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A Straightforward Approach for the One-pot Synthesis of Cyclic Polymer from RAFT Polymer *via* Thiol-Michael Addition†

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Junfei Zhao, Yanyan Zhou, Yu Zhou, Nianchen Zhou, Xiangqiang Pan, Zhengbiao Zhang* and Xiulin Zhu

Cyclic polymer has aroused more research interests in recent years. However, the effective synthetic approach for cyclic polymer is still lack, and developing novel and effective approach for the synthesis of cyclic polymer is highly desirable. Herein, a straightforward approach for the effective synthesis of cyclic polymer is illustrated. First, reversible addition-fragmentation chain transfer (RAFT) polymerization was implemented by using chain transfer agent with furan-protected maleimide at R group. The linear precursor RAFT poly(methyl methacrylate) (PMMA) was then dissolved in solvent with highly dilute concentration and heated to 110 ^{o}C to de-protect the maleimide followed by aminolyzing thiocarbonylthio to thiol group at room temperature. Upon the release of thiol, simultaneous intramolecular ring closure *via* thiol-maleimide Michael addition happened to afford cyclic PMMA. The cyclic PMMA was subjected to SEC, NMR and MALDI-TOF mass spectroscopy, which provided convincing evidence for successful preparation. The yield of the cyclic PMMA reached to 80% without no purifications. The versatility of this one-pot approach was verified by using either a functional monomer or a trithiocarbonate as chain transfer agent. Interestingly, the linear RAFT polymer mediated by symmetric trithiocarbonate chain transfer agent produced cyclic polymer with half molecular weight due to its intrinsic mechanism. This work undoubtedly offered a novel and effective approach for synthesizing cyclic polymer. The preparations of other topological cyclic polymers are also envisioned by employing different structures of chain transfer agents through this approach.

Introduction

Comparing with their linear precursors, cyclic polymers have no chain ends and express as the ring topology. This unique topology often brings some different properties with respect to the linear ones, such as smaller hydrodynamic volume, increased glass transition temperature (T_g), higher density, lower intrinsic viscosity, lower translational friction coefficient, higher refractive index and slower hydrolytic degradation profiles.[1-5] During the past decade, increasing attentions have been paid to the cyclic polymer-related area. However, despite that the synthesis techniques for cyclic polymers have been explored and many clever methods have been developed, the effective synthesis of cyclic polymers still remains a challenging task for polymer chemists. Generally, the synthetic strategy of cyclic polymers contains two categories: the ring-expansion[6,7,8-13] and ring-closure strategies[14]. The latter is popularly used due to more accessible monomers and easier control over molecular weights and topologies of the linear precursors. The ring-closure method includes intermolecular and intramolecular reactions, wherein the linear precursors with high degree of chain end fidelity with excellent modifiability are prerequisites. Living anionic[15] and cationic polymerizations[7] enabled the synthesis of well-defined linear precursors with high chain end fidelity, which can undergo further chain end modifications toward reactive chain ends. Controlled radical polymerizations with more moderate polymerization conditions and more accessible monomers, such as atom transfer radical polymerization (ATRP) and RAFT polymerization, can also endow the polymers with highly active chain ends. Besides, the chemical

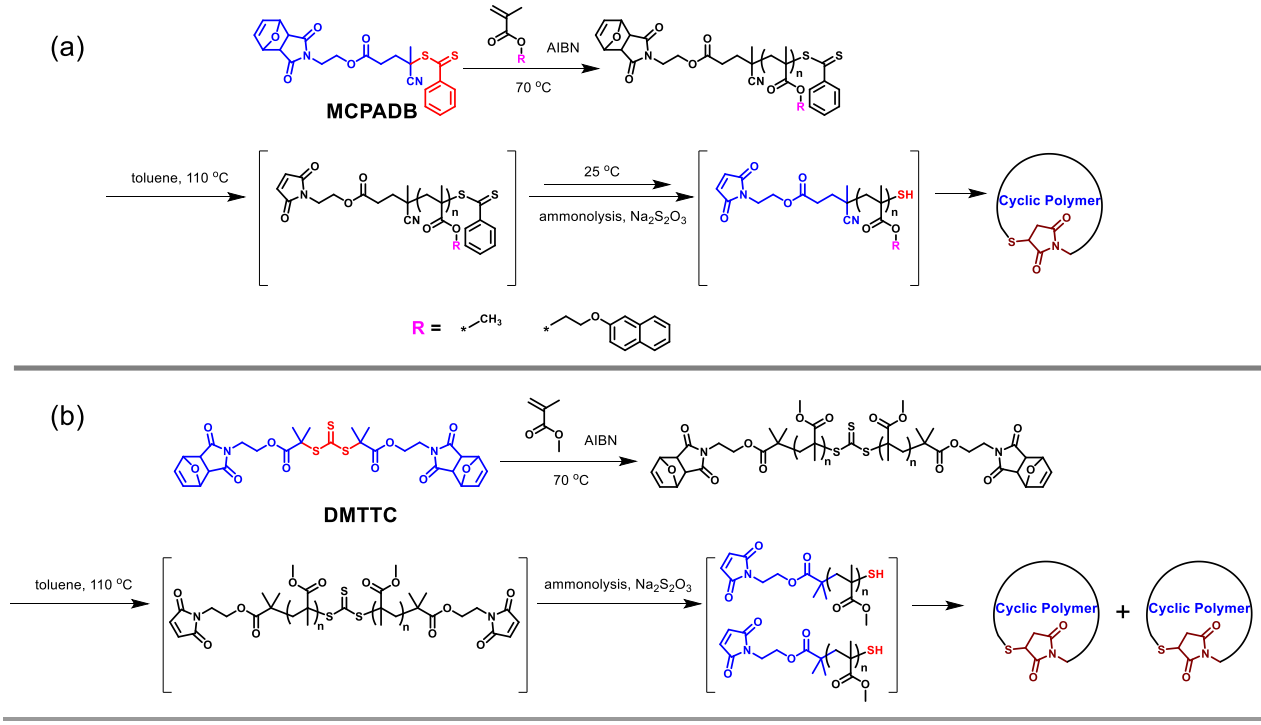
reaction used in ring-closure method plays vital role on the synthesis efficiency. Many highly effective chemical reactions, including copper-catalyzed azide-alkyne cycloaddition reaction (CuAAC),[16-19] olefin metathesis,[20,21] atom transfer radical coupling reaction,[22] Glaser coupling reaction,[23,24] Diels-Alder reaction,[25,26] thiol-ene (thiol-Michael addition) reaction[27,28] have been utilized for ring closure reactions for improving the output of cyclic polymer. To facilitate the ring closure and improve its efficiency, some smart approaches have been specially developed, such as electrostatic self-assembly and covalent fixation (ESA-CF),[29] dynamic covalent bonds,[30] rotaxane protocol[31]. Among them, ESA-CF[32-38] invented and developed by Tezuka *et al*. is highly attractive for its high efficiency and ability for constructing complex cyclic-based topological polymers. Our group has also reported a one-pot/one-step approach for highly effective synthesis of cyclic poly(alkyl methacrylate), which integrates the three steps (ATRP, terminal conversion and intramolecular CuAAC ring closure) into one step/one pot by judicious addition of a regulator.[39]

