Synthesis of Cyclic Polymers and Block Copolymers by Monomer Insertion into Cyclic Initiator by a Radical Mechanism

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ABSTRACT: Cyclic poly(methyl acrylate) with controlled ring size and narrow ring size distribution was successfully prepared by the ^{60}Co γ-ray-induced polymerization of methyl acrylate at −30 °C in the presence of cyclic initiator **3**. GPC, ^{1}H NMR, and MALDI−TOF confirmed the cyclic structure of the obtained polymers. With the same method and using cyclic PMA as macroinitiator instead of cyclic initiator **3**, amphiphilic cyclic block copolymers poly(*N*-isopropylacrylamide-*b*-methyl acrylate-*b*-*N*-isopropylacrylamide)s were obtained. The structures and compositions of the block copolymers obtained were investigated by GPC and NMR measurements. The living nature of the polymerization was supported by the linear evolution of molecular weight with conversion, constant concentration of chain radicals, and narrow molecular weight distribution. Thus, ring sizes and narrow distribution of cyclic polymers and cyclic block copolymers can be controlled.

Introduction

Cyclic polymers have novel properties different from their corresponding linear polymers.[1−6] Compared to other polymers with special architectures, such as star polymers, hyperbranched polymers, and dendrimes, the synthetic routes to cyclic polymers are less investigated. Cyclic oligomers have been known as minor byproducts in step-growth polymerizations due to ring−chain equilibrium reactions[7] and also in ring-opening polymerizations through backbiting reactions.[8,9] A series of cyclic oligo(alkylidene isophthalate)s have been prepared by the cyclo-depolymerization of the corresponding linear polymers in the presence of appropriate metal catalysts.[10−13] Colquhoun and co-workers[14] developed this method to prepare cyclic poly(ether sulfone)s containing from eight to at least 60 aromatic rings. Another method for preparation of cyclic polymers is through end-to-end ring closure reactions of linear polymer precursors in very low concentration.[15−18] Recently, this method is improved greatly.[19−21] Ishizu et al. synthesized cyclic poly(oxyethylene)s by Williamson etherification.[19] Tezuka et al.[20] suggested a remarkably efficient polymer cyclization method in which bifunctional poly(tetrahydrofuran)s (poly(THF)s) with terminal pyrrolidinium salt groups carrying dicarboxylate counteranions were prepared by an electrostatic self-assembly and covalent fixation strategy. Subsequent heat treatment of this ionic polymer precursors afforded cyclic poly(THF)s. Lepoittain et al.[21] prepared ring-shaped polystyrenes (PSt) by coupling two-end living PSt dianions precursor with 1,3-bis(1-phenylethylenyl)benzene (DDPE). To enhance the intramolecular over intermolecular reactions, Deffieux et al.[22,23] synthesized linear α-A and ω-B heterodifunctional polymers, and then intramolecular end-to-end cyclization reactions were performed under high dilution. All of these preparations are based on coupling reactions of telechelomers in dilute solution. Incomplete cyclizations or undesirable side reactions are common for the preparations; therefore, elaborate purification procedures are required to remove the acyclic contaminant. In addition, it is difficult to prepare the amphiphilic cyclic block copolymers using the coupling method. When they are prepared by end-to-end ring closure reaction of amphiphilic diblock copolymers, it may be difficult for two end groups to encounter each other due to the incompatibility of the two blocks. Therefore, the synthesis of cyclic polymers and block copolymers with narrow ring size distribution and controlled ring size and structure is exceedingly challenging.

Recently, a new synthetic route to cyclic polyethylenes has been developed, in which methylene groups were repetitively inserted into the carbon−boron bond[24] or the ends of growing polymer chains remain attached to a metal complex throughout the entire polymerization process.[25] However, these methods cannot be applied in the polymerization of conventional monomers, such as styrene (St) and methyl (meth)acrylates. In this paper, we report a new synthetic strategy for the synthesis of cyclic polymers and block copolymers by monomer insertion into a cyclic initiator, and the cyclic poly(methyl acrylate) (PMA) and cyclic triblock copolymer have been synthesized.

Experimental Section

Materials. *o*-Bromophenol (The First Shanghai Chemical Reagent Plant, >99%), 1,4-dibromobutane (Shanghai Chemical Reagent Co., 99.5%), and α,α′-dibromo-*p*-xylene (ACROS Organics) were used as received. Tetrahydrofuran (THF) was refluxed for 24 h over sodium and distilled prior to use. MA (Shanghai Chemical Reagent Co.) was dried over CaH_2 and distilled under reduced pressure prior to use. *N*-Isopropylacrylamide (NIPAAM, Kohjin Chemical Co. Ltd.) was recrystallized from the mixture of cyclohexane and benzene (65/35, v/v) and dried. All other reagents were of analytical grade and used as received.

Synthesis of 1,4-Bis(*o*-bromophenoxy)butane (1). Into a solution of *o*-bromophenol (20.76 g, 0.12 mol) in acetone (100 mL), K_2CO_3 (20.7 g, 0.15 mol) was added, and the mixture was stirred under a nitrogen atmosphere for 1 h. Then 1,4-dibromobutane (21.6 g, 0.1 mol) was dropped. The mixture was stirred at refluxing temperature for another 16 h and then

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cooled to room temperature. After most of acetone added was removed, CH_2Cl_2 (30 mL) and water (50 mL) were added. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 three times (3 × 20 mL). The combined extracts were washed with distilled water until neutral and then dried over anhydrous magnesium sulfate overnight. After the solvent was removed under reduced pressure, the crude product was recrystallized from benzene, and then the pure product was obtained as white crystal (34.5 g, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ (TMS, ppm): 1.8 (4H, 2 OCH_2CH_2); 3.9 (4H, 2 OCH_2CH_2); 7.0−7.4 (aromatic protons).

