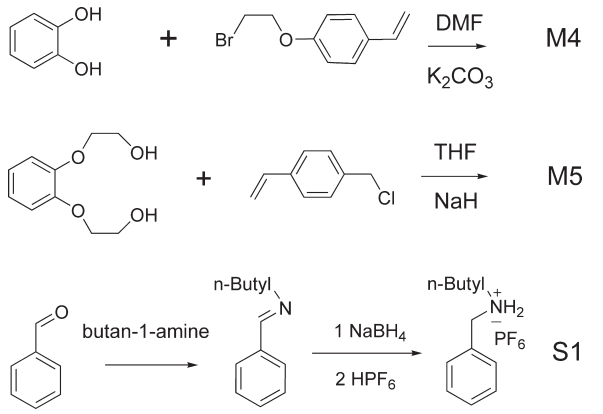
order to attain selective cyclocopolymerization to produce crown ether cavities on the main chain. In the present study, we synthesized and used a series of difunctional styrenic monomers with different spacers and rigidities (Scheme 1) in the preparation of the copolymers. The characterization and the recognition with organic ammonium salt of the resulting copolymers have been investigated.

EXPERIMENTAL SECTION

The chain transfer agent (CTA) benzyl dithiobenzoate was synthesized according to the literature.[33] 2,2′-Azobis(isobutyronitrile) (AIBN) (>98%, Tianjin Chemical Co.) was recrystallized from methanol twice, and maleic anhydride (>99%, Tianjin Guangfu Fine Chemical Research Institute) was recrystallized from $CHCl_3$ twice before use. 1,4-Dioxane was dried by sodium, distilled, and stored under nitrogen. Ethyl acetate, hexane, chloroform, and methanol were all purchased from Tianjin Chemical Co. and purified by distillation. Other reagents were used as received. The difunctional styrenic monomers 1,2-bis(2-(4-vinylphenoxy)ethoxy) ethane (**M1**),[34] 1,2-bis(2-(4-vinylbenzyloxy)ethoxy)-ethane (**M2**), and 1-((2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy)ethoxy)-ethoxy)ethoxy)methyl)-4-vinylbenzene (**M3**)[35] were synthesized according to the literature. The syntheses of 1,2-bis(2-(4-vinylphenoxy)ethoxy)-benzene (**M4**) and 1,2-bis(2-(4-vinylbenzyloxy)ethoxy)benzene (**M5**) are shown in Scheme 2.

Synthesis of M4. A mixture of catechol (0.72 g, 6 mmol), K_2CO_3 (3.00 g), 1-(2-bromoethoxy)-4-vinylbenzene (4.52 g, 20 mmol), synthesized according to the literature,[36] and dimethylformamide (10 mL) was stirred at 75 °C for 24 h. The mixture was diluted with water; the precipitate was collected and washed with cold water. The crude product was crystallized from ethyl acetate twice (2.03 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.23 (d, 4H, J = 8.8 Hz), 6.90 (m, 4H), 6.69 (d, 4H, J = 8.8 Hz), 6.57 (dd, 2H, J_1 = 10.8 Hz, J_2 = 17.6 Hz), 5.53 (dd, 2H, J = 17.6 Hz), 5.05 (dd, 2H, J = 10.8 Hz) 4.29 (t, 4H, J_1 = 4.0 Hz, J_2 = 4.8 Hz), 4.22 (t, 4H, J_1 = 4.8 Hz, J_2 = 4.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.0 (2C), 148.7 (2C), 135.7 (2C), 130.3 (2C), 126.9 (4C), 121.7 (4C), 115.4 (4C), 114.3 (4C), 111.2 (2C), 67.9 (2C), 66.3 (2C). HRMS Calcd for $C_{26}H_{26}O_4$ $[M + Na]^+$ 425.1729. Found: 425.1723.