In terms of the typical procedures for the preparations of cyclic polymers *via* ring-closure strategy, several steps in separate pots are usually needed. For example, with respect to the popular ATRP/CuAAC ring-closure synthetic route, three steps are usually required, *i.e.*, (1) ATRP initiated by an alkyn-bearing initiator, (2) chain end conversion from halogen to "clickable" azide group and (3) intramolecular ring closure *via* CuAAC click chemistry. Separation and purification of the intermediate polymer in each step are necessary for ensuring a high-efficiency preparation, which means low efficiency and low overall yield. Therefore, the synthetic efficiency of cyclic polymer is believed to be remarkably improved by eliminating the separation and purification of the intermediate linear polymer, that is, the one-pot synthesis of the cyclic polymer directly from the resultant polymer (fresh polymer) of “living” polymerization. To realize this, the installation of the (latent) reactive groups into the initiator or mediator for polymerization is required. Meanwhile, the judicious selection of type of “living” polymerization with these functionalized initiator/mediator is also equally important for the success of high-efficiency preparation of cyclic polymer.

It was well known that RAFT polymerization is a superior controlled radical polymerization (CRP) technique for its wide available monomers and good control over molecular weight.[40] During the past few years, RAFT agents with two dithioesters,[41] azido[42] or alkynyl,[43] thiolactone,[44] methylbenzaldehyde,[45] anthracene,[46] hydroxyl[28] were used to form the functional linear precursors and accomplish the ring closure reaction. Notably, the terminal thiocarbonylthio group of RAFT-made polymer can be easily and quantificationally converted to thiol group by facile aminolysis reaction.[47] The thiol group can undergo several types of click reactions, including radical-induced thiol-ene,[48] thiol-Michael addition,[49] thiol-bromo[50] *et al*.. Among them, the thiol-Michael addition click reaction is a good candidate for ring closure reaction for its mild condition, fast rate and high effectiveness.[51] Monteiro *et al.* used the thiol-Michael addition to produce the cyclic polymer from linear RAFT polymer, wherein the terminal thiol group was from thiocarbonylthio by aminolysis and the acrylate group was installed by post-modification.[28] As aforementioned, the post-modification and separation of the intermediate linear polymer means low efficiency. In order to realize the one-pot ring closure with thiol-Michael addition reaction, the R group of RAFT agent should be specially designed and installed with a (methyl) acrylate, maleimide or vinyl sulfone[51] functional group, which can be readily clicked with the generated thiol group from thiocarbonylthio group *via* thiol-Michael addition. However, these functional groups like (methyl) acrylate, maleimide or vinyl sulfone for ring-closure reaction cannot be intact, *i.e.*, they are easily polymerized under RAFT polymerization conditions. Thus, the facile protection and de-protection of these groups is required. It is well documented that maleimide protected by furan can be readily de-protected to release naked maleimide functional group *via* retro D-A reaction at 110 ^{o}C or higher temperature.[52] This furan-maleimide retro D-A reaction is highly attractive due to the easy release of furan from reaction system, no contamination, catalyst-free merit and quantitative yield.[53] The furan-maleimide retro D-A reaction has been used for constructing various topological polymers.[25]

Herein, a straightforward ring-closure by thiol-Michael addition with RAFT polymer as linear precursor was developed (Scheme 1). First, the RAFT-made precursor polymer was prepared by a RAFT agent with furan-protected maleimide installed at R group. Then, with RAFT polymer in dilute condition, the maleimide at α chain end was completely de-protected at 110 ^{o}C followed by the aminolysis of thiocarbonylthio to thiol group at moderate temperature in one pot. In the course of aminolysis and thereafter, the intramolecular ring closure *via* thiol-Michael addition facilely happened to form the cyclic polymer. RAFT agent with one trithiocarbonate and two furan-protected maleimide groups (Scheme 1) were designed and prepared aiming at the synthesis of topological cyclic polymers in one pot *via* similar procedures. This work provides an alternative and promising method for high-efficiency synthesis of *cyclic* polymers.

Scheme 1. Schematic illustrations of the one-pot approach for the synthesis of cyclic polymer from linear RAFT polymer



Experimental section

Chemicals and Solvents. Methyl methacrylate (MMA, Sinopharm Chemical Reagent, China, 99%) and methyl acrylate (MA, Sinopharm Chemical Reagent, China, ≥98.5%) were purified by distillation from calcium hydride under reduced pressure prior to use. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, TCI, >98%) was used as received. 2,2-Azobisisobutyronitrile (AIBN, Sinopharm Chemical Reagent, China, 98%) was purified by recrystallization from ethanol, Maleic anhydride (≥98.5%), Ethanolamine (>99%), Thionyl chloride ($SOCl_2$, ≥99.0%), N,N′-Dicyclohexylcarbodiimide (DCC, 99%), 4-dimethylaminopyridine (DMAP, >99%), Carbon disulfide(CS_2), Furan, tetrahydrofuran (THF), anhydrous ether, toluene, hexane, methanol and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without any further purification.