Synthesis of Cyclic Initiator 3. The Grignard reagent of dibromide **1** was prepared according to the method described in ref 26. Magnesium (0.33 g, 13.6 mmol) in a 250 mL three-necked flask was "activated" by purging purified nitrogen while stirring, until the magnesium became gray-black in color. Then THF (200 mL) was added, and compound **1** (2.727 g, 6.82 mmol) in THF (8 mL) was dropwise added in 1 h. The mixture was warmed to 40 °C. Into the reaction mixture, carbon disulfide (1.216 g, 16 mmol) was added in 30 min. After being maintained at 40 °C for 4 h, α,α′-dibromo-*p*-xylene (1.8 g, 6.82 mmol) in THF (8 mL) was added slowly in 1 h. The temperature was raised to 50 °C and maintained at this temperature for 2 days. Ice water was added, the organic layer was separated, and the water phase was extracted with diethyl ether (total 500 mL). The extracts and organic phase were combined, washed with water until neutral, and dried over anhydrous magnesium sulfate. After removal of solvent, the residue was purified on a silica column with dichloromethane/petroleum ether (30−60 °C) (v/v) as eluent. The cyclic initiator **3** was obtained as red solid (1.94 g, 57.6% yield); mp 91.7 °C (DSC measurement). ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 6.87−6.97, 7.24−7.36 (8H, aromatic Hs), 4.68 (4H, 2S−CH_2), 3.92 (4H, 2O−CH_2), 1.74 (4H, C−CH_2CH_2−C). Mass spectrum for $C_{26}H_{24}O_2S_4$: 496.0660 (26.37, 496.0659), 360.0300 (25.47), 328.0609 (22.32), 264.1145 (41.91), 221.0586 (14.33), 189.0406 (26.15), 137.0058 (100), 108.0042 (35.61), 104.0638 (25.30).

Polymerization of MA. The polymerization was carried out in sealed tubes. The general synthetic procedure is as follows. MA (0.8 g, 9.3 mmol), **3** (0.04 g, 0.08 mmol), and THF (8 mL) were added into a 10 mL glass tube. After the mixture was degassed by three freeze−evacuate−thaw cycles, the tube was sealed under vacuum and then subjected to ^{60}Co γ-irradiation at 80 Gy/min for 4 h. The tube was opened, and the polymer was precipitated by pouring a polymer solution in THF into excess petroleum ether (30−60°C) while stirring, obtained by filtration, and then dried in a vacuum at room temperature overnight. The cyclic PMA was obtained in 52% with $M_{n,NMR}$ = 5730 and M_w/M_n = 1.32. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.35−7.18, 6.84 (aromatic Hs), 4.85 (S−C*H*−COOMe), 3.90 (Ph−O−CH_2−), 3.62 (COOCH_3), 2.71 (Ph−CH_2−), 2.35 (−C*H*−COOMe), 2.12−1.35 (PhO−C−CH_2CH_2−C−OPh, −CH_2− in main chain).

Block Copolymerization of NIPAAM. Into a 10 mL glass tube, the cyclic macroinitiator PMA ($M_{n,NMR}$ = 5730, 0.278 g, 0.0485 mmol), NIPAAM (0.5 g, 4.42 mmol), and THF (4 mL) were added. The tube was sealed under vacuum after three freeze−evacuate−thaw cycles and subjected to ^{60}Co γ-irradiation at 80 Gy/min for 4 h. The final polymer was obtained by pouring the reaction mixture into excess petroleum ether (30−60 °C) while stirring and dried in a vacuum overnight. The cyclic PMA-*b*-PNIPAAM was obtained in 38% yield with $M_{n,NMR}$ = 9600 and M_w/M_n = 1.34. $(MA)_{67}$-*b*-$(NIPAAM)_{34}$. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.37−6.9 (aromatic Hs), 6.38−5.6 (N*H*), 4.79 (S−C*H*-CO), 4.04 (N−C*H*(Me_2)), 3.80 (Ph−O−CH_2), 3.65 (COOCH_3), 2.70 (Ph−CH_2−), 2.31(−C*H*−COOMe, −C*H*−CON−), 2.11−1.41 (PhO−C−CH_2CH_2−C−OPh, −CH_2− in main chain), 1.14 (CH_3 in NIPAM).

Characterization. ^{1}H NMR spectra were measured on a Bruker DMX-500 nuclear magnetic resonance instrument with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. The molecular weight and polydispersity indexes were determined on a Waters 150C gel permeation chromatograph (GPC) equipped with Ultrastyragel columns (500, 10^3, 10^4 Å) at 30 °C, using monodisperse polystyrene as calibration standard. THF was used as eluent at a flow rate of 1.0 mL/min. MALDI−TOF mass spectra of PMA were performed on a Bruker BIFLEX III equipped with a nitrogen laser (337 nm). The accelerating potential is 20 kV. Matrix (20 mg, 2,5-dihydroxybenzoic acid) and 1 mg of PMA were dissolved in 0.5 mL of THF. A 1 mL portion of the solution was deposited onto the sample target and allowed to dry in air at room temperature. Internal standards (peptide derivatives) were used to calibrate molecular weight.

Results and Discussion

Formation of Cyclic Polymers and Polymerization Mechanism. As we mentioned, the cyclic polyethylenes were prepared by repetitive methylene insertions into the carbon−boron bond of *B*-thexylborocane.[24] In this paper, we also prepare cyclic polymers by monomer insertion into a cyclic initiator. As shown in Scheme 1, using heat, UV, or γ-ray irradiations, the cyclic initiator is homolytically split into active and stable radicals. The former radical initiates the polymerization of monomer, forming propagating radical. In a local medium, the active chain radical propagates or terminates with the original stable radical, and they are competition reactions. When the propagation reaction is too fast, it is difficult for the propagating radical to react with the original stable radical because they diffuse apart. Fortunately, it will not occur because the rate constant (k_t) for termination is 10^2−10^6 times that (k_p) for propagation (generally, $k_p = 10^2$−10^4 and $k_t = 10^6$−10^8 L/(mol s); for methyl acrylate, $k_p = 2.09 \times 10^3$ and $k_t = 0.95 \times 10^7$ L/(mol s)).[27] Therefore, after the propagating radical reacts with several monomers, the propagating chain will reversibly terminate with the original stable radical. When the cyclic chain conformation is adjusted, this process will repeat again until a cyclic polymer with predetermined ring size is formed. Each initiating site has the same possibility to homolytically split, propagate, and terminate; thus, the ring size and its distribution can be controlled.

