Controllably Growing Topologies in One-shot RAFT Polymerization via Macro-latent Monomer Strategy

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Abstract The controlled and efficient synthesis of polymers with tailored topologies is challenging but important for exploring structure/property research. Herein, we proposed a concept of macro-latent monomer to achieve the controlled growth of polymer topologies. The macro-latent monomer was installed by a dynamic furan/maleimide covalent bond at the chain terminal. One-shot reversible addition-fragmentation chain transfer (RAFT) polymerization of styrene and the macro-latent monomer created controlled growth of polymer topologies. Low temperature such as 40 °C could not activate the macro-latent monomer and thus the polymerization created the homo-polystyrene. By contrast, high temperature of ~110 °C activated the macro-latent monomer, and a maleimide-terminated macro-monomer was released via the retro-Diels Alder reaction. This macro-monomer immediately joined the cross polymerization with styrene and thus produced the side chains. By delicately manipulating the polymerization temperature, the predetermined placement of the macro-latent monomer-derived polymeric side-chains created controllably growing topologies, including star-, n-shaped, and density-variable grafting copolymers. This work paved a new way for creating on-demand topologies and would greatly enrich the topology synthesis.

Keywords Latent monomer; Diels-Alder reaction; Maleimide; Styrene; Topologies

INTRODUCTION

The research on structure/property relationship and developing novel polymeric material is always the central research topic in polymer science. Topological polymers, such as cyclic, grafting, stars, dendrimer, etc., have aroused more and more attention because of their unique properties and thus specific applications. For example, compared with the linear counterparts, the cyclic polymers usually exhibit more compact hydrodynamic volume, lower viscosity, and higher glass transition temperature due to the endless architecture. The grafting copolymer and brush-like copolymers often possess unique and variable physical properties depending on the grafting density and the length of the side chains, which can be used as drug-delivery materials, rheology control agents, supersons elastomers, biosensors, nanowires, and lubricants. Dendritic polymer has been used as a commercial viscosity-reducing agent for improving the polymer processing due to its compact structure, high branching, and maximized terminal groups. For the structure/property research and potential applications, the controlled synthesis of on-demand topological polymers is a perquisite and crucial procedure, which, however, is sometimes challenging due to the uncontrollable intra-(inter)molecular reactions, and tedious steps including synthesis, purifications, and characterizations. To produce topological polymers via optimized and minimized synthetic procedures, scientists have made tremendous efforts and proposed the concept of transformable topologies. For example, Tezuka et al. developed the topological transformation from cyclic polyoctides to linear one by introducing the photo-cleavable o-nitrobenzyl group into the cyclic backbone. Upon photo irradiation, the o-nitrobenzyl group was cleaved to produce the linear counterpart with the same chain length and composition, but distinct properties. The convenient and effective transformation from linear to liquid and then cyclic topology was elegantly demonstrated by Takata et al. based on the rotaxane protocol by using a movable rotaxane unit in the linear backbone. The reversible topology transformation was also realized by using dynamic covalent bonds. Perrier et al. and Deffieux et al. incorporated the dynamic disulfide or iron tetraphenyl-porphyrin...
in the cyclic polymer, which can reversibly switch between linear and cyclic topology by manipulating the polymer concentration and reducing/oxidation atmosphere.\cite{38,39} Tezuka et al. and Zhao et al. demonstrated the light/heat induced reversible linear-cyclic topological conversion of polymers with terminal anthryl or coumarinyl end groups.\cite{38,39} Sumerlin et al. cleverly proposed the concept of macromolecular metamorphosis for topology transformation. Transformable polymers were equipped by the thermally labile furan/maleimide bonds, which were cleaved at elevated temperatures. Upon reacting with anthracene-containing templates, the released maleimide groups subsequently formed maleimide/anthracene cycloadducts, resulting in transitions in polymer architecture including transformation from an amphiphilic block copolymer to comb polymer, hydrophobic block copolymer, and star polymer, as well as from a segmented hyperbranched polymer to hydrophobic block copolymer and comb polymer.\cite{40,41} All these efforts have endowed effective approaches to achieve diverse topologies. However, toward the vast diversity of polymer topology and composition, the pursuit of versatile and efficient approaches to prepare the topological polymer has never stopped.