Analysis Techniques. The number-average molecular weight (M_n) and polydispersity ($Đ = M_w/M_n$) of the polymers were determined using a size exclusion column TOSOH HLC-8320 equipped with refractive index and UV detectors using two TSKgel Super Mutipore HZ-N (4.6 × 150 mm, 3 μm beads size) columns arranged in series, and it can separate polymers in the molecular weight range 500-1.9 × 10^5 g/mol. THF was used as the eluent at a flow rate of 0.35 mL/min at 40 ℃. Data acquisition was performed using EcoSEC software, and molecular weights were calculated with poly(methylmethacrylate) (PMMA) standards.

All ^{1}H NMR, ^{13}C NMR spectra were collected using a Bruker nuclear magnetic resonance instrument (300 MHz) using tetramethylsilane (TMS) as the internal standard at room temperature. NMR samples were prepared with concentrations of 10-20 mg/mL in $CDCl_3$ for ^{1}H NMR and 80-100 mg/mL for ^{13}C NMR. The ^{1}H NMR spectra were referenced to δ 7.26 ppm in $CDCl_3$, and ^{13}C NMR spectra were referenced to δ 77.00 ppm in $CDCl_3$.

^{1}H DOSY NMR experiments were conducted on Agilent Technologies 600 MHz DD2 spectrometer with PFG ^{1}H/^{19}F/X probe at 25 ℃, using *d*-chloroform as the solvent and tetramethylsilane (TMS) as an internal standard. For measurements of the self-diffusion coefficient, the solution concentration was 1.0 mg/mL, and a DBPPSTE_CC (DOSY Bipolar Pulse Pair Stimulated Echo with Convection Compensation) sequence was used. Diffusion attenuation curves were obtained at a sequential 15-step linear increase of the amplitude of the magnetic field gradient pulse in the range from 4.12 to 87.15 G/cm at fixed values of diffusion time Δ, δ_{pulse} gradient pulse duration (2.0 ms), and relaxation time d_1 (1 s). DOSY spectra were processed by Agilent's VnmrJ 3.2 software.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy were acquired on an UltrafleXtreme MALDI TOF mass spectrometer equipped with a 1 kHz smart beam-II laser. The instrument was calibrated prior to each measurement with external PMMA at the molecular weight under consideration. The compound trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, >98%) served as the matrix and was prepared in $CHCl_3$ at a concentration of 20 mg/mL. The cationizing agent sodium trifluoroacetate was prepared in ethanol at a concentration of 10

mg/mL. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). All samples were dissolved in THF at a concentration of 10 mg/mL. After sample preparation and solvent evaporation, the plate was inserted into the MALDI mass spectrometer. The attenuation of the laser was adjusted to minimize undesired polymer fragmentation and to maximize the sensitivity.

Differential scanning calorimetry (DSC) was performed with heating and cooling at a rate of 10 ℃ min^{-1} with a limited temperature from 60 ℃-150 ℃ on a Q200 differential scanning calorimeter (TA Instruments), and the glass transition temperature (T_g) was measured on the third cycle of a heat/cool/heat experiment.

Synthetic Procedures.

Polymerization of MMA with protected-maleimide RAFT agent MCPADB (*l*-PMMA-1): AIBN (15.4 mg, 0.0938 mmol), MCPADB (177.4 mg, 0.375 mmol) and freshly distilled MMA (2 mL, 18.9 mmol) were added into a 5 mL ampule. The mixture was degassed using three freeze/pump/thaw cycles under argon protection. After that, the ampoule was flame sealed and placed in a preheated 70 ℃ oil bath and allowed to stir under argon for 80 min. The ampule was cooled by immersion in ice water before the contents were dissolved in 5.0 mL of THF, and the resulting solution was precipitated into an excess of cold methanol twice with stirring. The product was collected by vacuum filtration, and dried in vacuo at 25 ℃ until a constant weight was recorded at room temperature to afford 0.5 g (Conversion = 26.5%) pink powder. The M_n and M_w/M_n values were determined by SEC (THF) with poly(methylmethacrylate) (PMMA) standards ($M_{n,SEC}$ = 4000 g/mol, $Đ$ = 1.13).

Cyclization of PMMA from *l*-PMMA-1: A 1000 mL three-necked flask equipped with a magnetic stirrer containing a 0.025 mM solution of *l*-PMMA-1 (50 mg, 1.25 $\times 10^{-5}$ mol) in toluene (500 mL) was degassed by bubbling with argon at room temperature for several hours. After that, the reaction mixture was allowed to stir at 110 ℃ for at least 8 hours under the protection of an argon flow and then cooled to 25 ℃, followed by adding a little amount reducing reagent ($Na_2S_2O_3$) and 5 mL DBU, the reaction was carried out at 25 ℃ for an additional 36 h. After evaporating toluene under reduced pressure, $CHCl_3$ (20 mL) was added and washed several times with saturated $NaHCO_3$ and NaCl solutions, dried over Na_2SO_4, concentrated in vacuo, and precipitated into hexane, filtered, and dried overnight in a vacuum oven at 25 ℃ to obtain a white solid (38 mg, yield: 80%, $M_{n,SEC}$ = 2300 g/mol, $Đ$ = 1.19).

Polymerization of 2NMA with protected-maleimide RAFT agent MCPADB (*l*-P2NMA): AIBN (1.60 mg, 0.00975 mmol), MCPADB (18.36 mg, 0.039 mmol) and 2NMA (0.5 g, 1.95 mmol) were dissolved in 1 mL toluene and added into a 5 mL ampule. The mixture was degassed using three freeze/pump/thaw cycles under argon protection. After that, the ampoule was flame sealed and placed in a preheated 60 ℃ oil bath and allowed to stir under argon for 5.5 h. The ampule was cooled by immersion in ice water before the contents were dissolved in 5.0 mL of THF, and the resulting solution was precipitated into an excess of cold methanol twice with stirring. The product was collected by vacuum filtration, and dried in vacuo at 25 ℃ until a constant weight was recorded at room temperature to afford 0.16 g (Conversion = 32 %) pink powder. The M_n and M_w/M_n values were determined by SEC (THF) with poly(methylmethacrylate) (PMMA) standards ($M_{n,SEC}$ = 5400 g/mol, $Đ$ = 1.22).