Although we have no ideas for designing a cyclic initiator for atom transfer radical polymerization (ATRP), we can design the cyclic initiator for nitroxide-mediated radical polymerization. Unfortunately, the polymers with complicated structure were obtained. Probably, the active and stable radicals, which are produced from homolytical decomposition of the cyclic initiator, diffuse thermally too fast. As a result, the reversible termination reaction with the original stable radical is impossible to occur. Obviously, decreasing the reaction temperature is necessary for reducing the diffusion rate and for suppressing the side reactions, such as chain-transfer reactions. Therefore, we synthesize the cyclic initiator **3** according to Scheme 2 and used it in the polymerization of MA at −30 °C under ^{60}Co irradiation, since γ-ray-induced polymerization is easier to operate at low temperature than with UV irradiation. For comparison, a polymerization was also carried out at 30 °C. The conditions and results are listed in Table 1. Considering the low active energy (29.7 kJ/mol) of propagation reaction of MA,[27] it is reasonable that the yields of polymers prepared at −30 °C are not much lower than those at 30 °C (see PMA1, PMA6, PMA3, and PMA7 in Table 1).

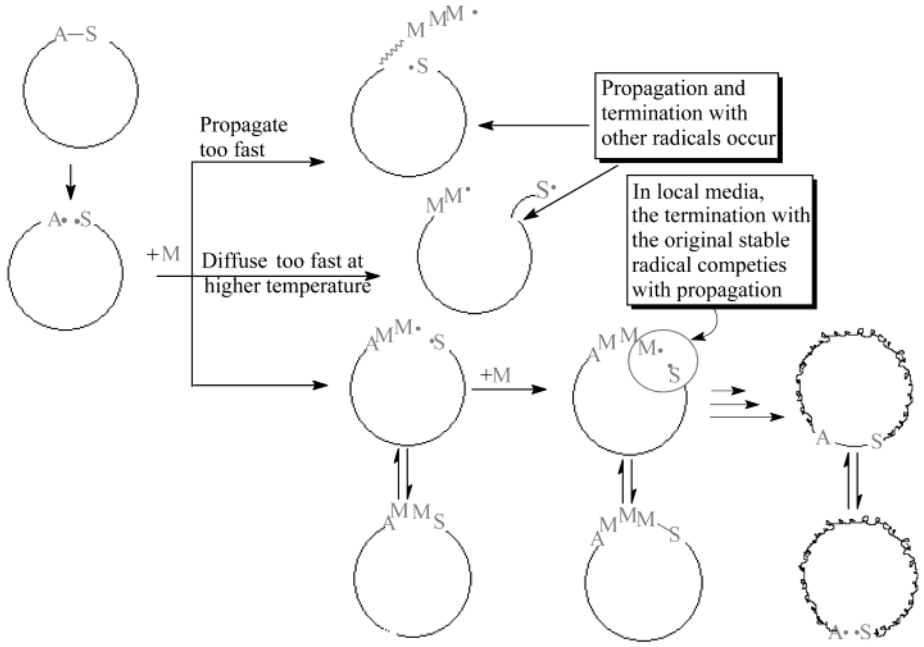
Characterization of the Cyclic Polymers. For determining cyclic structure of the polymers prepared

Table 1. Conditions and Results of γ-ray-Induced Polymerizations of MA Using Cyclic Initiator 3[a]

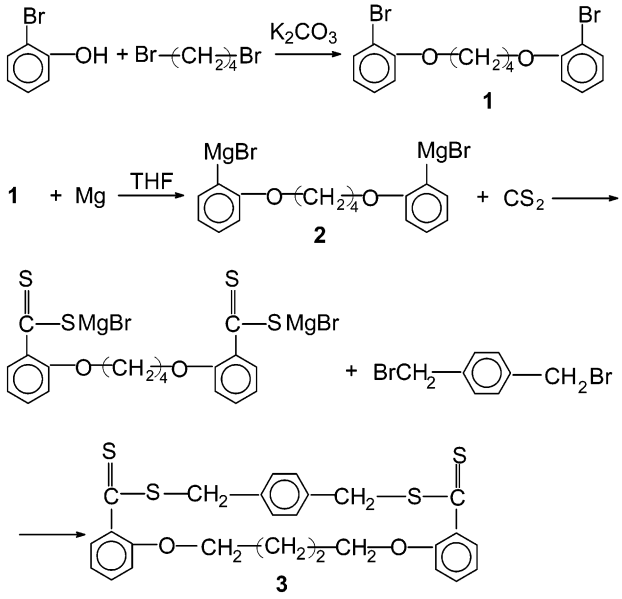
no.	temp (°C)	time (h)	yield [b] (%)	$M_{n,th}$[c] $\times 10^{-3}$	$M_{n,NMR}$[d] $\times 10^{-3}$	$M_{n,GPC}$[e] $\times 10^{-3}$	M_w/M_n[e]
PMA 1	−30	1	14	1.89	1.84	1.3	1.32
PMA 2	−30	2	30	3.53	3.55	2.7	1.30
PMA 3	−30	4	52	5.64	5.73	4.3	1.32
PMA 4	−30	6	66	7.11	7.19	5.4	1.31
PMA 5	−30	8	77	8.13	8.22	6.1	1.33
PMA 6	30	1	16				
PMA 7	30	4	59				

[a] Polymerization conditions: [MA]/[**3**] = 116/1 (molar ratio), MA: 0.8 g; dose rate = 80 Gy/min. [b] Calculated by weight method. [c] $M_{n,th}$ = conv × ($[M]_0/[I]_0$) × 86 + 496, where $[M]_0$ and $[I]_0$ are the initial molar concentrations of MA and **3**; 86 and 496 are the molecular weights of MA and **3**, respectively. [d] Calculated by eq 1. [e] Determined by GPC relative to polystyrene.