In recent years, our group proposed the concept of latent monomer for sequence control, which was demonstrated by using the furan protected maleimide as the latent monomer.\cite{42-45} The latent monomer cannot undergo radical polymerization. However, under high temperature (~110 °C), it can release maleimide via the retro Diels-Alder reaction. The released maleimide immediately copolymerizes with styrene via controlled radical polymerization, thus resulting in the segment with incorporated maleimide units. However, under ~40 °C, the retro Diels-Alder reaction cannot happen and no maleimide is released. The programmable changes of the polymerization temperature thus create the on-demand placements of maleimide units along the “living” polymer chain, and the sequence control is realized.\cite{46} Inspired by the latent monomer strategy, herein, we proposed a facile approach for creating controllably growing topologies by using macro-latent monomers via one-shot/one-pot controlled radical polymerization. By delicately manipulating the polymerization temperature, the predetermined installments of the macro-latent monomer-derived polymeric side-chains created controllably growing topologies, including star-, \(\pi\)-shaped and density-variable grafting copolymers (Scheme 1).

The “living” chain growth with simultaneous and controlled topology can be deliberately governed by many factors, including polymerization temperature, polymerization time for each temperature slot, and feed ratio of co-monomers. Therefore, this work paved a new way for facilely and efficiently creating on-demand topologies and greatly enriched the topology synthesis.

**EXPERIMENTAL**

**Materials**

All moisture/oxygen sensitive reactions were performed using standard glove box or Schlenk techniques under \(N_2\). Styrene (St, Sinopharm Chemical Reagent, 99%) and methyl methacrylate (MMA, Sinopharm Chemical Reagents, 99%) were inhibited during storage, and the inhibitor was removed by alkaline aluminum oxide column chromatography. 2,2-Azobisobutyronitrile (AIBN), 2,2′-azobis-(2,4-dimethylvaleronitrile) (ABVN), and 1,1′-azobis(cyclohexanecarbonitrile) (ACCN) were purchased from Sinopharm Chemical Reagent, China (98%) and purified by recrystallization from ethanol. 2-Cyanoprop-2-yl-1-dithionaphthalate (CPDN) was synthesized according to literature.\cite{46} Cuprous bromide (CuBr, Aldrich, 98%) was freshly purified by stirring in dilute acetic acid overnight, washing with ethanol, and drying under vacuum. N,N′,N″,N″′-pentamethyldiethylene-triamine (PMDETA, Energy Chemical, 99%), disiopropyl azodiformate (DIAD, 3A Chemicals, 98%), polyethylene glycol monomethyl ether (PEG-OH, TCI, average \(M_n=2000\) g/mol), N-methylmaleimide (MMI, Aldrich, 98%), 1,3,5-tri-tert-butylbenzene (TBB, energy chemical, 98%), and triphenylphosphine (PPh\(_3\), Adamas, 99%) were used as received. Furan, maleic anhydride, anhydrous ether, methanol, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and all other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. and used as received without any further purification. Tetrahydrofuran (THF), dichloromethane (DCM), N,N-dimethylformamide (DMF), and toluene were purified by passing through a purification column (Solvent Dispensing System; glass contour).

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**Scheme 1** Schematic diagram of the controllably growing topology in one-shot “living” polymerization by macro-latent monomer strategy.

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Analysis Techniques
The number-average molecular weight ($M_n$) and polydispersity index ($D = M_w/M_n$) of the polymers were determined using a size exclusion chromatograph (SEC) TOSOH HLC-8320 equipped with refractive index and UV detectors using two TSKgel Super 20 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 of 500−1×10^3 g/mol. THF or DMF was used as the eluent at a flow rate of 0.35 mL/min at 40 °C. Data acquisition was performed using EcoSEC software and molecular weights were calculated with polystyrene (PS) standards.

Proton nuclear magnetic resonance (1H-NMR) spectra of all samples were collected by a Bruker nuclear magnetic resonance instrument (300 MHz) using tetramethylsilane (TMS) as the internal standard at room temperature. NMR samples were prepared and tested in a raw sample with concentrations of 10−20 mg/mL in CDCl$_3$ or DMSO-d$_6$. The 1H-NMR spectra were referenced to δ 7.26 ppm in CDCl$_3$ or δ 2.54 ppm in DMSO-d$_6$.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on an UltraflexTM MALDI-TOF mass spectrometer equipped with a 1 kHz smart beam-II laser. The instrument was calibrated prior to each measurement with external poly(methyl methacrylate) (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 at a ratio of 10/1 (V/V). All samples were dissolved in chloroform 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.

Synthesis of Macro-latent Monomers

Synthesis of furan/maleimide adduct containing initiator (FMBr)$^{[47]}$
FMBr was synthesized according to Ref. [47] (Fig. S1 in the electronic supplementary information, ESI).