Cyclization of P2NMA from *l*-P2NMA: A 1000 mL three-necked flask equipped with a magnetic stirrer containing a 0.0185 mM solution of P2NMA (50 mg, 9.26 $\times 10^{-6}$ mol) in toluene (500 mL) was degassed by bubbling with argon at room temperature for several hours. After that, the reaction mixture was allowed to stir at 110 ℃ for at least 8 hours under the protection of an argon flow and then cooled to 25 ℃, followed by adding a little amount reducing reagent ($Na_2S_2O_3$) and 5 mL DBU, the reaction was carried out at 25 ℃ for an additional 36 h. After evaporating toluene under reduced pressure, $CHCl_3$ (20 mL) was added and washed several times with saturated $NaHCO_3$ and NaCl solutions, dried over Na_2SO_4, concentrated in vacuo, and precipitated into cold methanol, filtered, and dried overnight in a vacuum oven at 25 ℃ to obtain a white solid (35 mg, yield: 74%, $M_{n,SEC}$ = 4200 g/mol, $Đ$ = 1.27).

Polymerization of MMA with protected-maleimide RAFT agent DMTTC (*l*-PMMA-2): AIBN (10.3 mg, 0.0627 mmol), DMTTC (205.8 mg, 0.310 mmol) freshly distilled MMA (1 mL, 9.45 mmol) and toluene (2 mL) were added into a 5 mL ampule. The mixture was degassed using three freeze/pump/thaw cycles under argon protection. After that, the ampoule was flame sealed and placed in a preheated 60 ℃ oil bath and allowed to stir under argon for 2.5 h. The ampule was cooled by immersion in ice water, and the solution was precipitated into an excess of cold methanol twice with stirring. The product was collected by vacuum filtration, and dried in vacuo at 25 ℃ until a constant weight was recorded at room temperature to afford 0.090 g (Conversion = 9.5%) pink powder. The M_n and M_w/M_n values were determined by SEC (THF) with poly(methylmethacrylate) (PMMA) standards ($M_{n,SEC}$ = 7200 g/mol, $Đ$ = 1.40).

Cyclization of PMMA from *l*-PMMA-2: A 1000 mL three-necked flask equipped with a magnetic stirrer containing a 0.014 mM solution of *l*-PMMA-1 (50 mg, 6.94 $\times 10^{-3}$ mmol) in toluene (500 mL) was degassed by bubbling with argon at room temperature for several hours. After that, the reaction mixture was allowed to stir at 110 ℃ for at least 8 hours under the protection of an argon flow and followed by adding a little amount reducing reagent ($Na_2S_2O_3$) and 10 mL DBU, the reaction was carried out at 110 ℃ for an additional 36 h. After evaporating toluene under reduced pressure, $CHCl_3$ (20 mL) was added and washed several times with saturated $NaHCO_3$ and NaCl solutions, dried over Na_2SO_4, concentrated in vacuo, and precipitated into hexane, filtered, and dried overnight in a vacuum oven at 25 ℃ to obtain a white solid (30 mg, yield: 61%, $M_{n,SEC}$ = 3600 g/mol, $Đ$ = 1.66).

Results and Discussions

Synthesis of *l*-PMMA-1:

The synthetic route for the synthesis of cyclic polymer was quite straightforward as illustrated in Scheme 1. The RAFT polymerization was employed to prepare the functionalized macrocycle polymers.[44,45,54,55] After de-protection of the furan-protected maleimide at α-chain end and aminolysis of thiocarbonylthio at ω-chain end, the maleimide and thiol groups at α,ω-telechelic polymer were freshly obtained and used for the synthesis of cyclic polymer based on the versatile and high-efficiency thiol-Michael addition reaction.[28,56,57] As shown in the **Scheme 1(a)**, the functional RAFT agent (MCPADB) with furan-protected maleimide installed at R group was prepared firstly, which was characterized by ^{1}H NMR and ^{13}C NMR (**Figure S1**†). In this work, the maleimide of R group was protected by furan to avoid the undesired polymerization of maleimide group. A typical RAFT polymerization was implemented with MMA as model monomer, and the polymerization was stopped at about 30% conversion to guarantee a high degree of chain end fidelity. The linear PMMA was characterized by SEC, NMR and MALDI-TOF, and the number average molecular weight ($M_{n,SEC}$) was 4000 g/mol ($Đ$ = 1.13) with unimodal and symmetric distribution as shown in **Figure 1**. The chain end functionality of the thiocarbonylthio group was calculated as ~95% by comparing the protons on the benzene at the ω-chain end (h) to the vinyl protons at the protected maleimide of the polymer (a) using ^{1}H NMR spectroscopy (**Figure 2A**). The high chain end functionality (95%) ensured the following successful intramolecular cyclization.

Model reaction of de-protection of maleimide group and ammonolysis of thiocarbonylthio group:

To guarantee the effectiveness of the one-pot cyclization of the linear PMMA precursor as shown in Scheme, the complete de-protection of maleimide group and conversion of thiocarbonylthio group to thiol group were crucial. Therefore, model reactions of de-protecting maleimide group and aminolysis of thiocarbonylthio group were implemented, respectively. In the case of de-protection of maleimide group, the RAFT polymer was dissolved in toluene and heated at 110 ^{o}C for 8 hours (the experiment in detail were described in Supporting Information), the furan group at α-chain end was de-protected completely as confirmed by SEC and ^{1}H NMR measurement (**Figure S2**†). The SEC curve showed unobvious change after the de-protected reaction comparing with the original RAFT polymer. The ^{1}H NMR spectra displayed the complete the disappearance of the protons (a, b, c) at furan-protected maleimide group. Importantly, the thiocarbonylthio group was intact during de-protection process.

