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ARTICLE

Suzuki Coupling Reaction as Post-Polymerization Modification: A Promising Protocol for Construction of Cyclic-Brush Polymers and More

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Cyclic poly(4-bromostyrene) (*c*-PBrS), synthesized *via* combination of atom transfer radical polymerization (ATRP) and copper(I)-catalyzed azide_alkyne cycloaddition (CuAAC), was employed as a universal cyclic precursor to prepare cyclic-brush polymers by Suzuki coupling reaction. Cyclic functional poly[(4-methoxyphenyl)styrene] and cyclic-brush polystyrene have been achieved by Suzuki coupling reaction as post-modification, endowing excellent modification efficiency (~100%), *i.e.*, all the repeat units have been completely transformed to target ones. The obtained polymer structures were carefully characterized by NMR, GPC and MALDI-TOF mass spectra. This study undoubtedly offers a highly efficient and promising post-modification protocol to prepare the cyclic-brush polymers or more complex ones, the preparation of which is originally high challenging.

INTRODUCTION

Cyclic polymer as one of the oldest macromolecules, together with their derivative architectures with inherent cyclic topologies, are going through a reinvigoration due to the great development in organic synthesis and polymer chemistry.[1] Cyclic polymers with unique endless molecular topology have intrigued chemists by their unique physical properties from their linear counterparts, including a smaller hydrodynamic volume, less chain entanglement, higher thermostability, lower melt point as well as a different diffusion mode.[1] As well known, ring-closure and ring expansion methods, as two main synthetic strategies for cyclic polymers, have their respective pros and cros and supplement each other in the preparation of cyclic polymers including cyclic polystyrene,[2a] polyacrylate,[2b] polyester[2c] and polynorbornene,[2d] and complex cyclic topologies like theta,[3a] eight,[3a] tadpole,[3b] block[3c] shapes. Recent studies endow the cyclic polymers with more diverse topological structures, including manacle-shaped cyclic polymers, bridged- and spiro-type multicyclic polymers.[3d] These expansions of topological architectures are envisaged to endow the cyclic polymers with unique properties or functions.

Post-polymerization modification of polymer is considered as a powerful strategy for implanting the polymer precursors with various architectures and functionalities.[4] In this respect, several efficient organic reactions, such as Michael-type addition,[5] amine reaction with active esters[6] and Huisgen 1,3-dipolar cycloaddtion reaction[7] were reported successfully to functionalize polymer precursors. By introducing post-polymerization modification into the synthesis of cyclic polymers, a variety of topological cyclic polymers can be constructed. For example, Zhang and Tew *et al.* judiciously used thiol-ene chemistry to link the cyclic poly(5-hydroxy-1-cyclooctene) to produce the novel cyclic polymer gels.[8] CuAAC and nucleophilic substitution of activated esters with amines were also implemented to construct functionalized polymers, for example, comb-like cyclic polymers, cyclic gels and cyclic dendronized polymers.[9] Furthermore, metallo-supramolecular interaction inducing formation of metallo-supramolecular cyclic polymers was also successfully achieved.[10] More recently, cyclic-brush polymers and gels from cyclic polymer precursor were introduced by triazabicyclodecene-catalyzed cyclic ester ring-opening polymerization.[11] These examples undoubtedly proved that the post-polymerization modification was a powerful protocol for building cyclic-based topological polymer. It is noteworthy that the chemical reaction used for post-polymerization modification must be highly efficient to guarantee the uniform of the formed architecture, as summarized by Klok *et al.*.[12] Therefore, the utilization of high efficient reactions for post-polymerization modification of cyclic polymer can not only enrich the architectures of cyclic topological polymers, but also enabling these polymers with novel functions. Suzuki coupling reaction, which formed new carbon-carbon (C-C) bonds, showed high efficiency in post-functionlization of the precursor polymers. Holdcroft *et al.* reported that the poly(3-bromo-4-hexylthiophene)

was conveniently functionalized *via* the Suzuki coupling reaction with high efficiency (>99%) with respect to that Heck coupling reaction (29-51%).[13] Up to now, the post polymerization modifications of cyclic polymers via Suzuki coupling reaction have not been achieved.

Herein, we report the modular constructions of cyclic-brush polymers by utilizing Suzuki coupling reaction for post-polymerization modification. The cyclic polymer precursor, cyclic

PBrS (*c*-PBrS), was synthesized by combining ATRP and CuAAC intermolecular ring closure. The post-polymerization modifications of *c*-PBrS to cyclic poly[(4-methoxyphenyl)styrene] (*c*-PMOPS) and cyclic-brush polymer (*c*-PS-*g*-PS) are successfully achieved with high efficiency by Suzuki coupling reaction, as illustrated in Scheme 1. The current study provided a promising protocol for efficient preparations of cyclic-brush polymers or other complex topological cyclic-based polymers.