Scheme 2. Synthesis of Difunctional Styrenic Monomers M4 and M5 and the Organic Ammonium Salt S1

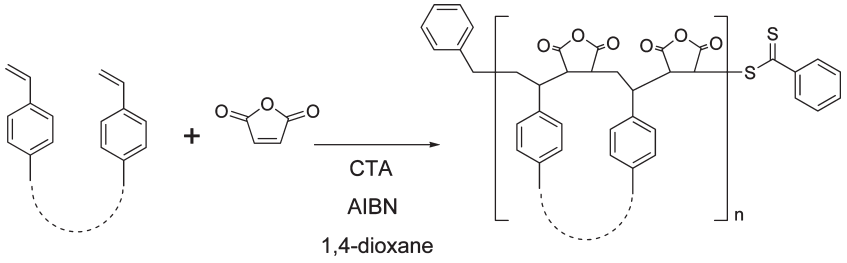


Synthesis of M5. A mixture of 1,2-(2-hydroxylethoxy)benzene (990 mg, 5 mmol), synthesized according to the literature,[37] and NaH (288 mg, 12 mmol) in 40 mL of dry THF was stirred in an ice bath for 1 h and then at room temperature for 2 h. After the addition of a 10 mL of THF solution of 4-vinylbenzyl chloride (1.82 g, 12 mmol), the mixture was stirred at room temperature for 1 h and then refluxed for 12 h. The mixture was cooled down, filtered, and concentrated under reduced pressure, neutralized by the addition of a dilute acid (50 mL, pH = 2), and extracted with dichloromethane (3 × 50 mL). The extract was washed three times with brine, then dried over $MgSO_4$, and concentrated. The product was purified by column chromatography (hexane/ethyl acetate, 10:1 (v/v)) to afford a viscous liquid of pure **M5** (1.74 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37 (d, 4H, J = 8.0 Hz), 7.30 (d, 4H, J = 8.0 Hz), 6.93 (m, 4H), 6.70 (dd, 2H, J_1 = 11.2 Hz, J_2 = 17.8 Hz), 5.73 (dd, 2H, J = 17.8 Hz), 5.23 (dd, 2H, J = 11.2 Hz), 4.61 (s, 4H), 4.25 (t, 4H, J_1 = 5.2 Hz, J_2 = 4.8 Hz), 3.84 (t, 4H, J_1 = 4.8 Hz, J_2 = 5.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.0 (2C), 137.8 (2C), 136.8 (2C), 136.5 (2C), 127.8 (4C), 126.1 (4C), 121.6 (4C), 114.9 (4C), 113.6 (2C), 72.9 (2C), 68.9 (2C), 68.5 (2C). HRMS Calcd for $C_{26}H_{26}O_4$ $[M + Na]^+$ 453.2042. Found: 453.2036.

Copolymerization of M1 with MAn. All the difunctional styrenic monomers copolymerizations with MAn were conducted under the same conditions (Scheme 3). In a typical reaction, benzyl dithiobenzoate (14 mg, 0.057 mmol), AIBN (3 mg, 0.018 mmol), **M1** (354 mg, 1 mmol), and MAn (980 mg, 10 mmol) were added to a dry 100 mL Schlenk tube equipped with a stirring bar under nitrogen. The tube was degassed and purged with nitrogen for 1 h. 1,4-Dioxane (50 mL) was added into the tube under a nitrogen atmosphere. Next, the tube was sealed with a septum, and residual oxygen in the mixture was removed by three freeze−pump−thaw cycles. The reaction mixture was allowed to thaw and was immersed in a preheated oil bath at 60 °C for 6 h. The tube was placed into ice water in order to quench the reaction. The solvent was mostly removed under reduced pressure. The conversion of **M1** was determined by ^{1}H NMR to be >99%. The reaction mixture was precipitated in excess methanol. The precipitate was washed several times with methanol and dried under vacuum to give 525 mg of **P1** as a pink powder. The copolymers **P2** (528 mg), **P3** (495 mg), **P4** (489 mg), and **P5** (546 mg) were obtained from the copolymerization of MAn with **M2**, **M3**, **M4**, and **M5**, respectively.

