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A method for preparing water soluble cyclic polymers

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ABSTRACT

A novel ring-closure method was developed to specifically focus on the preparation of water soluble cyclic polymers. The well-defined linear polymers were synthesized by a standard RAFT polymerization using a functional RAFT agent **1**. The cyclic polymers were then obtained by virtue of an efficient bromomaleimide-thiol substitution reaction to ring-close the linear precursors. This technique is unique in that it not only produces various well-defined water soluble cyclic polymers with high efficiency and topology purity, but also employs the environmentally benign solvent, water, as the ring-closure reaction media.

1. Introduction

Cyclic polymers, as one of the oldest topological polymers, have rejuvenated recently due to the significant achievements in cyclic polymer synthesis [1–6]. With the endless molecular topology, cyclic polymers have markedly different characteristics than their linear counterparts, such as a smaller radius of gyration and hydrodynamic volume, lower melt viscosity, and higher thermostability. To date, the known synthesis methods for cyclic polymers can be generalized into two categories: the ring-expansion and ring-closure strategies.

In the ring-expansion approach, the cyclic polymers are formed by a continuous insertion of monomer units into the activated cyclic chains. Because the cyclic polymers remain intact during the whole ring expansion process, this strategy can produce pure cyclic polymers with high molecular weight at concentrated solution and even in bulk. However, the ring-expansion approach is hardly to control the molecular weight and polydispersity of the resultant cyclic polymers [7–11]. In addition, it is difficult to produce the topological polymers derived from monocyclic polymers, such as the theta, eight, and tadpole shape polymers.

In the ring-closure method, cyclic polymers are prepared by applying highly efficient coupling chemistry to end-functionalized linear telechelic polymers. Especially when click chemistry is combined with controlled polymerization, this approach has demonstrated its power in the preparation of varied cyclic polymers with controlled molecular weight and low polydispersity [12–14]. In addition to the simple monocyclic topology, the ring-closure strategy can produce the cyclic polymer derivatives with complex architectures, such as theta and eight shapes conveniently [15–18]. However, the disadvantages are also obvious in this approach.

One of the main problems lies in the requirement of highly diluted coupling reaction condition to avoid the intermolecular reaction. Usually, this concentration goes to 10^{-5} M, which means that the preparation of 100 mg cyclic polymers needs around 1 L solvent [12,14,19]. As the environmental pollution becomes a very heavy topic nowadays, the utilization of huge amount of toxic organic solvents should be viewed as a significant limitation for producing cyclic polymers. Nearly all of the current ring-closure methods, however, are developed using the hazardous organic solvents as reaction media. Resultantly, the unique ring-closure techniques are urgently needed to produce cyclic polymer in the environmentally benign reaction media, such as water. In addition, since the natural bioorganic transformations are all carried out in water, the water solubility is a fundamental prerequisite for cyclic polymers when used in biology fields. From this point, it is again necessary to develop efficient ring-closuring techniques specifically focusing on the preparation of water soluble cyclic polymers.

The critical issue for producing cyclic polymers in water is to choose the right coupling reaction which has a high efficiency using water as reaction media. In 2009, Baker and co-workers discovered that bromomaleimides undergo rapid and highly efficient substitution reaction with thiol group in aqueous solution [20]. Subsequently, they demonstrated that this reaction can be utilized to prepare protein-polymer conjugates with high efficiency [21–23]. Just recently, this chemistry was extended into polymer synthesis field [24,25]. Robin et al. designed a novel dibromomaleimide reversible addition-fragmentation chain transfer (RAFT) agent, various well-defined polymers with dibromomaleimide end group were then produced by RAFT polymerization. The high

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reactivity of the end dibromomaleimide was demonstrated by reacting with a model thiophenol chemical [24].

Inspired by this, we developed a unique ring-closure method for the preparation of water soluble cyclic polymers by combining RAFT polymerization and bromomaleimide-thiol substitution reaction herein. Fig. 1 shows the main process. In the first step, the well-defined water soluble linear polymers were synthesized by RAFT polymerization using a functional RAFT agent **1**. As the second step, in the linear precursor water solution, the reducing agent $NaBH_4$ was used to cut the thiocarbonylthio group and release the thiol group, the cyclic polymers were then obtained in situ by virtue of thebromomaleimide-thiol substitution reaction.