Scheme 1 Synthetic routes for the cyclic functional polymer poly[(4-methoxyphenyl)styrene] and cyclic polymer brush[a].
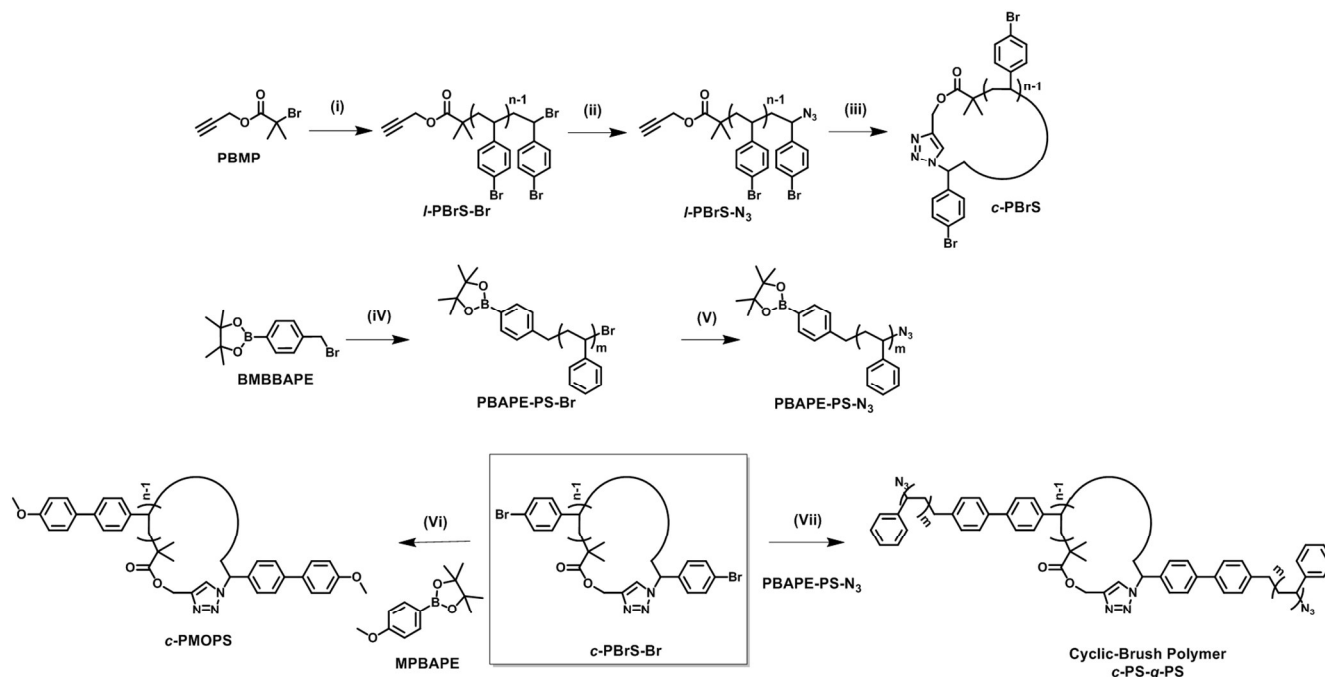
[a]Reaction conditions: (i) BrSt, CuBr$_2$, AsAc, PMDETA, anisole, 90 °C, 140 min, 25%; (ii) NaN$_3$, DMF, 25 °C, 84%; (iii) CuBr, PMDETA, toluene, 60 °C, 66%; (iv) St, CuBr, bpy, toluene, 110 °C, 14%; (v) NaN$_3$, DMF, 25 °C, 83%; (vi) Pd(PPh$_3$)$_4$, K$_2$CO$_3$ (2 M; aq), THF, 80 °C, 84%; (vii) Pd(PPh$_3$)$_4$, K$_2$CO$_3$ (2 M; aq), THF, 80 °C.

Experimental section

Materials. 4-Bromostyrene (BrSt, 99%, J&K Chemical) and styrene (St, 99%, Sinopharm Chemical Reagent Co., Ltd.) were dried over CaH$_2$ and purified by distillation under reduced pressure. Cuprous bromide (CuBr, Aldrich, 98%) was freshly purified by stirring in glacial acetic acid overnight, washed with ethanol, and dried in vacuum. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA, 99%, Energy Chemical) was dried with 4Å molecular sieves and distilled under vacuum. Sodium azide (NaN$_3$, ≥ 99.5%, Sigma-Aldrich), ascorbic acid (AsAc, 99.7%, Sinopharm Chemical Reagent Co., Ltd.), 4-bromotoluene (AR, Sinopharm Chemical Reagent Co., Ltd.), 4-methoxyphenylboronic acid pinacol ester (99%, Su Kailu chemical technology Co., Ltd.), 4-(bromomethyl)benzeneboronic acid pinacol ester (98%, Su Kailu Chemical Reagent Co., Ltd.) and tetrakis(triphenylphosphine)-palladium(0) (97.0%, TCI) were used as received. All solvents were dried with 4Å molecular sieves before use. Other chemicals were purchased from Shanghai Chemical Reagent Co. Ltd., China and used without further purification except mentioned specifically. The synthesis and characterization of prop-2-

yn-1-yl 2-bromo-2-methylpropanoate (PBMP) was described in the Supporting Information.

Characterization. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz) with CDCl$_3$, DMSO-d_6 and THF-d_8 as solvent and tetramethylsilane(TMS) as an internal standard. The number-average molecular weight (M_n) and polydispersity ($Đ = M_w/M_n$) of polymers were obtained by a HLC-8320 SEC (TOSOH) equipped with a refractive index detector. The SEC was performed using THF as the eluent at a flow rate of 0.35 mL/min and 40 °C on two TSKgel Super Mutipore HZ-N columns (4.6 × 150 mm, 3 μm particle size) in series with molecular weights ranging from $7 \times 10^2 - 2 \times 10^5$ g/mol. The PS standards purchased from TOSOH were used as the calibration. Crude polymer was purified by an Agilent PL-50 preparative SEC system equipped with a manual injector and differential refractive index detector in THF at 40 °C (flow rate: 3 mL/min) on a PLgel 10 μm MIXED-D, 300 × 25 mm preparative SEC column. The THF solution of dried crude polymer at 15-20 mg/mL concentration was filtered through a 0.45 μm PTFE syringe filter prior to inject. Different fractions were collected manually and analyzed by the TOSOH HLC-8320 SEC as described above. FT-IR spectra were

recorded on a Bruker TENSOR-27 FT-IR spectrometer using KBr disk method. GC analysis was performed on Varian CP3800 with a flame ionization detector equipped with HP-5 capillary (internal diameter = 0.25 mm, length = 30 m). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra was collected on a Bruker UltrafleXtreme (MALDI-TOF/TOF) mass spectrometer equipped with a 1 kHz smart beam-II laser. Both matrix (2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB)) (20 mg/mL) and all samples (10 mg/mL) were dissolved in chloroform, respectively. The cationizing agent sodium trifluoroacetate was dissolved in ethanol (10 mg/mL). The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). Differential scanning calorimetry (DSC) was performed at heating and cooling rates of 10 °C/min with a limited temperature from 0 °C – 200 °C on a 200Q differential scanning calorimeter (TA Instruments), and the glass transition temperature (T_g) was measured on the third cycle of a heat/cool/heat experiment.