Synthesis of *N*-*n*-Butylbenzylammonium Hexafluorophosphate (S1). **S1** was synthesized according to the literature procedure with minor modifications (Scheme 2).[38] Butan-1-amine (10 mmol) was added to a solution of benzaldehyde (10 mmol) in anhydrous toluene (20 mL). The resulting mixture was heated at 110 °C for 3 h and then evaporated to dryness. Then the crude product was dissolved in MeOH

Scheme 3. Difunctional Styrenic Monomers Copolymerized with MAn



The dashed flexible spacers contain tri- or tetra(ethylene glycol) moieties

(15 mL). $NaBH_4$ (30 mmol) was then added to the solution at 0 °C, which was stirred for 8 h after warming to room temperature. Water (10 mL) was added carefully to quench the excess $NaBH_4$. The solvent was then evaporated, and the residue was partitioned between water and $CHCl_3$. The organic extracts were dried, and the solvent was removed in vacuo. The residue was dissolved in THF, and 10 mmol of HPF_6 was added to the solution. THF was removed after the mixture was dried over $MgSO_4$. The solid was washed by $CHCl_3$ to yield **S1** (2.78 g, 90%) as a white powder.

Characterization. The number-average (M_n) and the weight-average molecular weights (M_w) and the polydispersity index (PDI) of the polymers were determined by size exclusion chromatography (SEC) by the use of an Agilent Technologies 1200 series SEC equipped with a G1362A differential refractive index detector, with THF as eluent at a flow rate of 1.0 mL/min. Polystyrene standards were used for the calibration of molecular weight. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Avance spectrometer at room temperature, with TMS as the internal standard. Thermogravimetric analysis (TGA) was performed on a Q500 thermogravimetric analyzer under nitrogen atmosphere (60 mL/min) at a heating rate of 10 K/min. FT-IR spectra were recorded with KBr pellets of solid samples on a Bruker Tensor 27. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Biflex III spectrometer equipped with a 337 nm nitrogen laser. 2,5-Dihydroxybenzoic acid was used as the matrix. The mass spectra were acquired in a linear mode at an acceleration voltage of +19 kV. High-resolution mass spectrometry (HRMS) was performed on a Varian QFT-ESI instrument.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Copolymers. Compared with **M1** and **M2**, **M4** and **M5** are more rigid due to the presence of an aromatic ring. The length of the spacer increases from **M1** to **M2** and to **M3** to increase the ring size in the resulting copolymers (Scheme 1). A low initial monomer concentration ($[monomer]_0$ = 0.02 M) was used to favor intramolecular propagation and to suppress any intermolecular propagation that may lead to uncyclized repeating units. It well established that an alternating copolymer will be preferentially obtained when styrene is copolymerized with MAn.[27,28] Increasing the concentration of the comonomers can generally promote the formation of charge transfer complex between the comonomers,[27] which facilitates the formation of an alternating copolymer. Since a high concentration of difunctional styrenic monomer may lead to potential problems of cross-linking, we opted to increase the concentration of MAn to promote the formation of the charge transfer complex and to enhance intramolecular cyclization. We also tried to decrease the molar ratio of MAn to difunctional styrenic monomer. Precipitation occurred during the polymerization when the molar ratio of MAn to difunctional styrenic monomer was lower than 5. When this molar ratio was 7, the conversion of difunctional styrenic monomers reached 99% in 48 h. The molar ratio of MAn to difunctional styrenic monomers was optimized to be 10, which afforded high cyclization yields even under dilute conditions. All resulting copolymers are soluble in organic solvents such as acetone and THF, which indicates that the cyclizations were efficient enough to prevent cross-linking. The ^1H NMR spectra of the copolymers are listed in Figure S1. The complete disappearance of the vinyl proton resonances indicates an efficient cyclocopolymerization and rules out the presence of detectable vinyl pendant groups within the copolymer backbone. The existence of MAn was confirmed by FT-IR spectra (Figure S2), showing two new strong absorption peaks at 1857 and 1780 cm^{-1} assigned to the characteristic carbonyl absorption of MAn. In this work, the copolymers were precipitated in methanol at the room temperature. Concerns of possible opening of the anhydride ring are eased by the attenuated total reflection (ATR) FT-IR spectra of the polymers obtained without the use of KBr, where no absorption was observed in the region of 3000−3500 cm^{-1}. The small absorption observed in this region in the FT-IR spectra may be caused by the water moisture in the KBr used. The IR spectra are shown in the Supporting Information (Figure S2).