2. Experimental

2.1. Materials

Bromobenzene, carbon disulfide (CS_2), maleimide, bromine, 4,4′-azobis(4-cyano-1-pentanol), 1-propanethiol, triphenylphosphine (PPh_3), diisopropylazodicarboxylate (DIAD), and sodium borohydride were purchased as regent grade from Aldrich, Acros, Alfa Aesar and used as received. Ethyl acetate, diethyl ether, methanol, chloroform, dichloromethane (DCM), tetrahydrofuran (THF) were purchased as regent grade from Beijing Chemical Reagent Co. and used as received unless otherwise noted. *N*-isopropylacrylamide (NIPAM) was purified by recrystallization in a mixture of n-hexane and toluene. *N,N*-dimethylacrylamide (DMAM) was dried over CaH_2 and distilled before use. 2,2′-Azoisobutyronitrile (AIBN) was recrystallized from ethanol and stored at 4 °C. 2,3-Dibromomaleimide [26], 2-bromomaleimide [27], and 4-Cyano-4-((thiobenzoyl)sulfanyl)pentanol (**a**in Fig. 2) [28] were synthesized according to the previous literature.

2.2. Preparation of 2-dibromo-3-propylsulfanyl-maleimide (b in Fig. 2)

A methanol solution (20 mL) of sodium acetate (360 mg, 4.39 mmol) and propanethiol (304 mg, 4.00 mmol) was dropwised into a methanol solution (16 mL) of 2,3-dibromomaleimide (2.04 g, 8 mmol)over 1 h. On completion of addition, the solution was stirred at room temperature for another 3 h. After that, the solution was concentrated and the crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 3/1) to produce the yellow solid product (520 mg) with a yield of 52%.

2.3. Preparation of RAFT agent 1

4-Cyano-4-((thiobenzoyl)sulfanyl)pentanol (**a**) (661 mg, 2.49 mmol), 2-dibromo-3-propylsulfanyl-maleimide (**b**) (520 mg, 2.08 mmol), and PPh_3 (654 mg, 2.49 mmol) were dissolved in anhydrous THF (10 mL). After cooled the mixture to 0 °C in an ice/water bath, DIAD (502 mg, 2.49 mmol) was dropwised into the solution and left it to stir for 30 min. The solution was then warmed to room temperature and kept stirring for another 12 h. After that, the solvent was removed under reduced pressure and the crude mixture was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 9/1) to afford the red oil product (486 mg) with a yield of 47%.

2.4. Preparation of Linear PDMAM

A mixed solution of DMAM (1.1 g, 11.11 mmol), RAFT agent 1 (53 mg, 0.11 mmol), and AIBN (3.5 mg, 0.02 mmol) was degassed via three freeze–thaw–pump cycles. After stirring for 5.5 h at 60 °C, the reaction was terminated by exposing system to air. The polymer was precipitated from an excess of mixture of ether and petroleum ether (v/v = 1/3) three times. After drying overnight in a vacuum oven at room temperature, the light red product was obtained with a yield of 22.11%. The monomer conversion was obtained from ^{1}H NMR with 23.94%.

2.5. Preparation of cyclic PDMAM

After dissolving linear PDMAM (20 mg) in water (100 mL) 1 h, $NaBH_4$ (80 mg, 2 mmol) was added and the solution was kept stirring for 24 h at room temperature. After that, the reaction solution was concentrated by vacuum evaporation to produce the cyclic PDMAM.

2.6. Preparation of linear PNIPAM

A mixed solution of N-isopropylacrylamide (4 g, 35.34 mmol), RAFT agent (176 mg, 0.35 mmol), AIBN (12 mg, 0.07 mmol), and DMF (4 g) was degassed via three freeze–thaw–pump cycles. After stirring for 24 h at 60 °C, the reaction was terminated by exposing system to air. The polymer was precipitated from an excess mixture of ether and petroleum ether (v/v = 1/3). After drying overnight in a vacuum oven at room temperature, the light red product was obtained with a yield of 17.21%. The monomer conversion was obtained from ^{1}H NMR with 19.74%.