Synthesis of macro-latent monomer based on homo-poly(styrene) (M-PS)
St (50 mL, 436.6 mmol), FMBr (1.559 g, 4.366 mmol), CuBr (619.3 mg, 4.366 mmol), and PMDETA (1513.3 mg, 1484 μL, 8.732 mmol) were placed in a 100 mL Schlenk flask. After three freeze-pump-thaw cycles, the mixture was filled with argon, immersed in a water bath preheated at 45 °C, and stirred for 5 h. Then the reaction was terminated by cooling to −24 °C. Straightway the mixture was precipitated in petroleum ether (PE) with stirring and a crude polymer was obtained after dried under reduced pressure. The crude polymer was dissolved in moderate THF to be passed through a basic Al$_2$O$_3$ chromatographic column to remove copper compounds and precipitated in PE with stirring. A white powder was obtained by extraction filtration and finally dried under reduced pressure (FM-PS, $M_{n,SEC}$=2.1 kDa, $D$=1.05 (Fig. S4 in ESI)).

Synthesis of macro-latent monomer based on poly(methyl methacrylate) (FM-PMM)
MMA (40 mL, 377.2 mmol), FMBr (1.346 g, 3.772 mmol), CuBr (54.11 mg, 0.3772 mmol), and PMDETA (130.7 mg, 156.9 μL, 0.7544 mmol) were placed in a 100 mL Schlenk flask. After three freeze-pump-thaw cycles, the flask was filled with argon, immersed in a water bath preheated at 45 °C, and stirred for 2 h. Then the reaction was terminated by cooling to −24 °C. Straightway the mixture was precipitated in petroleum ether (PE) with stirring and a crude polymer was obtained after dried under reduced pressure. The crude polymer was dissolved in moderate THF to be passed through a basic Al$_2$O$_3$ chromatographic column to remove copper compounds and precipitated in PE with stirring. A white powder was obtained by extraction filtration and finally dried under reduced pressure (FM-PMM, $M_{n,NAME}$=2358.1 g/mol). SEC results: $M_{n,SEC}$=2.6 kDa, $D$=1.09 (Fig. S5 in ESI).

Synthesis of macro-latent monomer based on poly(styrene-co-maleimide) (FM-PS-co-M)
St (50 mL, 436.4 mmol), MML (4.844 g, 43.64 mmol), FMBr (1.559 g, 4.364 mmol), CuBr (62.6 mg, 0.4364 mmol), and PMDETA (75.63 mg, 90.79 μL, 0.4364 mmol) were placed in a 100 mL Schlenk flask. After three freeze-pump-thaw cycles, the flask was filled with argon, immersed in a water bath preheated at 45 °C, and stirred for 10 h. Then the reaction was terminated by cooling to −24 °C. Straightway the mixture was precipitated in cool methanol with stirring and a crude polymer was obtained after dried under reduced pressure. The crude polymer was dissolved in moderate THF to be passed through a basic Al$_2$O$_3$ chromatographic column to remove copper compounds and then precipitated in cool methanol with stirring. A white powder was obtained by extraction filtration and finally dried under reduced pressure (FM-PS-co-M, $M_{n,NAME}$=2077.8 g/mol). SEC results: $M_{n,SEC}$=1.6 kDa, $D$=1.07 (Fig. S6 in ESI).

Synthesis of hydrophilic macro-latent monomer based on PEG (FM-PEG)
Maleimide (33.0 g, 340 mmol) was dissolved in 400 mL of toluene, and then furan (50.0 g, 735 mmol) was added to the above solution. The reaction was stirred at 90 °C for 24 h. The product was precipitated out of solution, collected via vacuum filtration, and washed with fresh toluene. The final product furan-protected maleimide was dried and collected in the form of a white solid (52.7 g, 93.9% yield).
Furan-protected maleimide (1.99 g, 12.1 mmol), PEG-OH (8.02 g, 4.01 mmol), and PPh$_3$ (1.59 g, 6.05 mmol) were added to a 100 mL round-bottom flask with 65 mL of DCM and...
cooled to 0 °C with stirring. Then, DIAD (1.25 mL, 6.05 mmol) was added dropwise to the above mixture. After standing by in ice water bath for 30 min, the reaction was stirred for 48 h at room temperature. Afterwards, the solvent was removed by reduced pressure distillation, and 50 mL of ultrapure water was added. The remaining PEG-OH, DIAD, and PPh$_3$ were washed with 100 mL of ethyl acetate and the water was removed by freeze-drying to collect crude product. The crude product was dissolved in moderate DCM and precipitated in 400 mL of anhydrous diethyl ether with stirring. A white product was dissolved in moderate DCM and precipitated in 100 mL of ethyl acetate and the water was re-

**Typical Procedures for RAFT Polymerization**

**Typical procedures for RAFT polymerization of St and M-PS at 110 °C**

The polymerization was carried out in a baked Schlenk tube under argon protection. St (2.0 mL, 17.5 mmol), M-PS (1.5277 g, 0.875 mmol), CPDN (0.0474 g, 0.175 mmol), ACCN (0.0213 g, 0.0875 mmol), and 1,3,5-tri-tert-butylbenzene (TBB) (1.699 g, 6.9 mmol) were added into a glass tube. The solvent (toluene, 2.0 mL) was added to increase the uniformity of the system and used as the internal standard in the polymerization. Then, the mixture was degassed by three freeze-pump-thaw cycles. The reaction tube was placed in an oil bath kept at 40 °C. At determined time interval, an aliquot was taken out with a syringe under argon, and the reaction was terminated by cooling to −24 °C. Immediately, monomer conversion was determined by $^1$H-NMR spectroscopy and SEC traces.