Scheme 1



Scheme 2



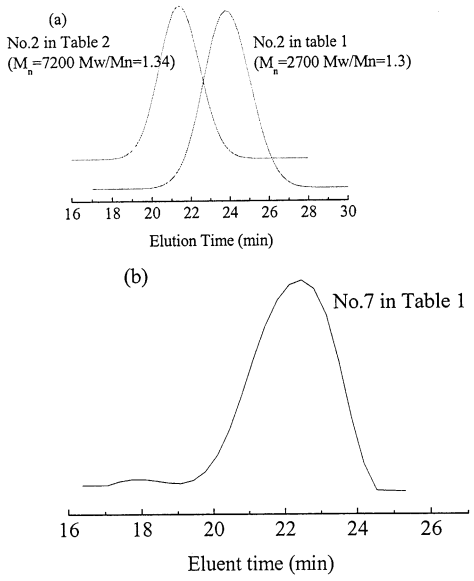
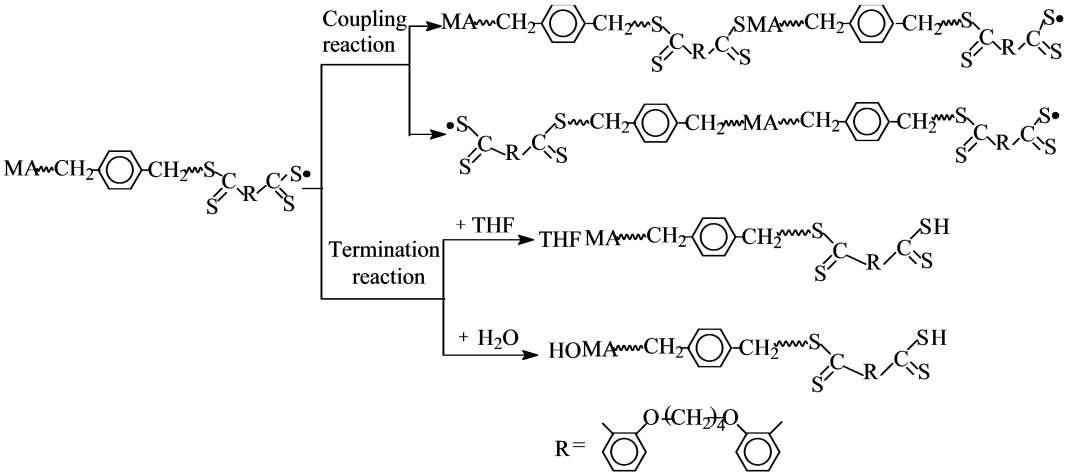


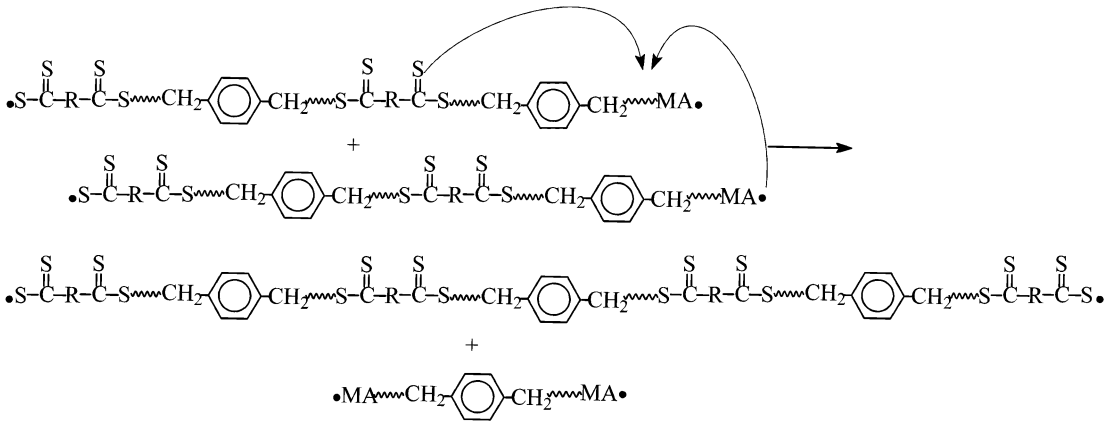
Figure 1. GPC curves of (a) cyclic PMA prepared at −30 °C (no. 2 in Table 1) and cyclic triblock copolymer, PNIPAAM-*b*-PMA-*b*-PNIPAAM, prepared at −30 °C (no. 2 in Table 2); (b) the PMA prepared at 30 °C (no. 7 in Table 1).

at −30 °C, their GPC traces were measured, and one typical GPC curve of PMA prepared at −30 °C is shown in Figure 1a. In principle, a single and symmetrical peak indicates that the polymerization proceeds via one polymerization mechanism. On the basis of our previous investigations, [28−31] under ^{60}Co irradiation, the weak bond, C−S bond, in cyclic initiator **3** undergoes homolytical cleavage to form benzyl radical and a stable sulfur radical. The former radical initiates the polymerization, forming the propagation chain, which terminates with the original stable sulfur radical. The polymerization continues to form cyclic polymers. If the

Scheme 3



Scheme 4



propagating radical is far from the original stable sulfur radical, coupling reactions and/or termination reactions with impurities in the polymerization system may compete to form a linear polymer, as shown in Scheme 3.

When considering the chain-transfer reactions with thiocarbonate group, as shown in Scheme 4, the polydispersity index of the polymers obtained will become broader as the conversion increases because the transfer reaction of one propagating radical with one cyclic will form one chain containing more than one initiator residue. Further chain transfer reactions will produce polymers with quite different molecular weights. The higher the conversion, the higher the molecular weight of the polymer obtained. The polydispersity index of the polymers obtained from the chain-transfer reactions becomes broader. The data listed in Table 1 show that the molecular weight distributions remain low and almost constant with increasing conversion. Thus, the chain-transfer reactions shown in Scheme 4 are negligible for the polymerization at −30 °C.

Although the linear polymerization may not produce the polymer with narrow molecular weight distribution (Scheme 3), its GPC curve may also show one single, symmetric peak. To identify which mechanism occurred for the polymerization at −30 °C, we carried out the polymerization at 30 °C since increasing the temperature will increase the diffusion rate of the radicals and favor the formation of linear polymers. The GPC curve of the polymers obtained at 30 °C in Figure 1b shows a large broad peak and a small peak. This is consistent with the polymers formed at −30 °C being cyclic because increasing the temperature will enhance the linear polymerization rate, forming more linear polymers.