Usually, the ω-terminal thiocarbonylthio can be facilely converted to thiol group by aminolysis with n-butylamine under mild conditions.[58,59] However, since that the n-butylamine can also readily react with maleimide *via* Michael addition,[51] the utilization of n-butylamine as the aminolysis agent was improper in this work. Based on this consideration, the tertiary amine, DBU was explored to serve as aminolysis agent, since that tertiary amine cannot react with malaimide *via* Michael addition. Model experiments with DBU as aminolysis agent was conducted to confirm its effectiveness, and the DBU treated polymer was characterized by SEC (**Figure S2A**†), ^{1}H NMR (**Figure S2B**†) and MALDI-TOF mass spectroscopy (**Figure S3A**†). The SEC curve also showed unobvious change after the aminolysis reaction except small amount of thiol-thiol coupling reaction with double molecular weight (**Figure S2A**†). From **Figure S2B**†, the chemical shifts of the "protected" maleimide protons (a, b, c) at 6.54, 5.28, and 2.89 ppm were intact, and benzene protons (h) of terminal thiocarbonylthio of the precursor linear polymer at 7.34-7.90 ppm disappeared, demonstrating the ease of conversion of thiocarbonylthio by DBU. The MALDI-TOF mass spectroscopy was utilized to confirm the successful aminolysis of thiocarbonylthio, and the results were presented in **Figure S3A (**ESI†). The peaks were separated by the molecular weight of a single MMA unit (100.05 mass units). Both of the furan-protected maleimide and thiol group were liable upon laser irradiation in MALDI TOF mass spectroscopy, therefore, and one furan molecular and one S atom were detached during MALDI TOF mass spectroscopy test. A representative m/z value of 2874.45 Da. corresponding to the 26-mer of PMMA with sodium was in good agreement with the calculated mass of thiol-terminated PMMA ($[M_{26}$+Na-Furan-S$]^+$, cal. 2874.45 Da.). To validate the detach of S atom during MALDI TOF mass spectroscopy, a representative thiol-Michael addition reaction was carried out. Methyl acrylate (MA) was used to react with the fresh thiol group on the polymer ***l*-PMMA-1-SH** in situ. That is, a small amount of DBU, together with MA and ***l*-PMMA-1** was added to toluene and the mixture was stirred at 25 ℃ for a predetermined time. The MALDI-TOF mass spectrum (**Figure S3B**†) of the resultant product showed a peak m/z value of 2992.72 Da. corresponding to the 26-mer of ***l*-PMMA-1-MA** with a sodium ion, matching well with the calculated mass ($[M_{26}$+Na-Furan$]^+$, cal. 2992.46 Da.). All of these convincing data suggested a successful aminolysis of thiocarbonylthio to thiol group by using DBU, and the fresh thiol group was highly active for the subsequent thiol-Michael addition reaction. Therefore, in this work, DBU was used as aminolysis agent of thiocarbonylthio group under argon atmosphere at mild condition. The reducing agent $Na_2S_2O_3$ was also added to avoid thiol-thiol coupling reaction.

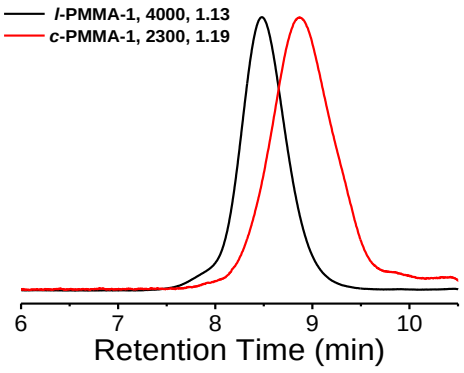


Figure 1. SEC RI traces of linear (black) and cyclic polymers (red) (**PMMA-1**). THF was used as the eluent, and PMMA standards were used for the calibration. All SEC traces were normalized to height.

Synthesis of *c*-PMMA-1 from *l*-PMMA-1 in one pot:

The unimolecular/intramolecular heterodifunctional approach[16,28] was the most commonly used cyclization method for its high efficiency among various cyclization methods.[14,16,60] After polymerization, the RAFT polymer was dissolved in toluene with a highly dilute concentration (2.5×10^{-5} mol/L).[16] Then, the furan group at α-chain end was de-protected and completely removed by heating at 110 °C for 8 hours.[61] Therefore, after deprotection of the maleimide group of the linear RAFT polymer in the highly dilute toluene solution, then cooled to 25 ℃, DBU and $Na_2S_2O_3$ were added directly and maintained at room temperature for 36 hours. After evaporation of the solution, almost white polymer (**Figure S4†)** was obtained and fully characterized by SEC, NMR, MALDI-TOF mass spectroscopy, differential scanning calorimetry (DSC) and ^{1}H DOSY NMR. From **Figure 1**, the SEC trace of the resultant polymer was unimodal and symmetric distribution. Meanwhile, it exhibited a longer retention time (M_p = 2500 g/mol, time of M_p = 8.87 min) than the linear RAFT polymer (M_p = 4400 g/mol, time of M_p = 8.48 min) and no obvious shoulder peak at shorter retention time was observed. This result implied that the intermolecular coupling reaction (either thiol-thiol coupling or thiol-Michael addition) of the linear precursor can be ignored. And, most of the linear RAFT polymer was transformed to the cyclic ones since that the cyclic polymer had reduced hydrodynamic volume compared with it linear counterpart.[14] Since that the hydrodynamic volume was greatly reduced after cyclization, the cyclic polymer might be presented as knotted ring form.[62] To further validate the reduced hydrodynamic volume after cyclization, the ^{1}H DOSY NMR spectra of linear and cyclic polymers were shown in **Figure S5†**, respectively. The measured diffusion coefficient (D) was 2.90×10^{-10} m^2/s for linear polymer, 3.36×10^{-10} m^2/s for cyclic polymer. Based on the Stokes − Einstein equation, the corresponding hydrodynamic diameter (D_h) of linear polymer and cyclic polymer was 2.68 and 2.32 nm, respectively. These results further supported the successful one-pot cyclization. The ^{1}H NMR spectra of ***c*-PMMA-1 (B)** and linear PMMA precursor ***l*-PMMA-1 (A)** were shown in **Figure 2**, respectively. The chemical shift of the "protected" maleimide protons (a, b) and benzene protons (h) of the precursor polymer disappeared, demonstrating the removal of furan and thiocarbonylthio groups. Furthermore, the protons of the "protected" maleimide (2.89 ppm, c) shifted to 2.74 ppm (c') and c'' included in the peak of main chain after the successive reactions in one pot, *i.e.*, deprotection of furan, aminolysis of thiocarbonylthio group and thiol-Michael addition. Besides, ^{13}C NMR spectra of ***c*-PMMA-1 (D)** and the PMMA precursor ***l*-PMMA-1 (C)** were shown in **Figure 2**, the chemical shift of the "protected" maleimide carbons (m, n) and the benzene carbon (f) of the precursor polymer disappeared. The chemical shift of the "de-protected" maleimide carbons (g', g") moved to 38.93 and 32.82 ppm (original g, at 47.48 ppm), and the signals of another "de-protected" maleimide carbonyl carbon (k') shifted to 165.67 ppm (k, original at 176.08 ppm). This NMR result provided clear evidence for the successful de-protection, aminolysis and cyclization in one pot.