Synthesis of Linear Poly(4-bromostyrene) (*l*-PBrS-Br). Freshly distilled 4-bromostyrene (15.93 g, 87.0 mmol), PBMP (178.4 mg, 0.87 mmol), CuBr$_2$ (55.8 mg, 0.25 mmol), PMDETA (86 mg, 0.50 mmol), AsAc (87.5 mg, 0.50 mmol) and anisole (10 mL) were added to a 25 mL Schlenk flask. This reaction mixture was degassed by three freeze-pump-thaw cycles, sealed under N$_2$, and heated at 90 °C with stirring for 140 min. The reaction was quenched by cooling the reaction mixture to 0 °C and diluted with 2 mL THF. The copper salts were removed by passage through a short neutral alumina column. After the solvent was removed, the concentrated product was precipitated into an excess of methanol twice, isolated by filtration. Drying under vacuum afforded the polymer as a white powder (4.03 g, 25%). $M_{n,NMR}$ = 5.6 kg/mol. SEC results: $M_{n,SEC}$ = 3.8 kg/mol, $M_{w,SEC}$ = 4.0 kg/mol, Đ = 1.05.

Synthesis of *l*-PBrS-N$_3$. *l*-PBrS-Br (1.00 g, 0.179 mmol) was loaded into a 25 mL round bottomed flask along with NaN$_3$ (0.24 g, 3.58 mmol) and DMF (10 mL). The solution was allowed to stir at room temperature for 24 h, filtered through a short neutral alumina column prior to precipitation into methanol, and followed by filtrating and dried *in vacuo* at 25 °C to give a white solid (0.84 g; Yield: 84%). $M_{n,NMR}$ = 5.6 kg/mol, $M_{n,SEC}$ = 3.9 kg/mol, $M_{w,SEC}$ = 4.1 kg/mol, Đ = 1.05.

Synthesis of *c*-PBrS. Toluene (850 mL) were loaded into a 1000 mL three-necked round-bottom flask equipped with a magnetic stirrer, sparged with argon for at least 0.5 h. CuBr (282 mg, 1.97 mmol) and PMDETA (618 μL, 2.95 mmol) were introduced into the flask under protection of argon flow in order. The *l*-PBrS-N$_3$ (150 mg, 2.68 × 10^{-2} mmol) in 20 mL of toluene were bubble with argon for at least 15 min and added to CuBr/PMDETA mixture at 60 °C via syringe pump at a rate of 0.6 mL/h under the protection of argon flow. After the addition of the polymer solution, the reaction mixture was further stirred for 24 h. After cooling, the copper salts were removed by passage through a short column of silica gel. After drained off toluene, the column was eluted by THF to collect the crude mixture. The mixture was evaporated, precipitated into methanol and isolated by vacuum filtration. Drying under vacuum afforded the polymer as a white powder (0.12 g, yield: 80%). The crude polymer was purified by preparative SEC (yield: 66%).

$M_{n,NMR}$ = 5.6 kg/mol, $M_{n,SEC}$ = 3.3 kg/mol, $M_{w,SEC}$ = 3.4 kg/mol, Đ = 1.04.

Synthesis of 4-methoxy-4'-methyl-1,1'-biphenyl (MMBP). 4-Bromotoluene (431.0 mg, 2.52 mmol) and 4-methoxyphenylboronic acid pinacol ester (MPBAPE) (884.9 mg, 3.78 mmol) was loaded into a 50 mL round bottomed flask along with THF (21 mL) and K$_2$CO$_3$ aqueous solution (2.0 M, 10.5 mL), sparged with argon for at least 30 min, and heated at 80 °C with stirring. Pd(PPh$_3$)$_4$ (43.7 mg, 3.78×10^{-2} mmol) were introduced into the flask under protection of argon flow. The liquid products were analyzed using an Varian CP3800 GC with a HP-5 capillary every two hour. The solution was allowed to stir for 9 h. Upon evaporating off the solvent, ethyl acetate (50 mL) was added. The organic layer was separated and washed with brine and dried over anhydrous Na$_2$SO$_4$. After the solvent was removed by rotary evaporation, the crude product was purified with column chromatography on silica gel with petroleum ether: ethyl acetate (25:1 and then 15:1, v/v) as the eluent to yield MMBP as a white solid. Yield: 89%. ^{1}H NMR (300 MHz, CDCl$_3$, ppm, δ): 7.52-7.49 (d, 2H, phenyl), 7.46-7.43 (d, 2H, phenyl), 7.23-7.20 (d, 2H, phenyl), 6.98-6.95 (d, 2H, phenyl), 3.84 (s, 3H,-ArOCH$_3$), 2.38 (s, 3H, -ArCH$_3$).

Preparation of *c*-PMOPS. *c*-PBrS (33 mg, 0.175 mmol of bromostyrene repeating units) and MPBAPE (122.9 mg, 0.525 mmol), THF (3 mL), K$_2$CO$_3$ aqueous solution (2.0 M, 1.5 mL) and Pd(PPh$_3$)$_4$ (6.1 mg, 5.25 × 10^{-3} mmol) was loaded into 25 mL Schlenk flask in order. This reaction mixture was degassed by three freeze-pump-thaw cycles, sealed under argon, and heated at 80 °C with stirring for 7 h. The yellow organic layer was separated, filtered through a short neutral alumina column prior to precipitation into methanol, and isolated by filtration. Drying under vacuum afforded the polymer as a pole yellow solid (31 mg, yield: 84%). $M_{n,SEC}$ = 4.1 kg/mol, $M_{w,SEC}$ = 4.2 kg/mol, Đ = 1.03.