For determining further the cyclic structure of the polymer, ^{1}H NMR spectra of the cyclic PMA were measured, and a typical spectrum is shown in Figure 2b. Except for characteristic peaks of PMA: δ = 1.4−1.9 (a), 2.3 (b), and 3.6 (c), the signal at δ = 4.8 (d) corresponds the methine proton of MA unit next to sulfur, the peak of the methlyene protons between benzene and the sulfur groups at δ = 4.7 in Figure 2a is completely disappeared, and moves to δ = 2.74 (f) in Figure 2b. This suggests that all the cyclic initiator **3** participated in the initiation. In addition, the signal appeared at δ = 3.9 (e) indicates the existence of methylene groups next to ether oxygen in the **3** unit. The integration ratio of the peaks at δ = 4.8, 3.9, and 2.74 is 1/2/2, which is a strong evidence to support that the cyclic initiator is completely transferred to the polymer. Comparison with the ^{1}H NMR spectrum of the PMA prepared at 30 °C in Figure 2C, the small signals at δ = 4.06 and 4.22 may represent two terminal methine protons respectively next to alkoxy and hydroxyl groups; other small signals at δ = 4.66, 5.29, and 5.90 are not clear now. All these signals must be related to the ring opening of cyclic PMA to form linear polymers. Assuming that each cyclic polymer contains one cyclic initiator unit, the number-average molecular

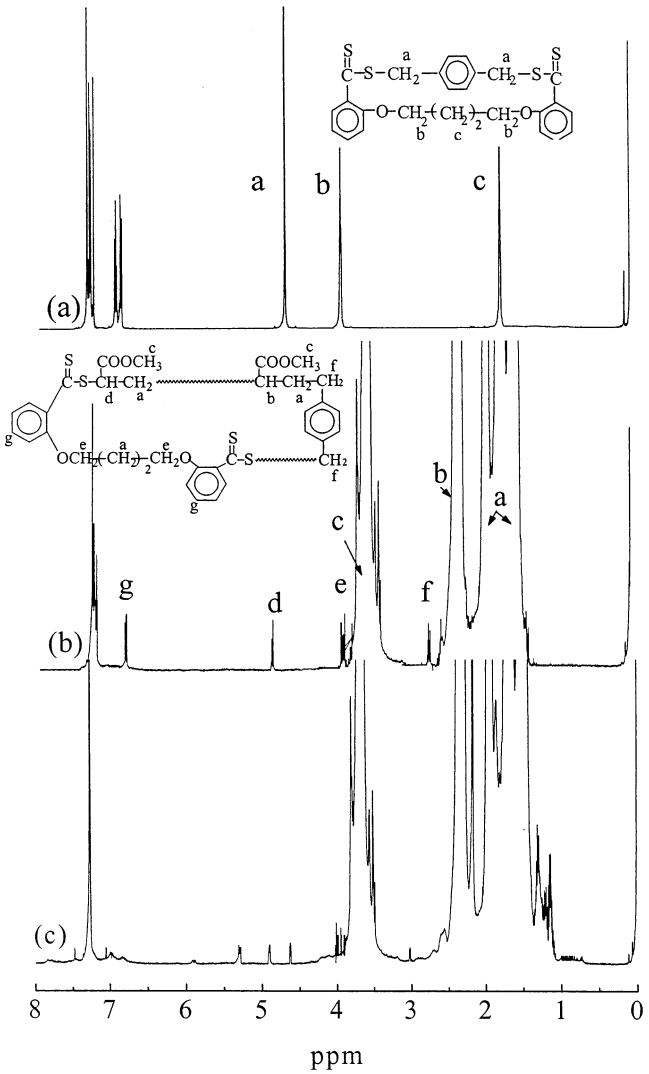


Figure 2. ^{1}H NMR spectra of (a) cyclic initiator **3**, (b) cyclic PMA (no. 1 in Table 1), and (c) cyclic PNIPAAM-*b*-PMA-*b*-PNIPAAM.

weight, $M_{n,NMR}$, can be calculated according to eq 1

$$M_{n,NMR} = [(I_{3.6}/3)/(I_{4.8}/2)] \times 86 + 496 \qquad (1)$$

where $I_{3.6}$ and $I_{4.8}$ are the integral values of the peaks at $\delta = 3.6$ and 4.8; 86 and 496 are the molecular weights of MA and **3**, respectively. The $M_{n,NMR}$s of the polymers obtained were calculated and are listed in Table 1. The data listed in Table 1 demonstrate good agreement of $M_{n,NMR}$s with theoretical number-average molecular weight $M_{n,th}$, which cannot be resulted from linear polymerization (see Scheme 3). In addition, it is reasonable that $M_{n,GPC}$ are lower than $M_{n,NMR}$ or $M_{n,th}$ (Table 1) because the cyclic polymers have more compact structure in comparison with the corresponding linear polymers having similar molecular weight. This is another evidence of cyclic polymers formed.

A powerful evidence confirms that the polymers formed at −30 °C is their MALDI−TOF mass spectra. If the polymerization proceeds via monomer insertion into cyclic initiator, the cyclic polymers obtained contain only one cyclic initiator **3** unit. When the propagation radical is far from the original sulfur radical, the linear polymerization will occur; the resulting product should have end groups except cyclic initiator **3**. Figure 3 is

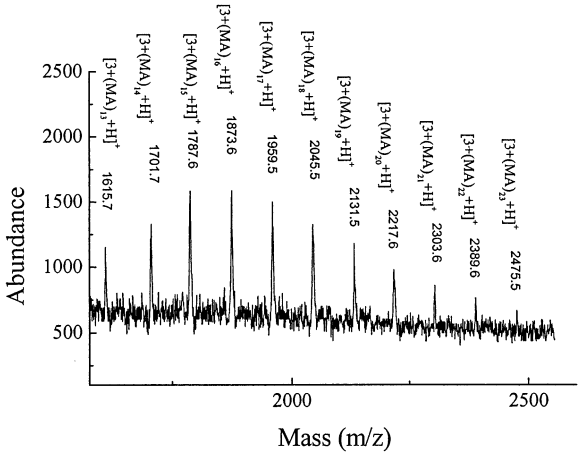


Figure 3. MALDI−TOF mass spectrum of cyclic PMA prepared by γ-ray-induced polymerization of MA in the presence of cyclic initiator **3** at −30 °C (no. 1 in Table 1). The molecular weight of each peak, $M_n = 496 + (n \times 86) + 1$, where 496 and 86 are molecular weights of cyclic initiator and MA, 1 is the atomic weight of H^+, and n is the degree of polymerization.