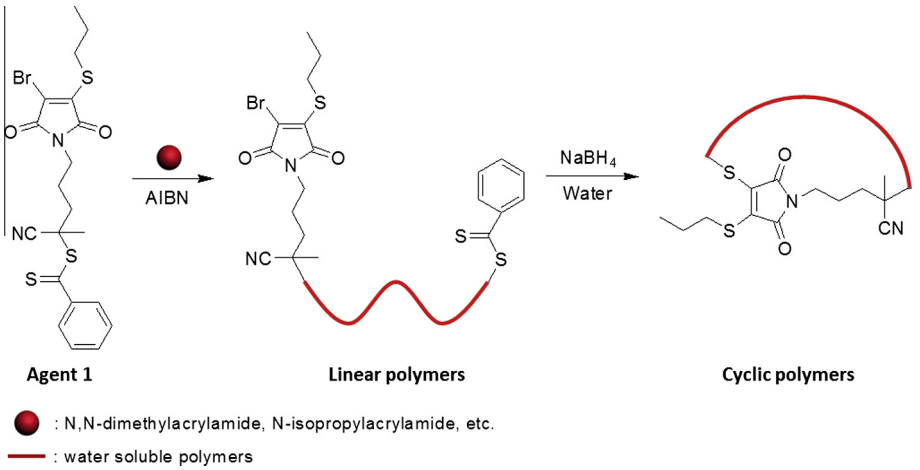

Fig. 1. The preparation of linear water soluble polymers by RAFT polymerization and the corresponding cyclic polymers by bromomaleimide-thiol substitution reaction.

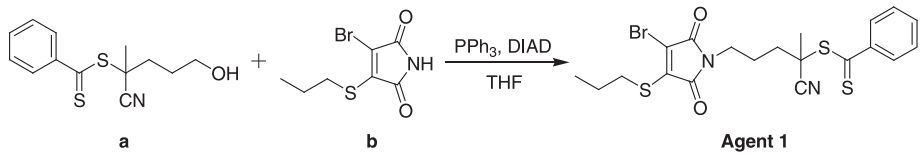

Fig. 2. Synthesis of functional RAFT agent **1**.

2.7. Preparation of cyclic PNIPAM

After dissolving linear PNIPAM (20 mg) in the mixture of water and methanol (v/v = 1/1, 100 mL) 1 h, $NaBH_4$ (80 mg, 2 mmol) was added and the solution was kept stirring for another 24 h at room temperature. Subsequently, the reaction solution was concentrated by vacuum evaporation to produce the cyclic PNIPAM.

2.8. Characterization

^{1}H NMR spectra were recorded on a Bruker DMX400 spectrometer at room temperature. Matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a BrukerBiflex III spectrometer equipped with a 337 nm nitrogen laser. Gel permeation chromatography (GPC) was performed with a Waters 515 pump, a Waters 2414 refractiveindex detector, and a combination of Styragel columns HT2, HT3, HT4, and HT5, the effective molecular weight range being 100–10 k, 500–30 k, 5 k–600 k, and 50 k–4000 k. Analysis was carried out in THF running with a flow rate of 1.0 mL/min at 35 °C. Polystyrene standards were used for the calibration.

3. Results and discussion

Functional RAFT agent **1** was synthesized by an efficient mitsunobu coupling reaction between 4-cyano-4-((thiobenzoyl)sulfanyl)pentanol (**a**) and 2-dibromo-3-propylsulfanyl-maleimide (**b**) (Fig. 2). The corresponding ^{1}H NMR and peak assignments were shown in Fig. 3A.