Synthesis of PBAPE-PS-Br. 4-(Bromomethyl)benzeneboronic acid pinacol ester (51.6 mg, 0.174 mmol), CuBr (0.174 mmol, 25 mg), freshly distilled styrene (1.82 g, 17.4 mmol), bpy (54.4 mg, 0.348 mmol), and toluene (2 mL) were added to in a 10 mL ampoule. The mixture was degassed using three freeze-pump-thaw cycles, and heated at 110 °C with stirring for 100 min. The reaction mixture was dissolved in THF, precipitated into methanol, and isolated by vacuum filtration. The white polymer was dried under vacuum. (0.25 g, 14%). $M_{n,NMR}$ = 2.9 kg/mol, $M_{n,SEC}$ = 2.8 kg/mol, $M_{w,SEC}$ = 3.4 kg/mol, Đ = 1.22.

Synthesis of PBAPE-PS-N$_3$. PBAPE-PS-Br (1.00 g, 0.345 mmol) was loaded into a 25 mL round bottomed flask along with NaN$_3$ (0.45 g, 6.90 mmol), and DMF (10 mL). The solution was allowed to stir at room temperature for 24 h, filtered through a short neutral alumina column prior to precipitation into methanol and followed by filtrating and drying in vacuo at 25 °C to give a white solid. (0.83 g, 83%). $M_{n,NMR}$ = 2.9 kg/mol, $M_{n,SEC}$ = 2.8 kg/mol, $M_{w,SEC}$ = 3.4 kg/mol, Đ = 1.20.

Preparation of *c*-PS-*g*-PS. *c*-PBrS (24 mg, 0.127 mmol of bromostyrene repeating units) and PBAPE-PS-N$_3$ (1.1 g, 0.382 mmol), THF (2.2 mL), K$_2$CO$_3$ aqueous solution (2.0 M, 1.1 mL) and Pd(PPh$_3$)$_4$ (4.4 mg, 3.82 × 10^{-3} mmol) was loaded into 25 mL Schlenk flask in order. This reaction mixture was degassed by three freeze-pump-thaw cycles, sealed under argon, and heated at 80 °C

with stirring for 7 h. The yellow organic layer was separated, filtered through a short neutral alumina column prior to precipitation into methanol, and isolated by vacuum filtration. Drying under vacuum afforded the polymer as a light brown solid. The crude polymer was purified by preparative SEC (yield: 11%). $M_{n,SEC}$ = 30 kg/mol, $M_{w,SEC}$ = 32 kg/mol, $Đ$ = 1.07.

Results and Discussions

The general synthetic routes of functional cyclic polystyrene (PS) and cyclic PS brush are presented in Scheme 1, including three steps, *i.e.*, synthesis of *l*-PBrS, preparation of *c*-PBrS and post-polymerization of *c*-PBrS *via* Suzuki coupling reaction to yield *c*-PMOPS and *c*-PS-*g*-PS.

Synthesis of *l*-PBrS precursor and *c*-PBrS.

The universal cyclic polymer precursor, *c*-PBrS, was prepared by ATRP and CuAAC techniques, which was one of the most popular strategies for the preparation of cyclic polymers.[2a,14] In the current study, Activators Generated by Electron Transfer (AGET) ATRP[15] was used to synthesize *l*-PBrS-Br using prop-2-ynyl 2-bromo-2-methylpropanoate (PBMP) as the initiator. The results are shown in Fig. 1. As shown in Fig. 1, *l*-PBrS-Br with unimodal and symmetric distribution was obtained. The number average molecular weight and molecular weight distribution ($Đ = M_w/M_n$) measured by SEC ($M_{n,SEC}$) is 3.8 kg/mol and 1.05, respectively. Considering SEC measurement using PS standards for the calibration, the molecular weight was calculated to be 5.6 kg/mol by ^{1}H NMR spectroscopy ($M_{n,NMR} = (3 \times I_{6.00-7.80}/4 \times I_{3.90-4.60}) \times M_{BrSt} + M_{PBMP}$, where $I_{6.00-7.80}$ and $I_{3.90-4.60}$ are the integrals of the signals at 6.00-7.80 ppm and 3.90-4.60 ppm, M_{BrSt} and M_{PBMP} are the respective molecular weights of BrSt and PBMP, Fig. 2A), which agreed well with the theoretical value (4.8 kg/mol) ($M_{n,th} = ([BrSt]_0/[PBMP]_0) \times M_{BrSt} \times$ conversion $+ M_{PBMP}$, where M_{BrSt} and M_{PBMP} are the molecular weight of BrSt and PBMP). The good agreement of $M_{n,NMR}$ and $M_{n,th}$ denoted the well-controlled polymerization behaviour and relatively high end-functionality of the obtained *l*-PBrS-Br, ensuring the successes of further chain end transformations. Subsequently, the terminal bromide (Br) of *l*-PBrS (*l*-PBrS-Br) was transferred to azido-terminated *l*-PBrS (*l*-PBrS-N₃) *via* nucleophilic substitution reaction in DMF.[16] The obtained polymer was characterized by SEC, ^{1}H NMR and MALDI-TOF mass spectra. As presented in Fig. 1, SEC curve of *l*-PBrS-N₃ after modification also showed unimodal and symmetric distribution. The methyne proton signals of the end of *l*-PBrS-Br at 4.25-4.45 ppm shifted to 3.64-4.05 ppm, indicating the complete end group transformation from bromo to azido group in Fig. 2. The above results were further proved by MALDI-TOF mass spectra (Fig. S1, ESI†) of *l*-PBrS-Br and *l*-PBrS-N₃.
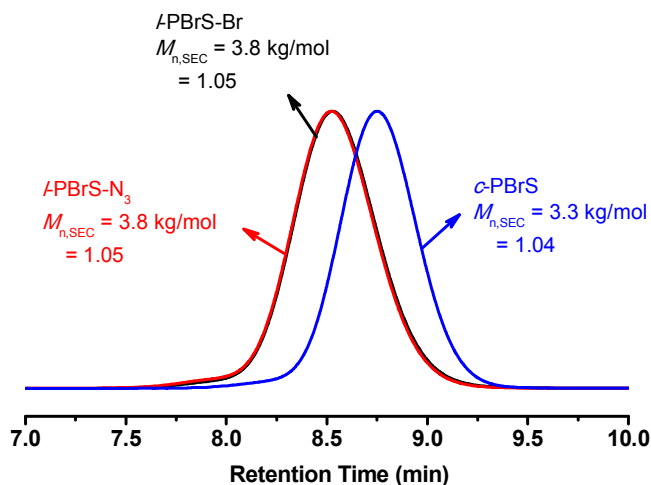