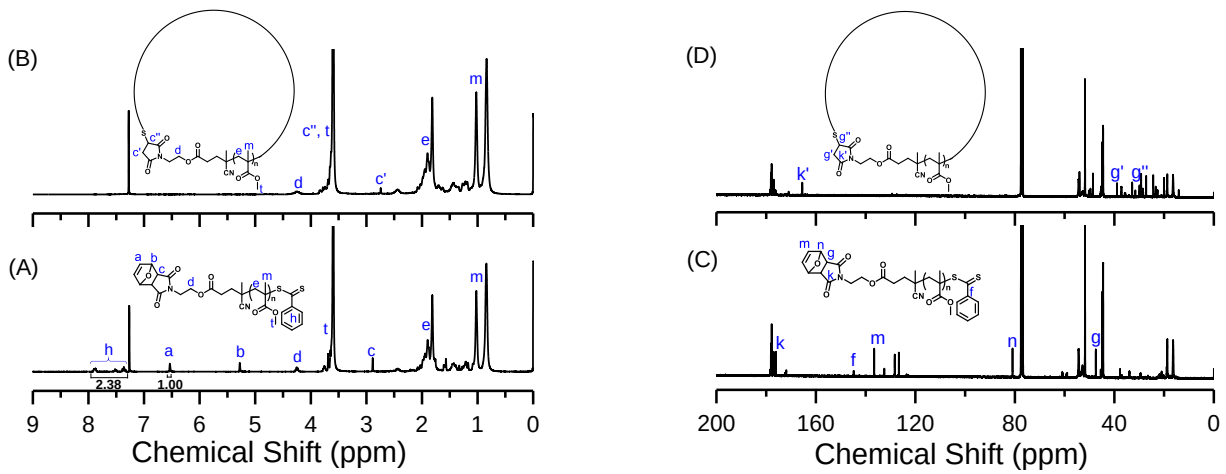


Figure 2. 300 MHz ^{1}H NMR spectra in $CDCl_3$ of (A) ***l*-PMMA-1**, (B) ***c*-PMMA-1**. And 75 MHz ^{13}C NMR spectra in $CDCl_3$ of (C) ***l*-PMMA-1**, (D) ***c*-PMMA-1**.

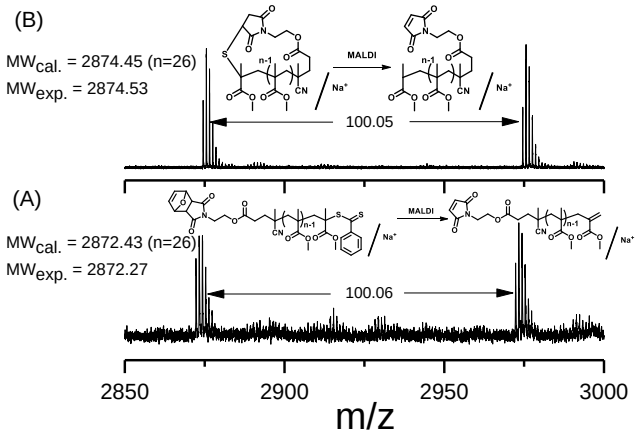


Figure 3. MALDI-TOF mass spectrum of ***c*-PMMA-1** was acquired in reflection mode by using Na salt as the cationization agent and a DCTB matrix.

The high-efficiency cyclization through a thiol-Michael click reaction was further confirmed by MALDI-TOF mass spectroscopy. The mass spectroscopy of linear precursor was also shown for better comparison (**Figure 3A**). The peaks were separated by the molecular weight of a single MMA unit. The representative m/z value of 2872.27 Da. corresponding to the 26-mer of PMMA with sodium agreed well with the calculated mass ([M_{26}+Na-furan-ArCSS]$^+$, cal. 2872.43 Da.). For the MALDI-TOF mass spectra of the cyclic polymer (**Figure 3B**), it was found that it exhibited a perfect spectrum with a uniform series of peaks recorded in reflection mode. A representative m/z value of 2874.53 Da. corresponding to the 26-mer of PMMA with sodium agreed well with the calculated mass ([M_{26}+Na-S]$^+$, cal. 2874.45 Da.). Since that the C-S bond of arising from thiol-Maleimide Michael addition was a relatively weak bond,[63-65] the laser irradiation imposed during MALDI-TOF mass spectroscopy detection probably destroyed the succinimide thioethers. The mass of S (32 m/z) was thus subtracted when calculating the theoretical one. Summary of molecular characterizations were shown in **Table S1**†. Besides, according to chain-end free volume theory, a cyclic polymer may have a higher glass transition temperature (T_g) than its linear precursor.[19] The glass transition behaviour of the linear and cyclic polymers was thus explored by using DSC. It was found that the T_g of the linear polymer (*l*-PMMA-1) was about 98.1 ℃, while it was 104.7 ℃ for the cyclic polymer (*c*-PMMA-1) (**Figure S6**†, ESI). This result further underpinned the successful preparation of cyclic polymer by one-pot method.

The chain of evidence including SEC, NMR, DSC, ^{1}H DOSY NMR and MALDI-TOF mass spectroscopy provided solid supports for the successful synthesis of cyclic polymer from linear RAFT polymer in one pot. It should be noted that the yield of the resultant cyclic polymer was 80% without any fractionations. While, the reported thiol-Michael ring closure *via* post-modification of the linear precursor gave 61% of yield after preparative SEC or fractionation precipitation.[28]

Synthesis of *c*-P2NMA from *l*-P2NMA:

Cyclic functional polymers were frequently reported to exhibit unique properties compared with their linear counterpart.[66] The versatility of the one-pot straightforward approach for the synthesis of cyclic polymer was testified by employing a functional monomer, 2-(naphthalen-2-yloxy)ethyl methacrylate (2NMA). And the functional monomer (2NMA) was designed and synthesized as confirmed by ^{1}H NMR and ^{13}C NMR (**Figure S7**†). The synthetic procedure was similar with that of ***c*-PMMA-1**. The resultant *cyclic* P2NMA (***c*-P2NMA**) was confirmed by elaborate characterizations, including SEC (**Figure 4**), NMR **(Figure 5A, 5B)** and MALDI-TOF mass spectroscopy (**Figure 5C**). The results uniformly proved that successful preparation of ***c*-P2NMA**, demonstrating good universality of the one-pot synthesis of cyclic polymer from RAFT polymer *via* thiol-Michael addition.