Good agreements between the $M_{n,SEC}$ measured by SEC and the $M_{n,NMR}$ by NMR were observed, while the PDIs were not very narrow (Table 1). The PDI increased with an increase in the monomer's spacer length from **P1** to **P2** and to **P3** even under the same reaction conditions, indicating that the cyclization becomes increasingly difficult to control as the spacer group becomes longer. The duration of cyclizations also increased from **P1** to **P2** and to **P3** with increasing spacer length of the monomers. In contrast, the yield decreased with the increase in the spacer length, which may be explained by the increased flexibility of the copolymer backbone caused by the spacer length. The resulting copolymers also have a higher solubility in methanol. For the same reason, solubility of the copolymers in chloroform also increased from **P1**, **P2** to **P3**. In previous reports,[12,39,40] the broadening of the PDI from the appearance of the shoulder on the high-molecular-weight side of the SEC curve is rather common in the course of cyclopolymerization of divinyl ether monomers, especially at high monomer conversions, where a

Table 1. Results of the RAFT Copolymerization of the Difunctional Styrenic Monomers M1−M5 with Maleic Anhydride in 1,4-Dioxane

copolymer	reaction time (h)	yield (%)[a]	$M_{n,NMR}$[b]	$M_{n,SEC}$[c]	PDI[c]	T_d (°C)[d]
P1	6	95	9600	8000	1.33	313
P2	24	89	9200	8400	1.52	296
P3	48	78	11400	12900	1.86	275
P4	6	80	8000	6500	1.51	316
P5	24	86	10800	9500	1.53	310

[a] Yield calculated from the soluble portion in methanol. The conversion of the difunctional styrenic monomers was >99% as determined by ^{1}H NMR. [b] $M_{n,NMR} = [M]_0/[CTA]_0 \times$ conversion (%) $\times$ molecular weight of monomer + molecular weight of CTA. [c] Determined by SEC. [d] The decomposition temperature is defined as the temperature at 5% weight loss, measured by TGA.

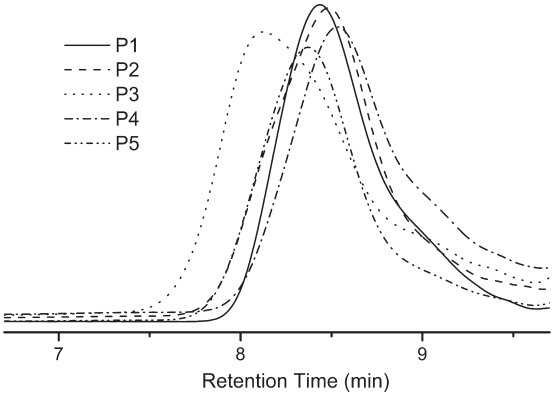


Figure 1. SEC curves of **P1**, **P2**, **P3**, **P4**, and **P5**.

minor extent of cross-linking and/or branching reactions may occur to consume the pendant unreacted vinyl groups and broaden the PDIs of the produced polymers. In this study, there is no apparent shoulder on the high-molecular-weight side of the SEC curves (Figure 1).

From the ^{1}H NMR spectra of **P1** and **P3**, molar ratio of difunctional styrenic monomers and MAn can be calculated directly by the relative integration of the proton resonances (Figures S3 and S4). They are both close to 1:2, indicating the good match between the observed and the proposed alternating structures of the comonomers. On the basis of the reactivity of the propagating radical and the comonomers, an alternating copolymer is preferentially obtained when styrene is copolymerized with MAn.[27,28] Charge transfer complexes should be formed between the monomers. Once the polymerization is initiated, the comonomer pair in the complex copolymerizes spontaneously to yield an alternating copolymer.