Fig. 1 SEC traces of *l*-PBrS-Br ($M_{n,SEC}$ = 3.8 kg/mol), *l*-PBrS-N₃ ($M_{n,SEC}$ = 3.8 kg/mol), *c*-PBrS (purified by prep SEC, $M_{n,SEC}$ = 3.3 kg/mol). THF was used as the eluent, and PS standards were used for the calibration.

The CuAAC intermolecular cyclization was performed in toluene using CuBr/PMDETA as catalysts. The polymer solution was slowly added into the catalyst solution *via* syringe pump to ensure the highly dilute concentration (3.2 ×10⁻⁵ M), guaranteeing the high priority of intramolecular cyclization.[17] After being purified by preparative SEC (Fig. S2, ESI†), the resulting *c*-PBrS were successfully characterized and deliberately analysis by SEC, FT-IR, ^{1}H NMR and MALDI-TOF mass spectra (Figs. 1-3 and S3, ESI†). The well-defined, symmetric and unimodal GPC elution curves for *c*-PBrS and their corresponding linear counterpart *l*-PBrS-N₃ are shown in Fig. 1, demonstrating that the resulting polymer has a significantly smaller hydrodynamic volume compared to its linear counterpart. Furthermore, in FT-IR spectra, the complete disappearance of the characteristic azide absorption signals at ~2100 cm⁻¹ and alkynyl at ~3300 cm⁻¹ found in Fig. S3 (ESI†) also provided the solid evidence for the successful ring closure. After cyclizcation, the disappearance of the signal of terminal alkynyl proton at 2.36 ppm (a) in the linear precursor was observed (Fig. 2C). And, the ^{1}H NMR spectrum of the *c*-PBrS (Fig. 2C) showed significant shifts at 4.60 ppm (b) and 4.84-5.00 ppm (g) compared with that of linear precursor *l*-PBrS-N₃, wherein peak b was ascribed to methylene protons adjacent to the triazole ring (original at 4.24-4.00 ppm) and peak g was ascribed to methine proton (original at 3.82-3.92 ppm), (Fig. 2B). Furthermore, the obtained polymer structure was carried out by MALDI-TOF mass spectra acquired in linear mode (Fig. 3A). The full spectrum of *c*-PBrS exhibits only one symmetric distribution. As expected, a representative peak m/z value of 5315.05 corresponding to the 28-mer of *c*-PBrS with sodium fitted well with the calculated mass ([M₂₈ + Na]⁺, Calcd: 5315.50). Therefore, the above chain of evidence confirmed the successful production of *c*-PBrS.
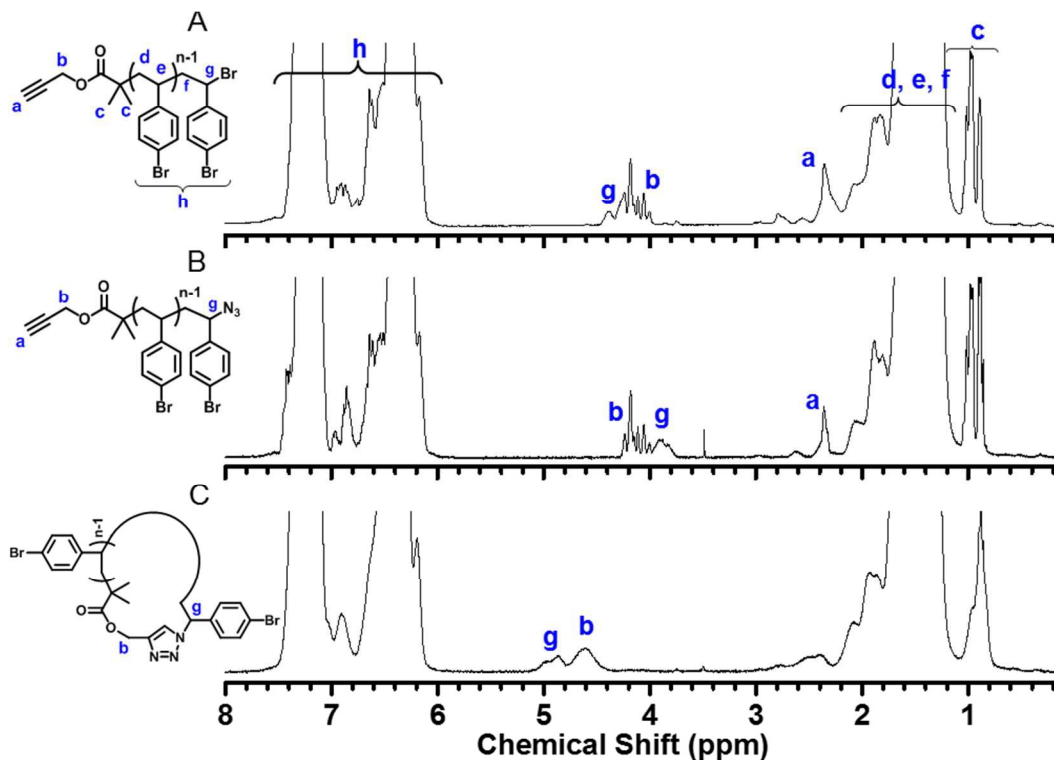
Fig. 2 ^{1}H NMR spectra in CDCl[3] of (A) *l*-PBrS-Br, (B) *l*-PBrS-N[3], (C) *c*-PBrS (purified by prep SEC).
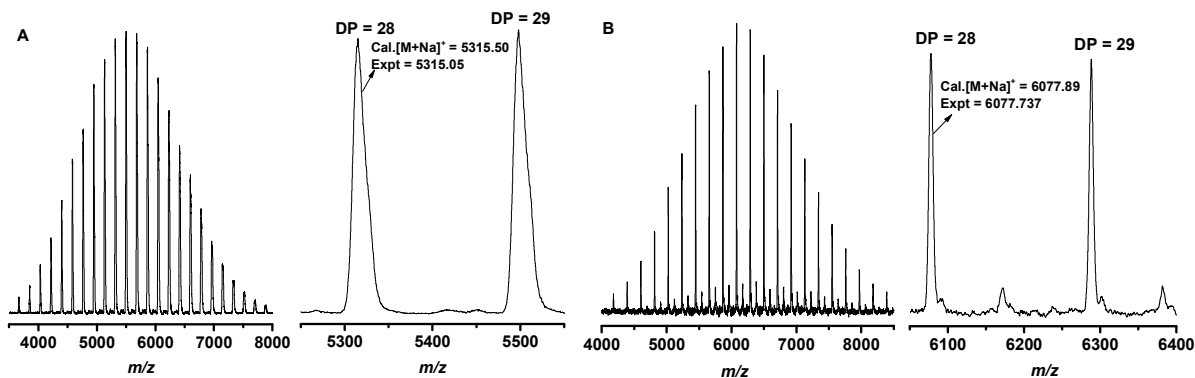