The agent **1** was then used to produce water soluble polymers (the first step in Fig. 1). The preparation of poly(*N,N*-dimethylacrylamide) (PDMAM) was firstly selected to demonstrated this concept. Table 1 shows the RAFT polymerization condition of PDMAM, in which the bulk polymerization of DMAM was performed at 60 °C and the DMAM/RAFT Agent/AIBN ratio was used as 100/1/0.2. After 5.5 h polymerization, a monomer conversion of 23.94% was obtained from ^{1}H NMR characterization of crude polymerization solution. The GPC curve is shown in Fig. 4A (black curve), in which a well-defined, monomodal, and symmetric peak was observed with M_n and M_w/M_n of 3360 and 1.06, respectively. Fig. 3B shows the ^{1}H NMR spectrum of purified PDMAM, where the three group peaks between 7.3 and 8.0 were inherent from the RAFT agent **1**, ascribing to the protons from the end benzene ring. This indicates the success of RAFT polymerization and the dithiobenzoate group was kept at the end of PDMAM polymer chain.

The cyclic PDMAM was subsequently prepared by a bromomaleimide-thiol substitution reaction to close the linear precursor in a highly diluted solution (the second step in Fig. 1). When dissolving 20 mg linear PDMAM in 100 mL water (the corresponding molar concentration is around $6 * 10^{-5}$ M), an excess of reducing agent $NaBH_4$ (80 mg) was used to cut the dithiobenzoate group and release the –SH at the end of polymer chain. The bromomaleimide-thiol substitution reaction was then carried out in situ to close the linear PDMAM and produce the cyclic polymers.

The GPC and MALDI-TOF MS were used to verify the successful cyclization. As shown in Fig. 4A and B, after the cyclization (red

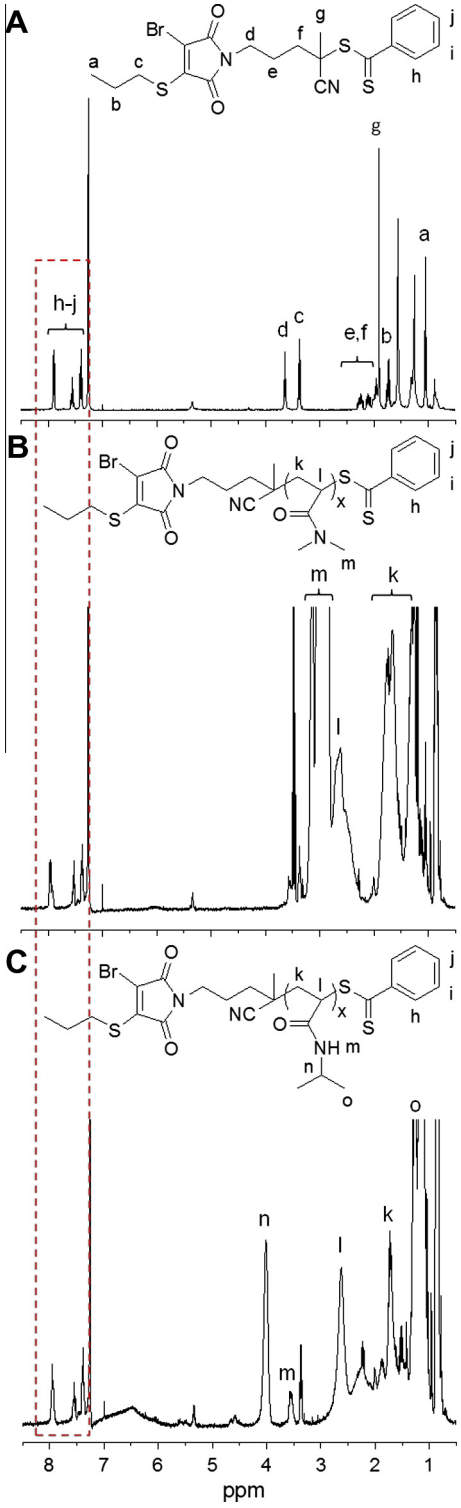

Fig. 3. ^{1}H NMR spectra of functional RAFT agent **1** (A), PDMAM (B), and PNIPAM (C) in $CDCl_3$.