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**RESULTS AND DISCUSSION**

In this work, the macro-latent monomer was the key component for the topology growth. Several macro-latent monomers were prepared by using furan/maleimide adduct containing initiator (FMBr, Scheme S1 and Fig. S1 in ESI) for atom transfer radical polymerization (ATRP). After ATRP, the furan/maleimide adduct was installed at a terminus and thus could act as the macro-latent monomer. For example, the FMBr initiated ATRP of styrene and methyl methacrylate created the macro-latent monomer, FM-PS (Figs. S2 and S3, macro-monomer M-PS in Scheme S2 and Fig. S4 in ESI) and FM-PMMA (Fig. S5 in ESI), respectively. ATRP copolymerization of styrene and maleimide created the macro-latent monomer, FM-PS-co-M (Fig. S6 in ESI). The hydrophilic PEG based macro-latent monomer (FM-PEG) was prepared by the Mitsunobu condensation reaction of PEG terminal hydroxyl and furan/maleimide adduct (furan-protected maleimide) (Figs. S7 and S8 in ESI). The hydrophilic PEG based macro-latent monomer (FM-PEG) was prepared by the Mitsunobu condensation reaction of PEG terminal hydroxyl and furan/maleimide adduct (furan-protected maleimide) (Figs. S7 and S8 in ESI). Considering the negative effects of the steric hindrance of the side-chain on polymerization rate, the molecular weights of these macro-latent monomers were kept at about 2.0 kDa for balancing the acceptable polymerization rate and suitable side chain length. All the macro-latent monomers possessed high chain end fidelities for ensuring controlled chain growth and topology uniformities. Taking FM-PS as an example, the SEC trace presented a unimodal and narrow molecular weight distribution (1.6 kDa, $D=1.08$, Fig. S2a in ESI). $^1$H-NMR results confirmed the successful preparation of FM-PS terminated by the furan/maleimide adduct (Fig. S2b in ESI). By quantitative calculations of the integration of the methenyl proton of $\alpha$-terminated furan/maleimide adduct (b, integration=2.00) and the methylene proton of the last St unit (j, integration=1.01) capped by $\omega$-terminal bromine, the high chain end fidelity up to 99% was confirmed. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy validated the high retention of the terminal furan/maleimide adduct (the furan was detached by the imposed laser energy during the MALDI TOF mass spectrometry test), i.e., almost every chain was terminated by the furan/maleimide adduct (Fig. S3 in ESI). Having these macro-latent monomers in hand, the manipulation of the reversible addition-fragmentation chain transfer (RAFT) polymerization enabled the controlled installation of the macro-monomer at the pre-designed position along the
“living” chain. That is, the low temperature at 40 °C could not release the macro-monomer via the retro Diels-Alder reaction, so no macro-monomer was placed into the polymer chain, and the homo-PS was created. Upon the transfer of the polymerization to another oil bath stabilized at 110 °C, the macro-monomer, i.e., the maleimide-terminated polymer, was immediately released and involved into the polymerization. As a consequence, the macro-monomer was placed at desired positions and created topological polymers. The programmable and deliberate manipulations of the feed ratios of the co-monomers, the onset of temperature change, and the duration of each temperature slot created on-demand topologies. It should be noted that the RAFT polymerization was used for guaranteeing the “living” chain growth with the simultaneous topology evolution (Scheme 2).

The one-shot RAFT polymerization of St and FM-PS was firstly conducted at 110 °C. In this work, the conversion of St (Conv.\textsubscript{St}) was estimated by \textsuperscript{1}H-NMR (Fig. 1A) by calculating the change of signal integration of methylene protons of the residual St at 5.69–5.80 ppm. The signal of methyl protons in

![Scheme 2](image)

**Scheme 2** Controlled topology growth by programmable manipulations of RAFT polymerization temperature by using FM-PS as the macro-latent monomer.