Fig.3 MALDI-TOF mass spectra using Na salt as the cationization agent and a DCTB matrix. (A) *c*-PBrS (purified by prep SEC) and (B) *c*-PMOPS, acquired in linear mode. Left: full spectra and right: magnified views of the spectra within a specific mass range.

Suzuki coupling of 4-bromotoluene and MPBAPE.

Suzuki coupling reation is a versatile and robust reaction, which tolerates a wide variety of functional groups, and gives high yields of product under the mild condition.[18] The above excellent superiorities of Suzuki reaction motivated us to examine the possibility of preparing cyclic-brush polymers by directly utilizing the Suzuki coupling of the side bromophenyl groups of the prepared *c*-PBrS. Prior to prepare the corresponding cyclic brush polymers, 4-bromotoluene and 4-methoxyphenylboronic acid pinacol ester were employed as model compounds to validate the efficiency of the Suzuki coupling. The conversions of 4-bromotoluene were determined by gas chromatogram with periodically sampling, and

the results are shown in Tables S1 (ESI†). As expected, Suzuki reaction shows its excellent efficiency with ~100% conversion under these conditions, and the conversion of 4-bromotoluene increased along with reaction time and completed within 7 hours. The structure of the resultant biaryls was distinctly confirmed by ^{1}H NMR spectra.

Suzuki Coupling of MPBAPE to *c*-PBrS.

The above investigation about the efficiency of model Suzuki reaction demonstrated an enormous potential to prepare uniform cyclic-brush polymers with perfect efficiency. The as-prepared cyclic *c*-PBrS of Scheme 1 contained activated bromophenyl moieties at each repeating unit. Therefore, by virtue of the excellent efficiency of Suzuki coupling reaction, *c*-PBrS can be a universal

template to prepare various cyclic-brush polymers with an inherent cyclic topology. First of all, the adaptability of Suzuki coupling was examined by using 1.5 equiv of 4-methoxyphenylboronic acid pinacol as small molecule. The resultant polymers after 7 hours reaction presented SEC traces with a small shoulder at high molecular weight, indicating the presence of a small amount of undesired polymer-polymer coupling. The polymer-polymer coupling was probably stemmed from the palladium-catalyzed Ullmann homocoupling of aryl bromides.[19] To avoid this side reaction, 3-fold excess of boronic acid pinacol was added. After 7 hours, the target polymer was yielded and isolated. The number average molecular weight ($M_{n,SEC}$) by SEC analysis was 4.1 kg/mol ($Đ$ = 1.04). Notably, no shoulder at high molecular weight were found, and the SEC curve showed unimodal distributions comparable with the starting c-PBrS, as shown in Fig. 4. ^{1}H NMR spectrum of the resultant polymer was shown in Fig. 5. The new appearance peak at characteristic chemical shifts (3.73 ppm) not found in the c-PBrS corresponded to the coupled methoxy protons of methoxyphenylstyrene repeat units. The integration ratio between peak a (CH$_3$O-, 3.73 ppm, integration area = 3.0) and peak b (-Ar-Ar-, 6.79-7.26 ppm, integration area = 8.05) confirmed the complete coupling at each repeat unit. ^{13}C NMR spectroscopy also verified the quantitative conversion from 4-bromo styrene to 4-(methoxyphenyl) styrene by the disappearance of peak 3' adjacent to the aryl bromide at 120 ppm, the new appearance of peaks 3, 6, 7 and 9 respectively at 55, 134, 138 and 160 ppm and the relocation of peaks 5 and 8 at 126-128 and 143 ppm in Fig. 6. Furthermore, the coupled polymer structure was thoroughly analyzed by MALDI-TOF mass spectra acquired in linear mode (Fig. 3B), and the spectra presented only one molecular weight distribution with a regular interval 210 Da corresponding to the methoxyphenylstyrene repeat unit of PMOPS. A representative peak of m/z at 6077.74 corresponding to 28-mer of poly[(4-methoxyphenyl)styrene] (PMOPS) matched well with the calculated mass ([M'$_{28}$ + Na]$^+$, Calcd: 6077.89). These results demonstrated the high efficiency of Suzuki coupling reaction for post modifications. As shown in the DSC traces of Fig. 9, c-PBrS has a glass transition temperature (T_g) at 143 °C, while PMOPS has a T_g value of 166 °C, demonstrating a significant change of thermal property between the starting cyclic polymer (c-PBrS) and the post-modified polymer (c-PMOPS).
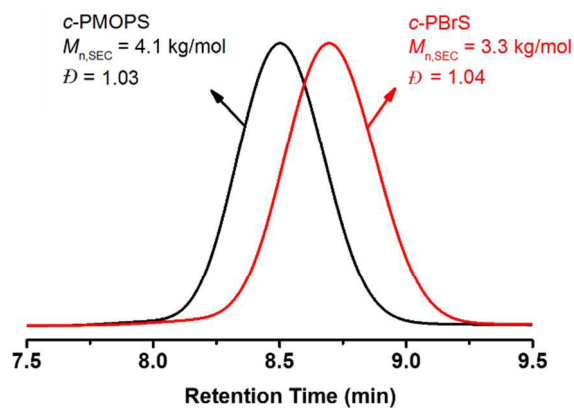