the MALDI−TOF mass spectrum of PMA1 (PMA1 in Table 1) and shows only one distribution consisting of a number of peaks with a peak-to-peak mass increase of 86 g mol^{-1}, which corresponds to the molecular weight of MA unit. This distribution could be assigned to the cyclic structure of PMA: [**3**-(MA)$_n$-H]$^+$, in which **3** and MA are cyclic initiator **3** and MA unit, respectively, and n is the degree of polymerization. The molecular weight of each peak can be calculated according to $M_n = 496 + (n \times 86) + 1$. The calculated values agree well with the corresponding experimental values, indicating that the polymer contains only one cyclic initiator **3** unit. Therefore, the pure cyclic PMA is ready formed. As we mentioned, raising the temperature will increase the diffusion rate of chain radicals, leading to the formation of linear polymers. As a comparison, the γ-ray-induced polymerization of MA was performed at 30 °C for 1 h, and the typical MALDI−TOF MS of the polymer obtained is shown in Figure 4. There are at least three distributions: one is assigned as cyclic PMA, [**3**-(MA)$_n$-H]$^+$; another two correspond to two linear PMAs, [**3**-(MA)$_n$-THF-H]$^+$ and [**3**-(MA)$_n$-H$_2$O-H]$^+$, which must result from the termination reactions of linear propagation radicals with THF and H_2O, respectively. When comparing the linear PMA, **3**-(MA)$_n$-THF, the relative amount of **3**-(MA)$_n$-H$_2$O is very small because THF is a solvent of the polymerization, but H_2O is a small amount of impurity in the polymerization system.

To confirm that the ring size of the polymers obtained can be controlled and its distribution is narrow, it is important to study whether the polymerization is of "living" nature. The relationship between $\ln([M]_0/[M])$ and polymerization time at −30 °C is a straight line, as shown in Figure 5a, indicating constant concentration of propagating radicals during the polymerization. A linear evolution of M_n with conversion as shown in Figure 5b suggests that the molecular weight of cyclic PMA obtained can be controlled by the molar ratio of monomer/initiator in the feed and polymerization time. Further evidence for the "living" nature is the narrow molecular weight distribution (MWD) (Figure 5b) and the single and symmetric peak (Figure 1a).

Synthesis of Cyclic Triblock Copolymer, Poly-(NIPAAM-*b*-MA-*b*-NIPAAM). With the same procedures of synthesizing cyclic PMA, the cyclic poly-

Table 2. Conditions and Results of Block Copolymerization of NIPAAM under ^{60}Co γ-ray Irradiation at −30 °C Using PMA3 as Macrocyclic Initiator[a]

no.	time (h)	yields[b] (%)	$M_{n,th(copolymer)}$[c] $\times 10^{-3}$	$M_{n,NMR(copolymer)}$[d] $\times 10^{-3}$	$M_{n,GPC(copolymer)}$[e] $\times 10^{-3}$	M_w/M_n[e]
1	2	21	7.86	7.9	5.8	1.33
2	4	38	9.57	9.6	7.2	1.34
3	6	51	10.9	11.0	7.9	1.33
4	8	61	12.0	12.1	8.6	1.35
5	12	76	13.5	13.6	9.5	1.34

[a] [NIPAAM]/[PMA3] = 100 (molar ratio); NIPAAM = 1 g, polymerization temperature: −30 °C; dose rate = 80 Gy/min. [b] Calculated with the gravimetrical method. [c] Calculated based on $M_{n,th(copolymer)}$ = conversion × ($[M]_0/[I]_0$) × 103 + 5730, where $[M]_0$ and $[I]_0$ are the initial concentrations of NIPAAM and macrocyclic initiator PMA3; 103 and 5730 are the molecular weights of NIPAAM and PMA3, respectively. [d] The $M_{n,NMR(copolymer)}$s were calculated by equation $M_{n,NMR(copolymer)} = [I_{4.1}/(I_{4.8}/2)] \times 103 + 5730$, where $I_{4.1}$ and $I_{4.8}$ are integral values of peaks at δ = 4.1 and 4.8, respectively. [e] Determined by GPC instrument.