The MALDI-TOF mass spectrometric results in Figure 2 are also in accordance with the structure of an alternating polymer. In the spectra, the main peaks are separated by a fragment mass corresponding to a repeating unit consisting of one difunctional styrenic monomer and two MAn monomers (structural pattern **A** in Scheme 4). For example, peaks A and B (Figure 2A) both correspond to the products of Na^+ cationization, and the interval between them correspond to the fragment mass of one difunctional styrenic monomer and two MAn (550 Da) as shown in pattern **A** in Scheme 4. In the enlarged spectra, one can observe the presence of minor peaks on the left side (for **P1** in Figure 2A and **P2** in Figure S7) or on both sides (for **P5** in Figure 2B) of each of main peaks. In the enlarged figure, one can clearly note that the interval between main peaks and the minor peaks are all 98 Da, which can be assigned to one unit of MAn (such as the interval between peaks D and E in Figure 2A). These differences can be attributed to the different terminal monomer patterns during polymerization (Scheme 4). Pattern **A**: the ends of polymer chain are different, being maleic anhydride and styrenic monomer, respectively. Pattern **B**: both ends terminate with the styrenic monomer (one MAn unit less). Pattern **C**: both ends terminate with MAn (one MAn unit extra). Patterns **B** and **C** may be less abundant than pattern **A**, even though all three patterns in the same group may contain the same number of styrenic monomers. In Figure 2A, the interval between peaks B and E (18 Da) correspond to a water molecule, since some of the anhydride groups may undergo a hydrolysis or absorb one water molecule at a high temperature with traces of moisture during the ionization experiments. The interval between peaks B and E (16 Da) may be caused by the different cationization or terminal chain transfer agent groups. In the MALDI-TOF mass spectrum of **P5** (Figure 2B), other minor peaks are present on both sides of the main peaks. The interval between main peaks A and B (626 Da) is fragment mass of structural pattern **A**. The intervals between peaks B and D or B and F are both 98 Da, corresponding to one unit of MAn, which can be also explained by the different terminal monomer patterns. Peaks B, D, and F correspond to the patterns **A**, **C**, and **B** in Scheme 4, respectively.

In this study, the design of the polymers is based on the well-known fact that styrenic monomers and MAn copolymerize to yield alternating copolymers with a regular sequence of the type $M_1M_2M_1M_2$.... This work is the first attempt to introduce relatively large crown ether rings on the main chain of polymers by the alternating copolymerization of difunctional styrenic monomers with MAn. It is known that comonomer pairs in the form of charge transfer complex M_1M_2 may be formed before the initiation, which helps the copolymerization of the monomers spontaneously in an alternating fashion.[27] Furthermore, if one considers the following reactions

$$\sim\!M_1\cdot + M_1 \xrightarrow{k_{11}} \sim M_1M_1\cdot \qquad \sim\!M_1\cdot + M_2 \xrightarrow{k_{12}} \sim M_1M_2\cdot$$

$$r_1 = k_{11}/k_{12}$$

$$\sim\!M_2\cdot + M_2 \xrightarrow{k_{22}} \sim M_2M_2\cdot \qquad \sim\!M_2\cdot + M_1 \xrightarrow{k_{21}} \sim M_2M_1\cdot$$

$$r_2 = k_{22}/k_{21}$$

where M_1 and M_2 represent MAn and styrene, respectively; the reactivity ratios r_1 and r_2 of the two monomers at 50 °C are 0.005 and 0.050, repectively.[41] These values indicate clearly that the two types of propagating species preferentially add the other monomer, not the monomer of its own kind. Under the dilute conditions (0.02 M) used in our study, which is lower than the concentration used by others in the cyclopolymerization of difunctional monomers,[3,17] it is even harder for the difunctional styrenic monomers to homopolymerize. Chances of any intramolecular cyclization of the two styrene moieties should be very low. Both the MALDI-TOF mass spectrometric data and the ^{1}H NMR spectroscopic data point to the formation of alternating copolymer structures as the major products. Theoretically, we cannot exclude the probability of adjacent identical monomer