![Fig. 1](image)

**Fig. 1** RAFT copolymerization of St and FM-PS. (A) \textsuperscript{1}H-NMR evolution of the raw polymerization solution with polymerization time. (B) SEC traces with polymerization time. \([\text{St}]_{0}/[\text{FM-PS}]_{0}/[\text{CPDN}]_{0}/[\text{ACCN}]_{0}=100/5/1/0.5\), St/toluene/DMF=4/3/1 (V/V/V), St=2.0 mL (17.5 mmol), temperature=110 °C, CPDN=0.175 mmol, ACCN=0.0875 mmol \((\text{Conv.}_{\text{St}} = (I_{5.69-5.80}^{0} - I_{5.69-5.80}^{t})/I_{5.69-5.80}^{0} \times 100\%\), Conv.\textsubscript{FM-PS} = \((A_{0} - A_{t})/A_{0} \times 100\%\) (Section A2 in ESI).

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toluene at 2.30 ppm was used as an internal standard. In some cases, DMF was used as a solvent for the calculation of St conversion by $^1$H-NMR. The conversions of macro-latent monomers were analyzed by the deconvolution of size exclusion chromatography (SEC) traces with 1,3,5-tri-tert-butylbenzene as the internal standard (Fig. 1B). The calculation detail is shown in Section A2 (in ESI). The results indicate the smooth growth of the "living" polymerization created the polymer with 5.9 kDa, which shifted to 10.9 kDa at 1.33 h and 12.6 kDa at 2.0 h. Finally, the polymer of 14.6 kDa was produced while only small fraction of FM-PS was left. These results implied that RAFT copolymerization maintained the “living” nature and thus ensured the topology and chain growth. It could be concluded that the macro-monomer was gradually consumed and incorporated into the “living” polymeric main chain, and the topology of the resultant polymer grew with time evolution. To clearly demonstrate the topology growth, the polymerization kinetics and the analysis of the co-monomer conversions are presented in Fig. 2. Fig. 2(a) shows that both of the co-monomers were gradually consumed, and approximately 80% of styrene and 95% of FM-PS were polymerized within 4 h. The results indicate the smooth growth of the “living” chain under 110 °C. The cumulative ($F_{\text{cum}}$) and instantaneous ($F_{\text{inst}}$) contents of styrene and M-PS are displayed in Fig. 2(b), which clearly demonstrate the statistical placements of the polymeric PS as the side chain along the growing chain, i.e., $F_{\text{inst}}$ of M-PS was approximately 5% during the whole chain growth. To further unambiguously illustrate the topology and chain growth, the SEC traces with the topology cartoons derived by $F_{\text{inst}}$ are summarized in Fig. 2(c). It should be noted that the topology of the resultant polymer was statistically deduced from the polymerization behavior, totally differing from those made by assembly or ligation of polymeric building blocks. It could be found that the topology grew from the initial linear one (2.0 kDa) to star-shape (or T-shape) (5.9 kDa), then n-shape (7.8 kDa), and finally the grafting polymer (14.6 kDa). These results confirmed the simultaneous topology and chain growth by using the macro-latent monomer strategy. By using the macro-monomer, that is, the maleimide-encapped PS with the removal of furan (M-PS), the polymerization under the identical conditions created different growth profiles compared with that with FM-PS (Fig. S9 in ESI). The macro-monomer was consumed and rapidly incorporated into the polymer because of the alternating copolymerization nature between St and maleimide. After the exhaustion of M-PS within 0.5 h, the “living” polymerization proceeded while producing the homo-PS segment. As a result, the polymerization created the topology from linear to grafting and the final tooth brush-like one. The shoulder peaks with higher molecular weights in Fig. S9 (in ESI) were caused by bi-radical terminations during the polymerization, which could be eliminated or depressed by decreasing the initiator concentration as shown in Figs. S11–S13 (in ESI).

As is well known, the retro Diels-Alder reaction for releasing polymerizable maleimide-derived macro-monomer was temperature dependent. Therefore, the growing topologies could be controllably manipulated by changing polymerization temperature. For example, the RAFT polymerization of St and FM-PS started at 40 °C. Maintaining 40 °C for 73 h, the retro Diels-Alder reaction could not be launched and thus the polymerization created the linear homo-PS segment (Fig. 3a). Then, the polymerization was quickly transferred to 110 °C. Under 110 °C, the retro Diels-Alder reaction happened and released the maleimide-encapped macro-monomer (M-PS),
which immediately participated in the copolymerization with St as shown in the polymerization kinetics (Fig. 3a). Fig. 3(b) displays the evolution of $F_{\text{cum}}$ and $F_{\text{inst}}$ of M-PS with normalized chain length, which indicates the distributions of the PS side chains along the main chain. The results indicate that after building the main-chain homo-PS segment, more and more side PS chains were gradually grafted onto the growing chain. The growing topologies were different from those without the temperature manipulation (Fig. 2b). The SEC traces clearly demonstrate the topology growth with chain evolution (Fig. 3c). The continuous release of M-PS enabled the “living” copolymerization creating the star-shaped (73 h + 25 min), $\pi$-shaped (73 h + 50 min), then tooth brush-like topology (73 h + 125 min).