Table 1
Synthesis and characterization of linear PDMAM and PNIPAM.

Run	Monomer[a]	Feed ratio[b]	Conv. (%)[c]	M_n[d]	M_w/M_n[d]
1	DMAM	100:1:0.2	23.94	3360	1.06
2	NIPAM	100:1:0.2	19.74	2290	1.07

[a] RAFT polymerization was performed at 60 °C.
[b] Initial molar ratio of monomer/RAFT Agent/AIBN.
[c] Calculated from the ^{1}H NMR spectrum.
[d] Calculated from GPC, in which THF were used as the eluent and polystyrene standards were used for the calibration.

Table 2
GPC characterization of linear and cyclic PDMAM and PNIPAM.

Run	Polymer	M_n[a]	M_w/M_n[a]
1	Linear PDMAM	3360	1.06
2	Cyclic PDMAM	2420	1.06
3	Linear PNIPAM	2290	1.07
4	Cyclic PNIPAM	1900	1.06

[a] THF was used as the eluent, and polystyrene standards were used for the calibration.

curve), the well-defined monomodal and symmetric peak shape was preserved but the whole peak position shifted to lower molecular weight direction completely compared to the linear precursor (black curve). Table 2 shows the GPC results of cyclic and linear PDMAM, where the same M_w/M_n and a M_n ratio of 0.72 between cyclic and linear PDMAM indicates the success of the ring-closure process from bromomaleimide-thiol substitution reaction [6,7,9]. To characterize the purity of the resultant cyclic topology, a log-normal distribution model [16,29,30] was used to simulate the molecular weight distributions of cyclic and linear PDMAM. As shown in Fig. 4B, the fitting curves (dash) from the log-normal distribution model excellently matched with the measured GPC curves, which demonstrated the high monocyclic topology purity of the resultant cyclic polymers.

Fig. 5 shows the MALDI-TOF mass spectra of linear PDMAM (A) and the cyclic counterparts (B). From the full spectra (left), the absolute M_n of 3750 and 3360 were obtained for the linear and cyclic PDMAM respectively. Comparing to the much smaller (0.72 times) apparent M_n of cyclic PDMAM than that of linear precursor from GPC (Table 2), the similar absolute M_n indicated a more compact molecular structure for cyclic PDMAM. This again confirmed the successful formation of cyclic PDMAM. In addition, the detailed descriptions of the MALDI-TOF mass spectra were shown in Fig. 5 (right). In the expanded spectrum of linear PDMAM (A), the marked peak at m/z = 3792.2 was ascribed to the linear PNIPAM$_{33}$/Na$^+$ (cal. = 3791.8). The corresponding cyclic counterpart was observed in the expanded spectrum of cyclic PDMAM (B) with a cleavage of propylthio group. As shown in Fig. 5B (right), the marked peak at m/z = 3532.1 was assigned to cyclic PDMAM$_{33}$-propylthio/K$^+$ (cal. = 3531.7). Furthermore, a regular m/z interval of 99.3 was observed between the major peaks in both cases, which corresponds to the molar mass of the DMAM monomer unit.

In addition, the molecular weight effect was explored on the ring-closure efficiency of bromomaleimide-thiol substitution reaction. To demonstrate this, the linear PDMAMs were synthesized with different M_n of 6410 and 12190 (Table S1). Their corresponding GPC curves show in Fig. S1 (black). After the cyclization, the GPC curve (red) shifted to lower molecular weight direction completely for the PDMAM with M_n of 6410 (Fig. S1A) (Table S2, Run 1 and 2). For the PDMAM with M_n of 12190 (Fig. S1B) (Table S2, Run 3 and 4), however, only lower molecular weight part curve shifted but the higher molecular weight part kept constant. These results indicate that bromomaleimide-thiol substitution reaction could be used to successfully ring-close the linear polymers with molecular weightlower than around 10,000.