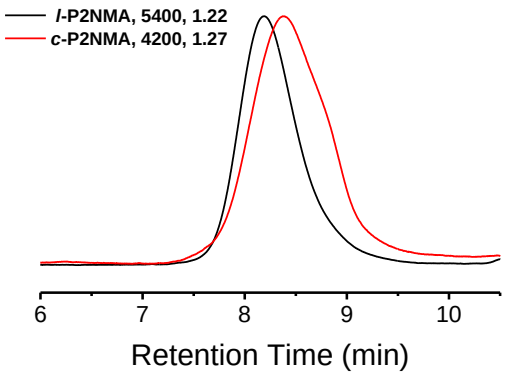


Figure 4. SEC RI traces of linear (black) and cyclic polymers (red) (**P2NMA**). THF was used as the eluent, and PMMA standards were used for the calibration. All SEC traces were normalized to height.

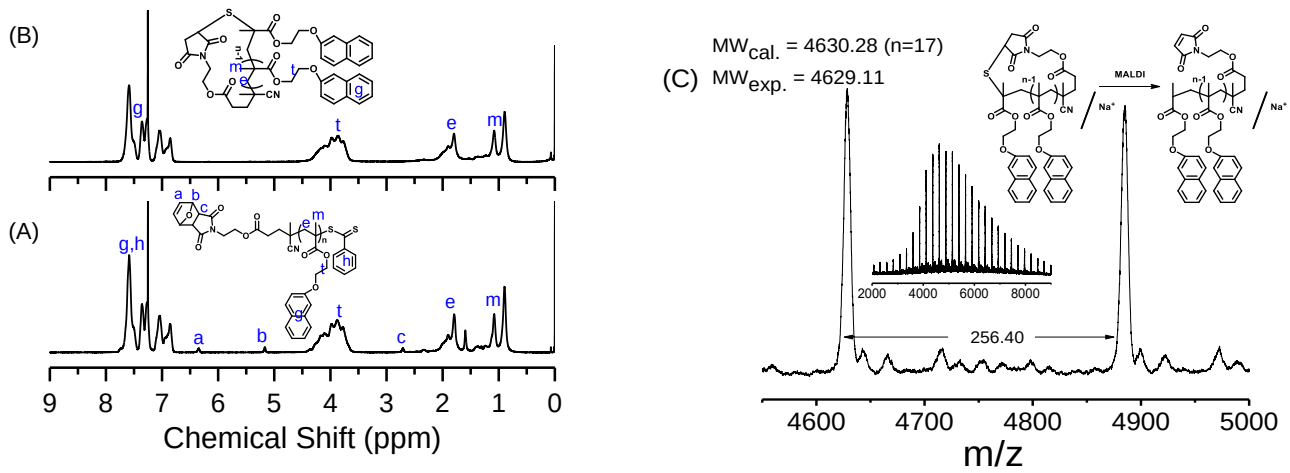


Figure 5. 300 MHz ^{1}H NMR spectra in $CDCl_3$ of (A) ***l*-P2NMA**, (B) ***c*-P2NMA**. (C) MALDI-TOF mass spectrum of ***c*-P2NMA** was acquired in linear mode by using Na salt as the cationization agent and a DCTB matrix.

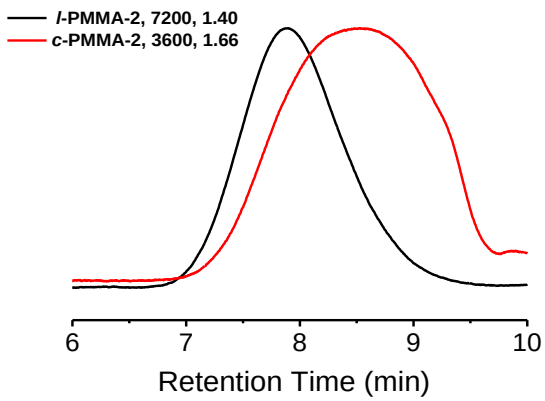


Figure 6. SEC RI traces of linear and cyclic polymers (**PMMA-2**). THF was used as the eluent, and PMMA standards were used for the calibration. All SEC traces were normalized to height.

Synthesis of *c*-PMMA-2 from *l*-PMMA-2 *via* thiol-Michael "click" chemistry:

This one-pot approach was also verified by using trithiocarbonate (**DMTTC**) as chain transfer agent for the RAFT polymerization (**Scheme 1(b)**). Two furan-protected maleimide moieties were installed at both R groups of the symmetric DMTTC. According to RAFT mechanism, the resultant RAFT polymer should possess trithiocarbonate group at the middle of the polymer chain. The one-pot preparation of the cyclic polymer from this RAFT polymer would split the chain into half, and thus the MW of cyclic polymer should only have the half value of its linear precursor RAFT polymer. As shown in the **Scheme 1(b)**, the functional RAFT agent (**DMTTC**) was designed and synthesized as confirmed by ^{1}H NMR and ^{13}C NMR (**Figure S8†**). Then, a typical RAFT polymerization was implemented and ceased at about 10% of monomer conversion to maintain a high degree of chain end fidelity. The linear PMMA was characterized by SEC, the number average molecular weight ($M_{n,SEC}$) was 7200 g/mol ($Đ$ = 1.40) with unimodal and symmetric distribution as shown in **Figure 6**. Upon the deprotection of furan, aminolysis of trithiocarbonate and thiol-maleimide Michael addition in one-pot process, the SEC of resultant polymer (**Figure 6**) showed the MW of 3600. This result denoted that the trithiocarbonate centered at the linear RAFT polymer was aminolyzed into two thiol groups, and the polymer chain was split into half as expected. The MWD of the resultant polymer was 1.60, which might be due to the broadening effects arising from the aminolysis of the trithiocarbonate groups.