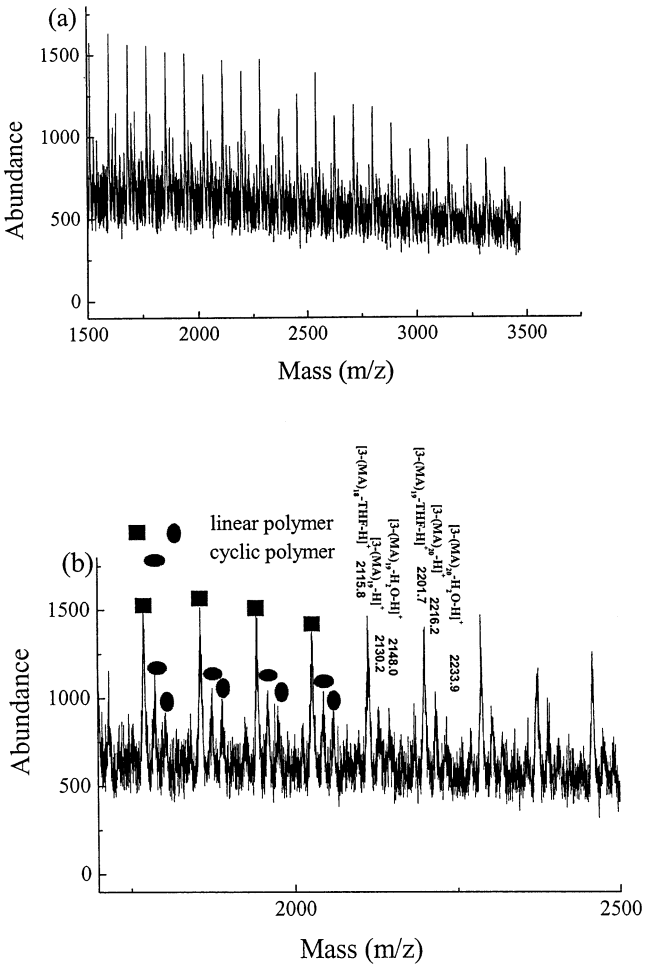


Figure 4. MALDI−TOF mass spectrum of PMA prepared by γ-ray-induced polymerization of MA in the presence of cyclic initiator **3** at 30 °C (no. 6 in Table 1) Full scan (a). Part of full scan (b). Cyclic PMA, horizontal oval: molecular weight of each peak $M_n = 496 + (n \times 86) + 1$; linear polymer, square: $M_n = 496 + (n \times 86) + 72 + 1$, where 72 is molecular weight of THF; vertical oval: $M_n = 496 + (n \times 86) + 18 + 1$, where 18 is the molecular weight of H_2O.

(NIPAAM-*b*-MA-*b*-NIPAAM) was prepared at −30 °C using macrocyclic PMA as initiator instead of cyclic initiator **3**. The results and conditions are listed in Table 2.

For confirming the formation of triblock copolymers, their ^{1}H NMR spectra were measured, and a typical spectrum is shown in Figure 6. The characteristic peaks of PNIPAAM can be observed. The signal at δ = 1.1 (a) is ascribed to the methyl protons, the signal at δ = 4.1 (b) belongs to the methine proton next to nitrogen, and the broad peak at δ = 5.8−6.5 (c) corresponds to N−H. The signal of ester methyl in the PMA unit appears at

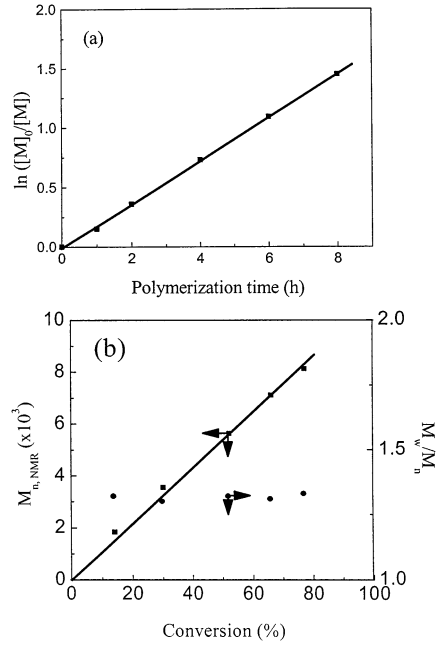


Figure 5. Relationship of ln($[M]_0/[M]$) vs polymerization time (a) and M_n vs conversion (b) for polymerization of MA under ^{60}Co irradiation at −30 °C in the presence of cyclic initiator **3**.

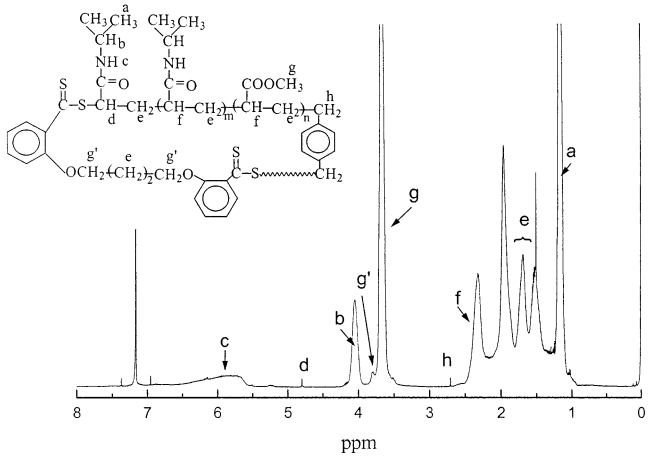


Figure 6. ^{1}H NMR spectrum of poly(NIPAAM-*b*-MA-*b*-NIPAAM) (no. 2 in Table 2).

δ = 3.6 (g). These facts evidence the formation of triblock copolymers. The signals at δ = 4.8 (d) and 2.74 (h) correspond to the methine proton next to sulfur and methylene protons adjacent to the phenyl group from initiator **3**, respectively, and their integral ratio is 1/2. This indicates that all the cyclic initiator **3** residues were transferred into the block copolymers. The number-average molecular weight $M_{n,NMR}$ of PNIPAAM block could be calculated on the basis of the integration ratio

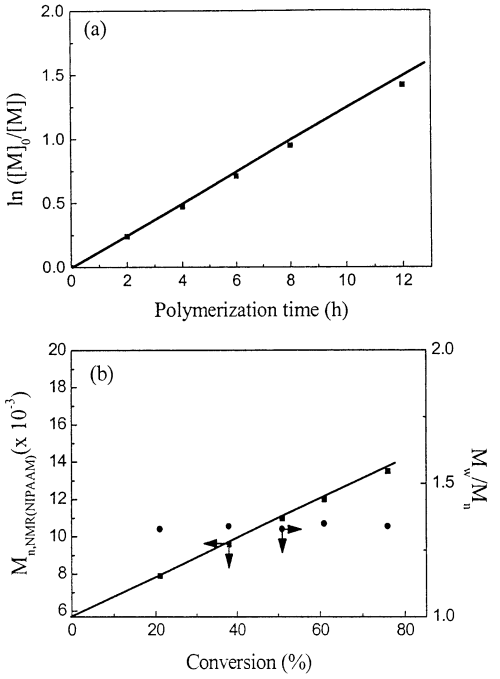


Figure 7. Relationship of $\ln([M]_0/[M])$ vs polymerization time (a) and M_n vs conversion (b) for block copolymerization of NIPAAM under ^{60}Co irradiation at −30 °C using PMA3 as macrocyclic initiator.

of the peak at $\delta = 4.1$ to that at $\delta = 4.8$. The results are listed in Table 2. The lower value of $M_{n,GPC}$ (copolymer) than that of $M_{n,NMR}$ for the block copolymers is an evidence that the triblock copolymers obtained are cyclic, since cyclic polymers have compact structure in comparison with the corresponding linear polymers.