Controlled topology growth could be created by deliber-

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In conclusion, the macro-latent monomer allowed the controlled topology growth. In general, the topology grew from the linear to the star, then n-, and finally grafting shape by controlled installations of the side chains along the “living” main chain. Fine topologies could be tailored by changing several polymerization factors, including the temperature mode, the duration of each temperature slot, and co-monomer feed ratios. Importantly, the macro-latent monomer can be diversified by using different chemical compositions, including homopolymer, copolymer, and hydrophilic polymers. This work provided a promising synthetic approach of topological copolymers via a one-shot and controlled manner, and thus greatly enriched the research of topological polymers.

Electronic Supplementary Information
Electronic supplementary information (ESI) is available free of charge in the online version of this article https://doi.org/10.1007/s10118-020-2463-1.

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REFERENCES

1. Huang, Z. H.; Zhou, Y. Y.; Wang, Z. M.; Li, Y.; Zhang, W.; Zhou, N. C.; Zhang, Z. B.; Zhu, X. L. Recent advances of CuAAC click reaction in building cyclic polymer. Chinese J. Polym. Sci. 2017, 35, 317–341.

2. Tang, H.; Tang, J.; Shen, Y.; Guo, W. X.; Zhou, M.; Wang, R. H.; Jiang, N.; Gan, Z. H.; Yu, Q. S. Comb-like poly(N-(2-hydroxypropyl) methacrylamide) doxorubicin conjugates: the influence of polymer architecture and composition on the biological properties. Chinese J. Polym. Sci. 2018, 36, 1225–1238.

3. Endo, K. Synthesis and properties of cyclic polymers. Adv. Polym. Sci. 2008, 217, 121–183.

4. Hoskins, J. N.; Grayson, S. M. Synthesis and degradation behavior of cyclic poly(ε-caprolactone). Macromolecules 2009, 42, 6406–6413.

5. Kricheldorf, H. R. Cyclic polymers: synthetic strategies and physical properties. J. Polym. Sci., Part A: Polym. Chem. 2010, 48, 251–284.

6. Yamamoto, T.; Tezuka, Y. Topological polymer chemistry: a cyclic approach toward novel polymer properties and functions. Polym. Chem. 2011, 2, 1930–1941.

7. Qiu, X. P.; Tanaka, F.; Winnik, F. M. Temperature-induced phase transition of well-defined cyclic poly(ε-isopropylacrylamide) in aqueous solution. Macromolecules 2007, 40, 7069–7071.

8. Lee, C. U.; Li, A.; Ghale, K.; Zhang, D. Crystallization and melting behaviors of cyclic and linear polypeptides with alkyl side chains. Macromolecules 2013, 46, 8213–8223.

9. Shin, E. J.; Jeong, W.; Brown, H. A.; Koo, B. J.; Hedrick, J. L.; Waymouth, R. M. Crystallization of cyclic polymers: synthesis and crystallization behavior of high molecular weight cyclic poly(ε-caprolactone). Macromolecules 2011, 44, 2773–2779.

10. Chen, R.; Nossarev, G. G.; Hogen-Esch, T. E. Synthesis and thermal and spectroscopic properties of macrocyclic vinyl aromatic polymers. J. Polym. Sci., Part A: Polym. Chem. 2004, 42, 5488–5503.

11. Zhang, S. S.; Cheng, X. X.; Wang, J. Z.; Zhang, Z. B.; Zhang, W.; Zhu, X. L. Synthesis of a cyclic-brush polymer with a high grafting density using activated ester chemistry via the “grafting onto” approach. Polym. Chem. 2018, 9, 5155–5163.

12. Zhang, S. S.; Tezuka, Y.; Zhang, Z. B.; Li, N.; Zhang, W.; Zhu, X. L. Recent advances in the construction of cyclic grafted polymers and their potential applications. Polym. Chem. 2018, 9, 677–686.

13. Lee, H. I.; Pietrasik, J.; Sheiko, S. S.; Matyjaszewski, K. Stimuli-responsive molecular brushes. Prog. Polym. Sci. 2010, 35, 24–44.

14. McKee, M. G.; Unal, S.; Wilkes, G. L.; Long, T. E. Branched polystyrenes: recent advances in synthesis and performance. Prog. Polym. Sci. 2005, 30, 507–539.