To explore the universality of this novel ring-closure technique, the preparation of cyclic PNIPAM was used as another example. By virtue of the agent **1**, RAFT polymerization of NIPAM was carried out in DMF solution at 60 °C (Table 1). A monomer conversion of 19.74% was obtained after 24 h reaction. Fig. 6A shows the GPC curve (black) of the resultant PNIPAM, where a monomodal and symmetric peak was obtained with M_n = 2290 and M_w/M_n = 1.07. From ^{1}H NMR spectrum of purified PNIPAM (Fig. 3C), the proton signals from end benzene ring were clearly observed at 7.3–8.0 ppm, inherited from the RAFT agent **1** (Fig. 3A). This indicated that the well-defined linear PNIPAM was prepared by RAFT polymerization using agent **1**. The 20 mg linear precursor was then dissolved into 100 mL mixed solvents of water and methanol (v/v = 1/1), where the methanol was used to improve the PNIPAM solubility in water. After cleaving the dithiobenzoate group by $NaBH_4$, the cyclic PNIPAM was obtained in situ by virtue of bromomaleimide-thiol substitution reaction. As shown in Fig. 6A and B, the GPC curve of cyclic PNIPAM (red) inherited the monomodal and symmetrical peak shape from its linear precursor (black), but the peak position shifted to lower molecular weight direction completely. A M_n ratio of 0.83 was obtained between cyclic and linear PNIPAM (Table 2), which is quite consistent with the value reported in the literature [14,19]. The log-normal distribution model was further used to investigate the topological purity of resultant cyclic PNIPAM. As shown in Fig. 6B, the simulation curves accurately fit the experimentally measured GPC curves, demonstrating a high monocyclic topology purity of the resultant cyclic polymers. These strongly supported the success the bromomaleimide-thiol substitution ring-closure technique for the preparation of cyclic PNIPAM.

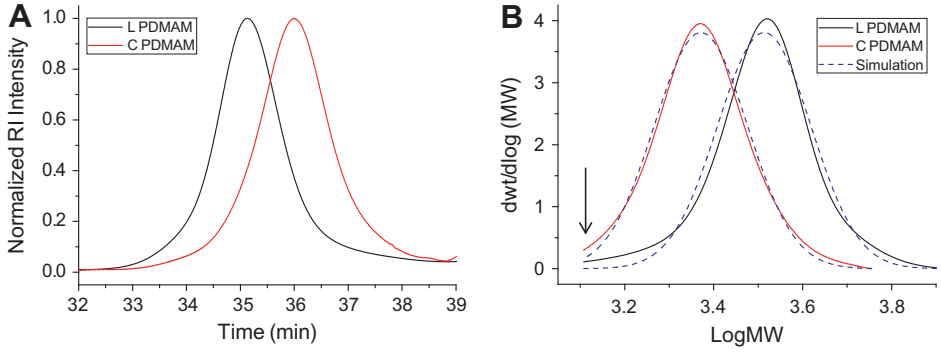

Fig. 4. (A) The GPC data (normalized RI intensity vs. time) for linear PDMAM (black) and cyclic PDMAM (red). (B) The GPC data (dwt/dlog (MW) vs. log MW) for linear PDMAM (black), cyclic PDMAM (red), and the corresponding log-normal distribution simulation (blue dash). The arrow indicates the low molecular weight integration limit of the used GPC. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