Fig. 4 SEC RI traces of c-PBrS (purified by prep SEC, $M_{n,SEC}$ = 3.3 kg/mol), c-PMOPS (c-PBrS : MPBAPE = 1 : 3, $M_{n,SEC}$ = 4.1 kg/mol). THF was used as the eluent, and PS standards were used for the calibration.
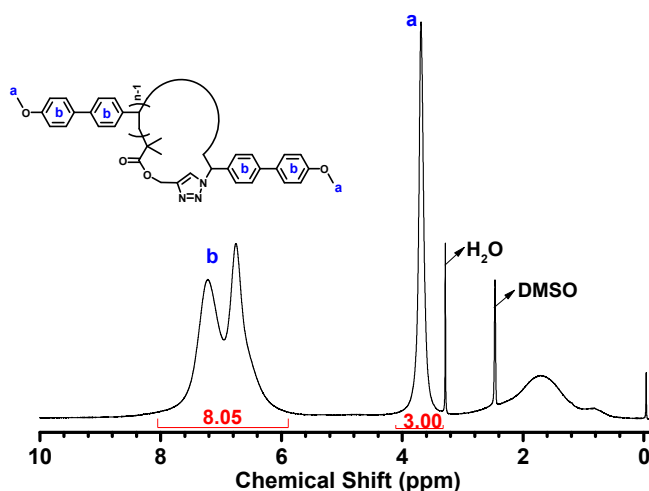

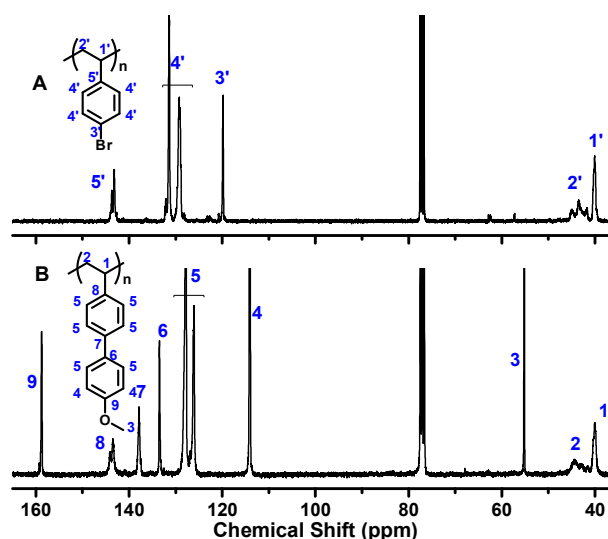**Fig. 5** ^{1}H NMR spectrum of poly[(4-methoxyphenyl)styrene] in DMSO-d_6.

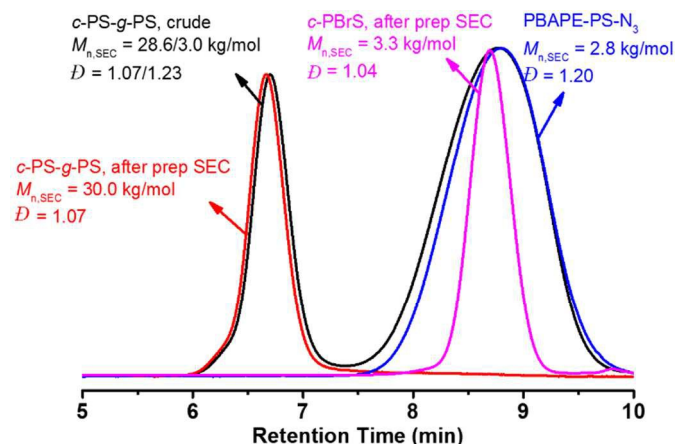**Fig. 6** ^{13}C NMR spectrum of c-PBrS (purified by prep SEC) and PMOPS in CDCl$_3$.

Fig. 7 SEC traces of cyclic polymer brush with PS side chains ($M_{n,SEC}$ = 28.6/3 kg/mol), c-PS-g-PS (purified by prep SEC, $M_{n,SEC}$ = 30.0 kg/mol), PBAPE-PS-N$_3$ ($M_{n,SEC}$ = 2.8

kg/mol) and *c*-PBrS (purified by prep SEC, $M_{n.SEC}$ = 3.3 kg/mol). THF was used as the eluent, and PS standards were used for the calibration.