15. Sheiko, S. S.; Sumerlin, B. S.; Matyjaszewski, K. Cylindrical molecular brushes: synthesis, characterization, and properties. Prog. Polym. Sci. 2008, 33, 759–785.

16. Zhang, M. F.; Müller, A. H. E. Cylindrical polymer brushes. J. Polym. Sci., Part A: Polym. Chem. 2005, 43, 3461–3481.

17. Feng, C.; Li, Y. J.; Yang, D.; Hu, J. H.; Zhang, X. H.; Huang, X. Y. Well-defined graft copolymers: from controlled synthesis to multipurpose applications. Chem. Soc. Rev. 2011, 40, 1282–1295.

18. Tan, H. G.; Xia, G.; Liu, L. X.; Niu, X. H.; Hao, Q. H. Surface patterns of a tetrahedral polyelectrolyte brush induced by grafting density and charge fraction. Chinese J. Polym. Sci. 2020, 38, 394–402.

19. Han, X. H.; Yang, X. W.; Chen, S.; Luo, H.; Zhang, D.; Zhang, H. L. Multiple effects tailoring the self-organization behaviors of triphenylene side-chain liquid crystalline polymers via changing the spacer length. Chinese J. Polym. Sci. 2018, 36, 960–969.

20. Johnson, J. A.; Lu, Y. Y.; Burts, A. O.; Xia, Y.; Durrell, A. C.; Tirrell, D. A.; Grubbs, R. H. Drug-loaded, bivalent-bottle-brush polymers by graft-through ROMP. Macromolecules 2010, 43, 10326–10335.

21. Hawker, C. J. Architectural control in living free-radical polymerizations—preparation of star and graft polymers. Angew. Chem. Int. Ed. 1995, 34, 1456–1459.

22. Pakula, T.; Zhang, Y.; Matyjaszewski, K.; Lee, H. I.; Boerner, H.; Qin, S.; Berry, G. C. Molecular brushes as super-soft elastomers. Polymer 2006, 47, 7198–7206.

23. Chen, J.; Huang, Z. Y. Elastic behavior of comb-like polymer chains. Chinese J. Polym. Sci. 2010, 28, 311–322.

24. Heinrich, C. D.; Thelakkat, M. Poly(3-hexylthiophene) bottlebrush copolymers with tailored side-chain lengths and high charge carrier mobilities. J. Mater. Chem. 2016, 4, 5370–5378.

25. Yuan, J. Y.; Xu, Y. Y.; Walther, A.; Bollisetty, S.; Schumacher, M.; Schmalz, H.; Ballauff, M.; Müller, A. H. E. Water-soluble organo-silica hybrid nanowires. Nat. Mater. 2008, 7, 718–722.

26. Lee, S.; Spencer, N. D. Poly(L-lysine)-graft-poly(ethylene glycol): a versatile aqueous lubricant additive for tribosystems involving thermoplastics. Lubr. Sci. 2008, 20, 21–34.

27. Kobayashi, M.; Terayama, Y.; Hosaka, N.; Kaido, M.; Suzuki, A.; Yamada, N.; Tonikai, N.; Ishihara, K.; Takahara, A. Friction behavior of high-density poly(2-methacryloyloxyethyl phosphorylcholine) brush in aqueous media. Soft Matter 2007, 3, 740–746.

28. Hong, C. Y.; You, Y. Z.; Liu, J.; Pan, C. Y. Dendrimer-star polymer and block copolymer prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization with dendritic chain transfer agent. J. Polym. Sci., Part A: Polym. Chem. 2005, 43, 6379–6393.

29. Tomalia, D. A.; Fréchet, J. M. J. Discovery of dendrimers and dendritic polymers: a brief historical perspective. J. Polym. Sci., Part A: Polym. Chem. 2002, 40, 2719–2728.

30. Sun, H.; Kabb, C. P.; Sims, M. B.; Sumerlin, B. S. Architecture-transformable polymers: reshaping the future of stimuli-responsive polymers. Prog. Polym. Sci. 2019, 89, 61–75.

31. Naoto, S.; Asai, S.; Tezuka, Y.; Yamamoto, T. Photoinduced topological transformation of cyclized polylactides for switching the properties of homocrypts and stereocomplexes. Polym. Chem. 2015, 6, 3591–3600.

32. Mo, B.; Liu, H.; Zhou, X.; Zhao, Y. Facile synthesis of photolabile dendritic-unit-bridged hyperbranched graft copolymers for stimulus-triggered topological transition and controlled release of Nile red. Polym. Chem. 2015, 6, 3489–3501.

33. Aoki, D.; Albara, G.; Uchida, S.; Takata, T. A rational entry to cyclic polymers via selective cyclization by self-assembly and topology transformation of linear polymers. J. Am. Chem. Soc. 2017, 139, 6691–6794.