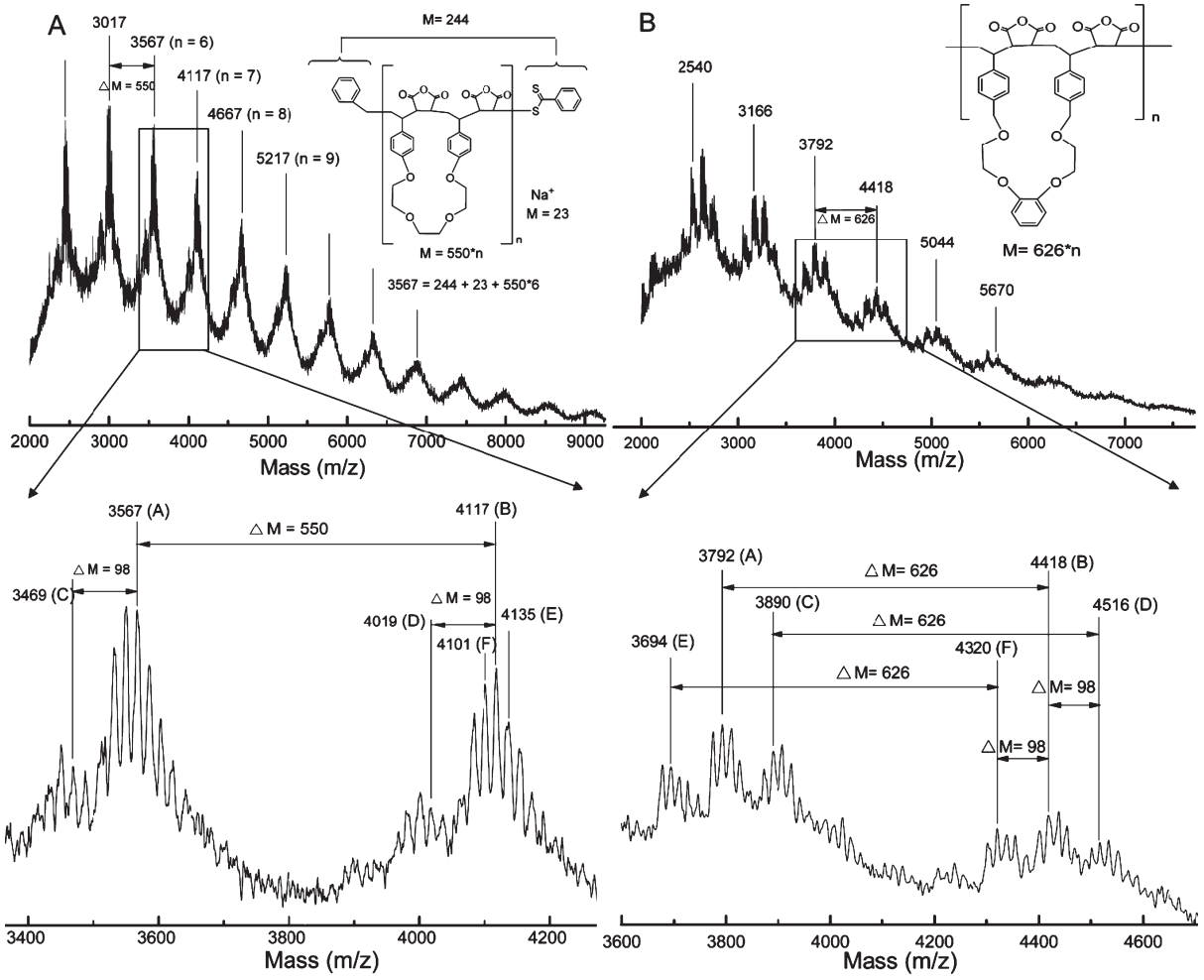
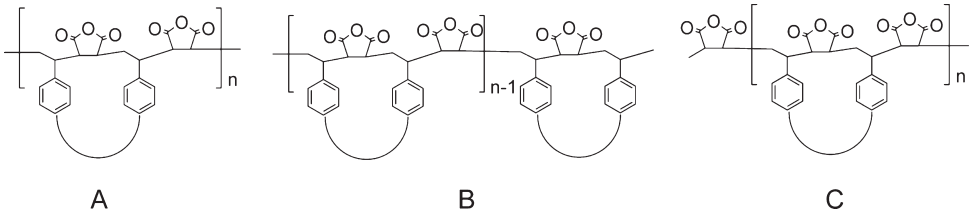


Figure 2. MALDI-TOF mass spectra of **P1** (A) and **P5** (B) and the enlarged regions of the spectra.