Suzuki Coupling of functional PBAPE-PS-N₃ to *c*-PBrS

Encouraged by these positive results from high-efficiency Suzuki coupling reaction, more complex topological cyclic-based polymers were envisaged, such as cyclic-brush architecture. The concept (Scheme 1, vii) can be demonstrated by the preparation of a cyclic-brush polymer with PS as grafting chains. The functional PS end-capped by an arylboronic pinacol ester group was designed and synthesized by ATRP by the utilization of an arylboronic pinacol ester-containing ATRP initiator (Scheme 1, iv). After ATRP, the terminal bromo groups were completely converted into azido moieties (PS-N₃) avoiding undesirable cross-coupling reactions between benzylic bromide derivatives and arylboronic ester.[20] Both PBAPE-PS-Br and PBAPE-PS-N₃ have symmetrical and unimodal SEC traces as shown in Fig.S4 (ESI†). The successful terminal conversion has been fully characterized by ^{1}H NMR spectra (Fig. S5, ESI†) and MALDI-TOF mass spectra (Fig. S6, ESI†). Cyclic-brush polymer was prepared under identical conditions as the model Suzuki-coupling reaction with a 3-fold excess of PBAPE-PS-N₃. The resultant cyclic-brush polymer was purified by pre-SEC to remove excess PBAPE-PS-N₃. From SEC curves shown in Fig. 7, it can be seen that the purified cyclic-brush polymer has an obvious shift to much higher molecular weight (30 k g/mol). The ^{1}H NMR (Fig. S4C) and ^{13}C NMR (Fig. 8) proved the successful preparation of cyclic-brush polymer. The DSC traces as shown in Fig. 9, the T_g value of resultant cyclic-brush polymer is between those of *c*-PBrS and PBAPE-PS-N₃, due to the change of free volume by introducing many branch points.[21,22,23] These results confirmed further that the Suzuki coupling reaction can be used as a promising protocol for constructing complex topological polymers. Actually, the termini azido groups at each branching end can also be utilized for further fabrication of more topological polymers *via* azide-alkyne "Click" reactions, undoubtedly offering an extendable cyclic template.
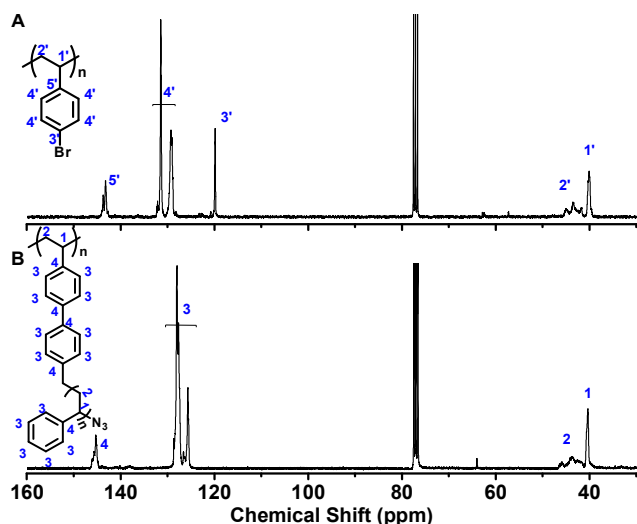

Fig. 8 ^{13}C NMR spectrum of *c*-PBrS (purified by prep SEC) and *c*-PS-*g*-PS (purified by prep SEC) in CDCl₃.
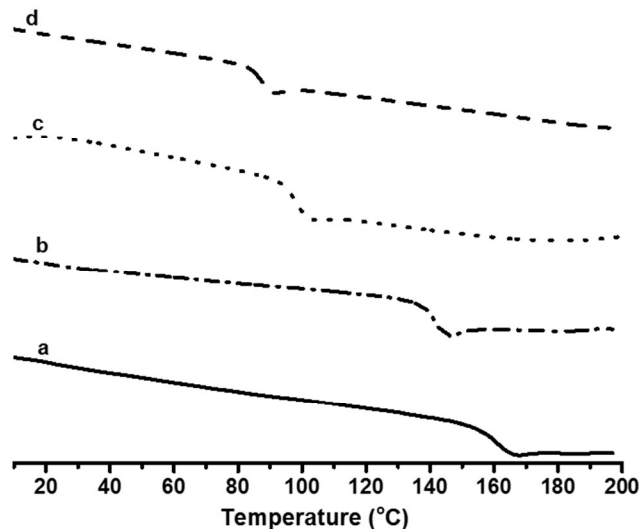

Fig. 9 DSC traces for (a) *c*-PMOPS, (b) *c*-PBrS, (c) *c*-PS-*g*-PS (d) PBAPE-PS-N₃. Heating rate of 10 °C/min; T_g measured on the third cycle of a heat/cool/heat experiment.

Conclusions

In summary, cyclic polymer precusor *c*-PBrS bearing bromobenzene moieties at each repeating unit has been successfully synthesized by combing ATRP and CuAAC cyclization reaction. The repeat units of *c*-PBrS were further converted *via* Suzuki coupling reaction. The results confirmed that the Suzuki coupling reaction was proved to a highly efficient post-polymerization modification protocol, *i.e.*, every repeat unit was transformed to the target. Cyclic-brush polymer with arylboronic pinacol ester-end captured PS as grafting chains were successfully constructed *via* Suzuki coupling reaction. Fully and careful characterizations confirmed further the entire post-polymerization modifications. It is believed that the Suzuki coupling reaction can be also facilely adapted in other topological polymers, such as linear, hyperbranched, dendrimer and so on. Differing from other post-polymerization modification methods, Suzuki coupling reaction can install new C-C bonds, which would undoubtedly introduce some novel chemical components to the target polymers. This work developed a novel and universal post-polymerization protocol for the preparation of cyclic-brush polymers, which would enrich the chemical structures of complex topological cyclic polymers and more.

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Notes and references

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