The ^{1}H NMR spectra of ***c*-PMMA-2 (B)** and the linear PMMA precursor ***l*-PMMA-2 (A)** were shown in **Figure 7**, respectively. The peaks of the "protected" maleimide protons of the precursor polymer at 6.52, 5.26 and 2.89 ppm disappeared, and no signals of protons (vinyl double bond of maleimide) appeared around 6.7 ppm. Furthermore, the MALDI-TOF mass spectroscopy in **Figure 7C** provided convincing evidence for the structure of cyclic PMMA: a representative peak m/z value of 2235.15 g/mol corresponding to the 20-mer of PMMA with sodium was in good agreement with the calculated mass ($[M_{20}+Na-S]^+$, cal. 2235.12 g/mol). Therefore, all of the obtained results strongly supported the molecular structures and uniformity of the resulting cyclic PMMA. By using such a symmetric trithiocarbonate as chain transfer agent for RAFT polymerization, the MW of resultant cyclic PMMA was only half of the linear precursor RAFT polymer. It was supposed that by using other structures of chain transfer agents, for example, a trifunctional and tetrafunctional chain transfer agents, more topological cyclic

polymers can be produced by this one-pot approach. The topological cyclic structures, such as tadpole- and spiro-shaped, have attracted more and more attention. However, the synthesis of these topological cyclic polymers is a highly challenging task for polymer chemists, and three or more steps of polymer synthesis were necessary required with a very low yield of the target polymer.[36,37,67-69] The advantage of the one-pot approach for the synthesis of cyclic polymer from RAFT polymer showed obvious advantages since it simplified the polymer synthetic procedures with multi-steps in one pot. The collections and purifications of the intermediate polymers were not needed, enabling a highly effective preparation of the topological cyclic polymers. The one-pot synthesis of topological cyclic polymers is ongoing in our lab.

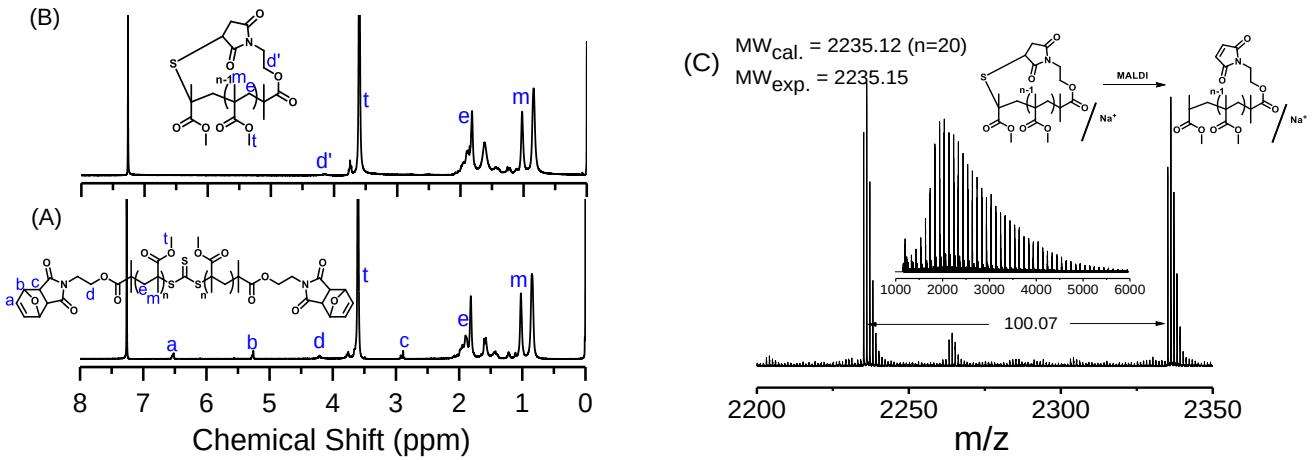


Figure 7. 300 MHz ^{1}H NMR spectra in $CDCl_3$ of (A) ***l*-PMMA-2**, (B) ***c*-PMMA-2**. (C) MALDI-TOF mass spectrum of ***c*-PMMA-2** was acquired in reflection mode by using Na salt as the cationization agent and a DCTB matrix.

Conclusion

In summary, a one-pot straightforward approach for synthesizing cyclic polymers was developed based on the deprotection of furan-protected maleimide, aminolysis of thiocarbonylthio and thiol-Michael addition reaction of linear precursor RAFT-made PMMA. The effectiveness of this approach was manifested by multi-step in one-pot reaction, no purifications and high yield (80%) of cyclic polymer. The versatility of this approach was verified by using functional monomer or trithiocarbonate as chain transfer agent. This work offers an alternative, effective and straightforward approach for preparing cyclic polymers. Some topological cyclic polymers can be also prepared by this one-pot approach.

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Notes and references

Suzhou key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, China. Tel/Fax: 86-512-6588-2787.
*To whom correspondence should be addressed. E-mail: zhangzhengbiao@suda.edu.cn.

† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/

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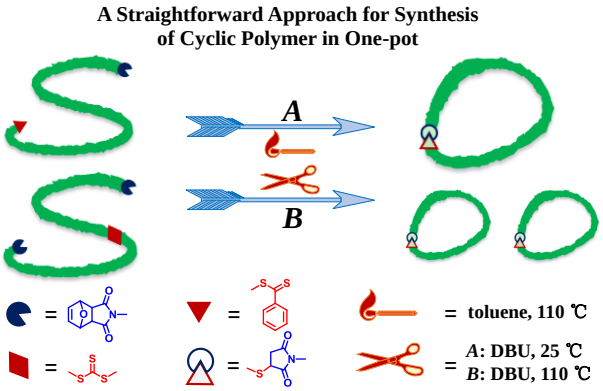

A Straightforward Approach for the One-pot Synthesis of Cyclic Polymer from RAFT Polymer *via* Thiol-Michael Addition

Junfei Zhao, Yanyan Zhou, Yu Zhou, Nianchen Zhou, Xiangqiang Pan, Zhengbiao Zhang* and Xiulin Zhu