Scheme 4. Different Structural Patterns of the Copolymers Observed in MALDI-TOF Mass Spectrometry



units in the copolymers obtained, but the data obtained indicates that the difunctional styrenic monomers preferentially copolymerize with MAn, yielding alternating copolymers. In the case of **M5** copolymerization with MAn, there may be trace amounts of adjacent MAn units close to the baseline noise of the enlarged part of the MALDI-TOF spectrum of **P5** (Figure 2B). This is not observed, however, for the other copolymers obtained as shown in Figure 2A for **P1** and Figure S7 for **P2**. Indeed, reports on the homopolymerization of MAn are rare due to MAn's very low homopolymerization reactivity.

Other matrices were also tested for the MALDI-TOF mass spectrometry of the copolymers, but the result was not satisfactory due to the low intensity of the signals, especially in the higher molecular region. It is possible that copolymer has a lower solubility in the mixture of THF and methanol, which may lead to insufficient mixing of the polymer and matrix, causing difficulty in the ionization of the polymer.[42]

To demonstrate the controlled character of these polymerizations, **M1** copolymerization with MAn was used as a model for the kinetic study at 60 °C. The samples were withdrawn from the copolymerization mixtures at prefixed time intervals, quenched in an ice bath, and promptly analyzed by SEC and ^{1}H NMR. As shown in Figure 3A, a nearly linear increase of M_n with conversion as well as the relatively narrow PDI values (1.3−1.5) reveals a constant number of propagating chains throughout the polymerization and the absence of nondegenerative chain transfer

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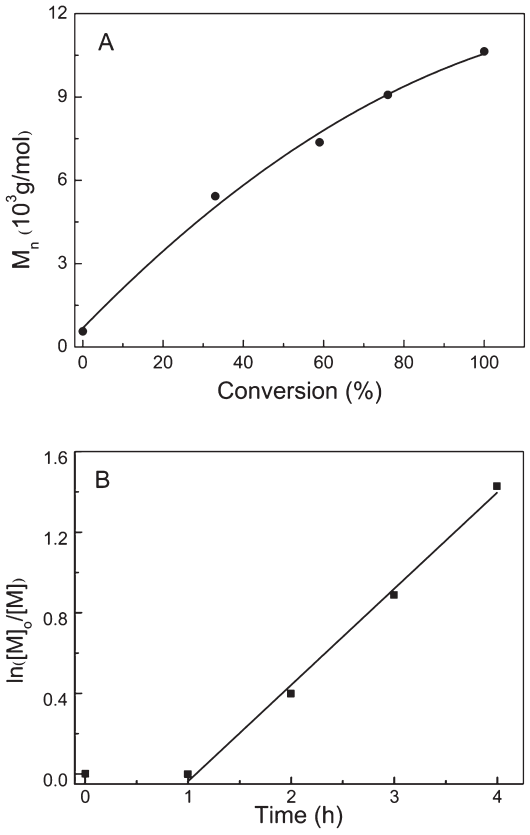

Figure 3. Kinetic study of **M1** cyclocopolymerization with MAn in 1,4-dioxane at 60 °C: (A) plot of M_n as a function of **M1** conversion; (B) plot of $\ln([M]_0/[M])$ as a function of reaction time.