34. Ogawa, T.; Nakazono, K.; Aoki, D.; Uchida, S.; Takata, T. Effective approach to cyclic polymer from linear polymer: synthesis and transformation of macromolecular [1]Rotaxane. ACS Macro Lett. 2015, 4, 343–347.

35. Aoki, D.; Uchida, S.; Takata, T. Star/linear polymer topology transformation facilitated by mechanical linking of polymer chains. Angew. Chem. Int. Ed. 2015, 54, 6770–6774.

36. Whittaker, M. R.; Goh, Y. K.; Gernici, H.; Legge, T. M.; Perrier, S.; Monteiro, M. J. Synthesis of monocyclic and linear polystyrenes using the reversible coupling/cleavage of thiol/disulfide groups. Macromolecules 2006, 39, 9028–9034.

37. Schappacher, M.; Deffieux, A. Reversible switching between linear and ring poly(EOs) bearing iron tetraphenylporphin rings triggered by solvent, pH, or redox stimuli. Macromolecules 2011, 44, 4503–4510.

38. Yamamoto, T.; Yagyu, S.; Tezuka, Y. Light- and heat-triggered reversible linear-cyclic topological conversion of telechelic polymers with anhydrol end groups. J. Am. Chem. Soc. 2016, 138, 3904–3911.

39. Zhao, Y.; Tremblay, L.; Zhao, Y. Phototunable LCST of water-
soluble polymers: exploring a topological Effect. Macromolecules 2011, 44, 4007–4011.
40 Sun, H.; Kabb, C. P.; Dai, Y.; Hill, M. R.; Ghiviriga, I.; Bapat, A. P.; Sumerlin, B. S. Macromolecular metamorphosis via stimulus-induced transformations of polymer architecture. Nat. Chem. 2017, 9, 817–823.
41 Bapat, A. P.; Ray, J. G.; Savin, D. A.; Hoff, E. A.; Patton, D. L.; Sumerlin, B. S. Dynamic-covalent nanostructures prepared by Diels-Alder reactions of styrene-maleic anhydride-derived copolymers obtained by one-step cascade block copolymerization. Polym. Chem. 2012, 3, 3112–3120.
42 Ji, Y.; Zhang, L.; Gu, X.; Zhang, W.; Zhou, N.; Zhang, Z.; Zhu, X. Sequence-controlled polymers with furan-protected maleimide as a latent monomer. Angew. Chem. Int. Ed. 2017, 56, 2328–2333.
43 Gu, X.; Zhang, L. Q.; Li, Y.; Zhang, W.; Zhu, J.; Zhang, Z. B.; Zhu, X. L. Facile synthesis of advanced gradient polymers with sequence control using furan-protected maleimide as a comonomer. Polym. Chem. 2018, 9, 1571–1576.
44 Meng, F. Y.; Zhang, Y. J.; Ding, K. S.; Liu, B. L.; Han, F. F.; He, Y. Y.; Zhou, N. C.; Zhang, Z. B.; Zhu, X. L. One-shot synthesis of sequence-controlled polymers with versatile succinimide motifs for post-modifications. React. Funct. Polym. 2019, 134, 67–73.
45 Zhang, L. Q.; Ji, Y. X.; Gu, X.; Zhang, W.; Zhou, N. C.; Zhang, Z. B.; Zhu, X. L. Synthesis of sequence-controlled polymers with pendant “clickable” or hydrophilic groups via latent monomer strategy. React. Funct. Polym. 2019, 138, 96–103.
46 Zhu, J.; Zhu, X. L.; Kang, E. T.; Neoh, K. G. Design and synthesis of star polymers with hetero-arms by the combination of controlled radical polymerizations and click chemistry. Polymer 2007, 48, 6992–6999.
47 Li, Y.; Zhou, Y. Y.; Zhou, Y.; Yu, Q.; Zhu, J.; Zhou, N. C.; Zhang, Z. B.; Zhu, X. L. Dynamic furan/maleimide bond-incorporated cyclic polymer for topology transformation. React. Funct. Polym. 2017, 116, 41–48.
48 Glassner, M.; Blinco, J. P.; Barner-Kowollik, C. Formation of nanoporous materials via mild retro-Diels-Alder chemistry. Polym. Chem. 2011, 2, 83–87.
49 Behrendt, F. N.; Schlaad, H. Metathesis polymerization of cystine-based macrocycles. Polym. Chem. 2017, 8, 366–369.
50 Pfeifer, S.; Lutz, J. F. A facile procedure for controlling monomer sequence distribution in radical chain polymerizations. J. Am. Chem. Soc. 2007, 129, 9542–9543.

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