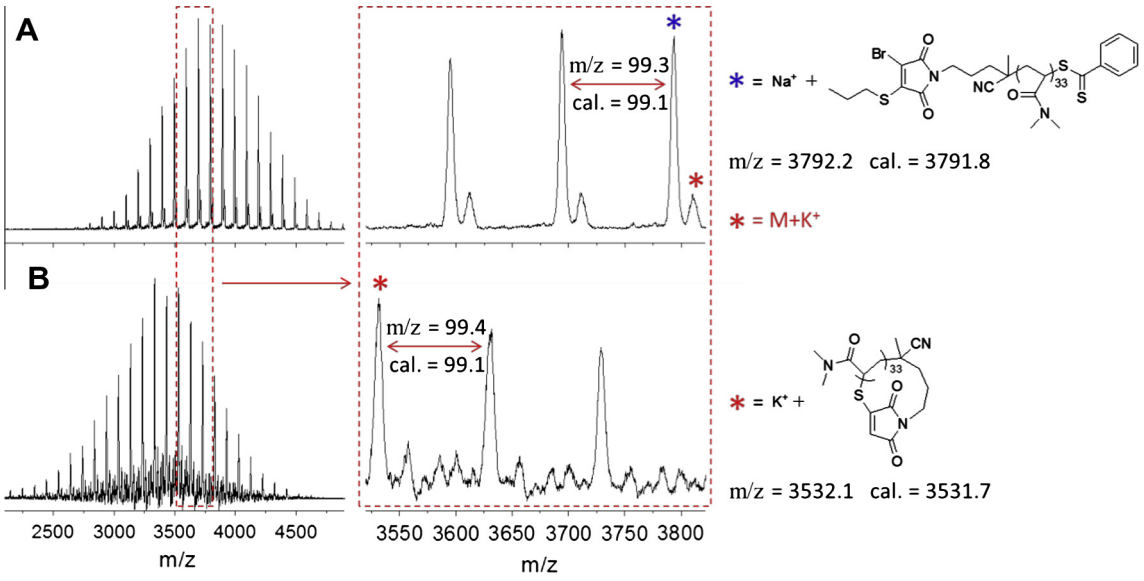

Fig. 5. MALDI-TOF mass spectra for linear PDMAM precursor and the corresponding cyclic PDMAM.

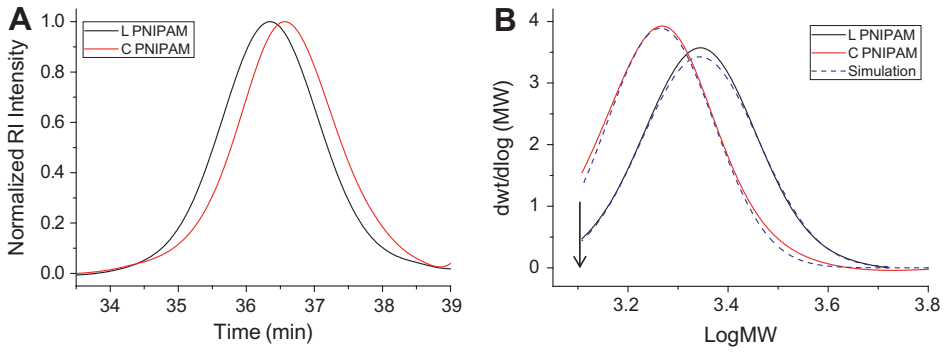

Fig. 6. (A) The GPC data (normalized RI intensity vs. time) for linear PNIPAM (black) and cyclic PDMAM (red). (B) The GPC data (dwt/dlog (MW) vs. log MW) for linear PNIPAM (black), cyclic PNIPAM (red), and the corresponding log-normal distribution simulation (blue dash). The arrow indicates the lowmolecular weight integration limit of the used GPC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion

We developed a unique ring-closure method for the preparation of water soluble cyclic polymers in this paper. As the first step, the functional RAFT agent **1** was designed and used to produce well-defined water soluble linear polymers, such as PDMAM and PNIPAM, by a standard RAFT polymerization technique. At the second step, when dissolving the linear precursors in the environmentally benign solvent water with a high dilution, the reducing agent $NaBH_4$ was used to cleave the dithiobenzoate group and release the thiol group at the end of polymer chain. The well-defined water soluble cyclic polymers were then obtained by an in situ ring-closure process from the efficient bromomaleimide-thiol substitution reaction. Since the linear polymer precursors were produced by the standard RAFT polymerization and the subsequent ring-closure process was carried out at an extremely mild reaction condition, we expect that this novel technique could become one of the basic tools for producing various well-defined water soluble cyclic polymers. In addition, inspired by the success for preparing monocyclic polymers, the preparation of varied water soluble cyclic polymer derivatives, such as tadpole and eight shape topological polymers, are exploring in our group based on the same chemistry.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.reactfunctpolym.2013. 11.006.

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