The formation of cyclic polymers can be further confirmed by the method similar to that of identifying the cyclic PMA with GPC measurements. A typical GPC curve of the block copolymer obtained at −30 °C is shown in Figure 2a (no. 2 in Table 1) and demonstrates a single and symmetrical peak. This might be resulted from the cyclic polymerization.

The block copolymerization also shows the living nature, which is supported by the following evidence: the linear relationship between the polymerization time and $\ln([M]_0/[M])$ (Figure 7a); the linear increase of $M_{n,NIPAAM}$ with the increasing NIPAAM conversion (Figure 7b); the relatively low polydispersity indexes ($M_w/M_n \sim 1.34$). Thus, the ring size of the polymer obtained can be controlled by monomer conversion. The narrow distribution of polymer ring size might be obtained.

The mechanism of the controlled cyclic block copolymerization at −30 °C using the macrocyclic PMA initiator under ^{60}Co γ-irradiation is similar to that of the homopolymerization of MA under the same conditions; the key point for the synthesis of cyclic block copolymers is reducing the diffusion rate, which can be achieved by lowering temperature.

Conclusion

The γ-ray-induced radical polymerization of MA at −30 °C using cyclic initiator **3** yielded pure cyclic PMA without specific purification procedure. The triblock copolymers, PNIPAAM−PMA−PNIPAAM, were successfully synthesized by the controlled γ-ray-induced radical polymerization of NIPAAM with macrocyclic PMA as initiator. The key point for preparing cyclic polymers is the reduced diffusion rate, which we obtained at lower polymerization temperature, such as −30 °C. The polymerization is proposed via repetitive monomer insertion into the cyclic initiator. The γ-ray-induced homopolymerization of MA in the presence of cyclic initiator **3** and the block copolymerization of NIPAAM with macrocyclic initiator are of "living" nature. The ring size of cyclic polymers and block copolymers can be controlled by the initial molar ratio of monomer to initiator and polymerization time. The ring size distribution is narrow.

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References and Notes

(1) Gan, Y.; Dong, D.; Carlotti, S.; Hogen-Esch, T. E. *J. Am. Chem. Soc.* **2000**, *122*, 2130.
(2) Cooke, J.; Viras, K.; Yu, G. E.; Yonemitsu, T.; Ryan, A. J.; Price, C.; Booth, C. *Macromolecules* **1998**, *31*, 3030.
(3) Kusmartssev, F. V. *Phys. Rev.* **1992**, *46*, 7674.
(4) Iwata, K. *Macromolecules* **1985**, *18*, 115.
(5) Cherayil, B. J.; Bwendi, M. G.; Miyake, A.; Freed, K. F. *Macromolecules* **1986**, *19*, 2770.
(6) Di Marzio, E. D. *Macromolecules* **1993**, *26*, 4613.
(7) Fawcett, A. H.; Mee, R. A. W.; McBride, F. W. *Macromolecules* **1995**, *28*, 1481.
(8) Clarkson, S. J.; Semlyen, J. A.; Horska, J.; Stepto, R. F. T. *Polymer* **1986**, *27*, 31.
(9) Sigwalt, P.; Masure, M.; Moreau, M.; Bischoff, R. *Macromol. Chem. Rapid Commun.* **1993**, *73*, 147.
(10) Hall, A. J.; Hodge, P.; McGrail, C. S.; Rickerby, J. *Polymer* **2000**, *41*, 1239.
(11) Bryant, J. J. L.; Semlyen, J. A. *Polymer* **1996**, *38* 2475.
(12) Hamilton, S. C.; Semlyen, J. A.; Haddleton, D. M. *Polymer* **1998**, *39*, 3241.
(13) Hubbard, P. A.; Brittain, W. J.; Mattice, W. L.; Brunelle, D. J. *Macromolecules* **1998**, *31*, 1518.
(14) Colquhoun, H. M.; Lewis, D. F.; Hodge, P.; Ben-Haida, A.; Williams, D. J.; Baxter, I. *Macromolecules* **2002**, *35*, 6875.
(15) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843.
(16) Ohtani, H.; Kotsuji, H.; Momose, H.; Matsushita, Y.; Noda, I.; Tsuge, S. *Macromolecules* **1999**, *32*, 6541.
(17) Iatrou, H.; Hadjichristidis, N. *Polym. Prepr.* **1999**, *40*, 1059.
(18) Gan, Y. D.; Zöller, J.; Yin, R.; Hogen-Esch, T. E. *Macromol. Symp.* **1994**, *77*, 93.
(19) Ishizu, K.; Akiyama, Y. *Polymer* **1997**, *38*, 491.
(20) Oike, H.; Mouri, T.; Tezuka, Y. *Macromolecules* **2001**, *34*, 6592.
(21) Lepoittevin, B.; Douges, M. A.; Masure, M.; Hemery, P.; Baran, K.; Cranail, H. *Macromolecules* **2000**, *33*, 8218.
(22) Rique-Lurbet, L.; Schappacher, M.; Deffieux, A. *Macromolecules* **1994**, *27*, 6318.
(23) Deffieux, A.; Schappacher, M.; Rique-Lurbet, L. *Polymer* **1994**, *35*, 4562.
(24) Shea, K. J.; Lee, S. Y.; Busch, B. B. *J. Org. Chem.* **1998**, *63*, 5746.
(25) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041.
(26) Moad, G.; Rizzardo, E.; Thang, S. H. PCT/US97/12540, 30.
(27) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley & Sons: New York, 1991; pp 274−275.
(28) Bai, R. K.; You, Y. Z.; Pan, C. Y. *Macromol. Rapid Commun.* **2001**, *22*, 315.
(29) You, Y. Z.; Bai, R. K.; Pan, C. Y. *Macromol. Chem. Phys.* **2001**, *202*, 1980.
(30) Bai, R. K.; You, Y. Z.; Zhong, P.; Pan, C. Y. *Macromol. Chem. Phys.* **2001**, *202*, 1970.
(31) Hong, C. Y.; You, Y. Z.; Bai, R. K.; Pan, C. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3934.

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