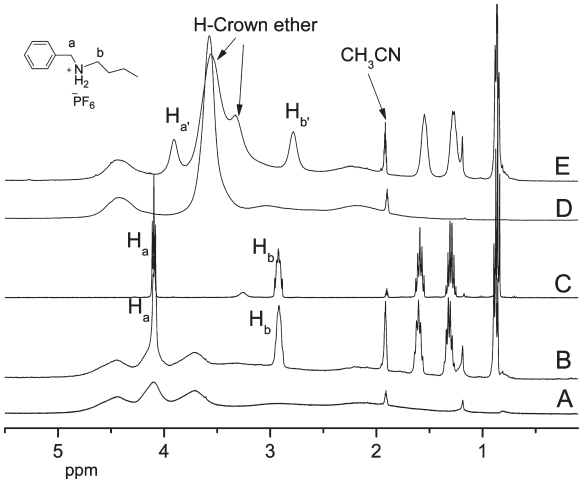

Figure 4. ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$, 5:1, v/v) of (A) **P5**, (B) **S1** mixed with **P5** (C) **S1**, (D) **P3**, and (E) **S1** mixed with **P3**. **S1** was added in equimolar amounts as the crown ether units in the polymers.

reaction. The linearity of the first-order kinetic plot (Figure 3B) for the copolymerization indicates a constant free radical concentration and the absence of significant termination reactions. Figure 3B also indicates the consumption of **M1** starting after an induction period of 1 h. The induction periods are often observed with CTAs in which the substitution group R reinitiates slowly[43−45] or preferentially adds back to CTA, such as the CTA possessing a cumyl R group.[46] These results indicate that the cyclocopolymerizations of **M1** with MAn proceeded in a controlled manner via RAFT. In contrast, in the case of conventional radical polymerization, precipitation was observed from the copolymerization mixture after 5 min, yielding a cross-linked polymer. This significant difference in the polymers obtained indicates that the slower propagation in the presence of CTA favors the selective cyclopolymerization process. If the efficiency of the cyclization were low, the number of the propagating ends per polymer chain would have increased by branching as the polymerization progressed. The polymer obtained did not contain any double bond moiety, as confirmed by ^{1}H NMR, which also supports the good selectivity of the cyclocopolymerization.

We also examined the interplay between the structure and the thermal properties of copolymers by TGA. The T_d decreases with increasing ring size and with decreasing ring rigidity (Table 1). In other words, a smaller ring size and a more rigid ring both lead to an increased stability of the copolymers.

Formation of Inclusion Complexes. The interaction between crown ether cavities and organic ammonium salts (**S1**) can help to establish the relative ring sizes and can be monitored by ^{1}H NMR spectroscopy as reported previously.[38,47,48] The ^{1}H NMR spectra were recorded after mixing **S1** and a copolymer sample for 30 min (Figure 4). No chemical shift change can be observed when **P5** is mixed with **S1**. When another copolymer **P3** with a larger ring on the chain is mixed with **S1**, the ^{1}H NMR spectra reveals that the characteristic peaks of H_a and H_b of the methylene group of **S1** shifts upfield from 4.11 and 2.94 ppm to 3.91 and 2.78 ppm, respectively. A portion of the proton signals of the crown ether units also shifts upfield from 3.55 to 3.33 ppm. These results suggest that the dialkylammonium ions are encircled by the crown ether cavities on the polymer backbone and that the match of ring size with the organic ammonium ion is crucial in the formation of inclusion complexes.

CONCLUSION

The cyclocopolymerizations of difunctional styrenic flexible monomers with MAn have been successfully carried out in high yield. The expected ratio of difunctional styrenic monomers to MAn in the ^{1}H NMR spectra of the resultant polymers, the MALDI-TOF mass spectrometric results, and their solubility in common organic solvents all indicate the formation of crown ether cavity-containing cyclocopolymers on the main chain. This cyclocopolymerization strategy provides a favorable condition to obtain alternating copolymers in high yields even in high dilution and without cross-linking products. The crown ether cavities in the copolymers exhibited a selective recognition for certain dialkylammonium ions and may be useful for other size selective complexations. This method leads a new path for cyclocopolymerization. In addition, the MAn moiety may be easily transformed into other functional groups, which is a subject of further studies.

ASSOCIATED CONTENT

Supporting Information. Figures showing IR, NMR, and MALDI-TOF mass spectra and TGA curves of the copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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