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Polymethylene-Based Eight-Shaped Cyclic Block Copolymers

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Supporting Information

ABSTRACT: A new strategy was developed for the synthesis of well-defined eight-shaped polymethylene (PM, equivalent to polyethylene)-based cyclic block copolymers, [c-(PM-b-PCL)]₂, according to the following four steps: (a) synthesis of a B-thexyl-boracyclic initiator by cyclic hydroboration of 1,4pentadiene-3-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate with thexylborane; (b) polyhomologation of dimethylsulfoxonium methylide using this boracyclic initiator to afford α,ω dihydroxyl linear PM (PM-OH)₂; (c) synthesis of 4-miktoarm star block copolymers, (PM-alkyne)₂-(PCL-N₃)₂, by esterification, deprotection, and ring-opening polymerization (ROP); and (d) intramolecular cyclization of (PM-alkyne)₂- $(PCL-N_3)_2$, under high-dilution condition by copper-catalyzed



"click" chemistry. All intermediates and final products were characterized by high-temperature gel permeation chromatography, proton nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, and differential scanning calorimetry. Initial studies on the thermal and self-assembly behavior of the cyclic block copolymers and their corresponding precursors revealed a significant influence of the cyclic structure on the properties.

INTRODUCTION

The relationship between polymer architecture and various properties is an important research subject in both academia and industry.1 Among different architectures, cyclic polymers, which contain a unique non-chain-end structure and different physical properties,^{2,3} have attracted considerable attention. Compared to their linear analogues, many differences on properties such as crystallinity, glass-transition temperature, and melt-flow dynamics, are discovered because of the absence of chain ends.⁴ Several novel model cyclic polymers were synthesized and investigated, including single cyclic poly-mers^{5–9} and complex cyclic polymers^{10–12} such as tadpole-shaped,^{13–15} sun-shaped,^{16–18} and eight-shaped.^{19,20} However, the polymers involved in the above examples are mainly polydienes, polycaprolactone (PCL), polystyrene, poly(2vinylpyridine), and poly(ethylene oxide). With respect to polymethylene (PM), there are only a few reports on the synthesis of homocyclic PM.²¹⁻²³

Polymethylene (equivalent to polyethylene, PE) is the most widely used polymer because of its low cost, excellent physical properties, and recyclability.²⁴ However, there are still some limitations in its applications in many areas. For example, poor adhesion and incompatibility have been found between PM and polar polymers; to overcome these disadvantages, it is very important to develop synthetic strategies toward novel PMbased polymeric materials.²⁵ Shea et al.²⁶⁻³⁰ have recently reported a new living method, namely, polyhomologation (or C1 polymerization), which is a powerful tool for the synthesis of well-defined functionalized linear polymethylenes.³¹⁻⁴⁵ In

this living C1 polymerization, boron compounds were used as initiators to polymerize dimethylsufoxonium methylide, leading to well-defined hydroxyl-functionalized polymethylene. Different PM-based (co)polymers were constructed by combining this efficient strategy with other polymerization methods, such as ring-opening polymerization (ROP),³² atom transfer radical polymerization (ATRP),³³⁻³⁶ reversible addition-fragmentation chain-transfer polymerization (RAFT),⁴⁵ and iodine transfer polymerization.⁴⁶ Recently, our group has also used polyhomologation to build welldefined PM-based architectures by designing/synthesizing novel borane initiators.^{47–55}

In our previous paper,²³ the synthesis of PE-based single cyclic block and tadpole copolymers was achieved by combining polyhomologation, Diels-Alder reaction (anthracene-terminated PE and an azido-maleimide derivative), ROP, chain-end transformation to introduce the alkynyl groups, and cyclization (Scheme 1a). In the present work, the synthesis of eight-shaped copolymers is based on a dihydroxy-protected diene (1,4-pentadien-3-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate) precursor and thexylborane chemistry to afford a difunctional boron initiator, followed by polyhomologation, first chain-end transformation to introduce alkynyl groups, ROP, second chain-end transformation to introduce azido groups, and cyclization (Scheme 1b). The development of this successful procedure was achieved after testing many different

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synthetic strategies, one of which is given in the Supporting Information.

EXPERIMENTAL SECTION

Materials. Ethyl formate (97%), vinylmagnesium chloride solution (1.6 M in tetrahydrofuran (THF)), copper(I) bromide (CuBr, 99.999%), borane dimethylsulfide complex solution (1.0 M in THF), 2,3-dimethylbut-2-ene (\geq 99%), ^tBu-P₂ (2.0 M in THF), sodium azide (NaN₃, 99.5%), 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (97%), amberlyst-15(wet) ion-exchange resin, 4-(dimethylamino)pyridine (DMAP, \geq 99%), trimethylamine N-oxide dihydrate (TAO·2H₂O, \geq 99%), and *N*,*N*'-dicyclohexylcarbodiimide (DCC, 99.8%) were purchased from Aldrich and used as received. N,N,N',N",N"-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) and ε caprolactone (CL, \geq 99%) were distilled over calcium hydride (CaH₂) under reduced pressure before use. Toluene was refluxed over sodium/benzophenone and distilled under nitrogen atmosphere just before use. Dimethylsulfoxonium methylide was prepared according to Corey's method followed by switching the solvent from THF to to lucas 41,56toluene.

Measurements. The high-temperature gel permeation chromatography (HT-GPC) measurements were carried out with Viscoteck 350 instrument equipped with two PLgel 10 μ m MIXED-B columns and 1,2,4-trichlorobenzene (TCB) as the eluent at a flow rate of 0.8 mL/min at 150 °C. The system was calibrated by PS standards. ¹H and ¹³C NMR spectra were recorded with a Bruker AVANCE III-400, 500, or 600 spectrometer, and Fourier transform infrared (FT-IR) spectra with a NICOLET iS10 FT-IR instrument. Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC1/TC100 system under an inert atmosphere (nitrogen). The sample was heated from room temperature to 150 °C, cooled to -40 °C, and finally heated again to 150 °C with a heating/cooling rate of 10 °C/min. The second heating curve was used to determine the melting temperature (T_m) . Dynamic light scattering (DLS) measurements were carried out with a Malvern Zetasizer Nano ZS equipped with a TurboCorr correlator. The light source was a 30 mW He-Ne laser emitting a vertically polarized light of 632.8 nm wavelength.

Synthesis of 1,4-Pentadien-3-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (Scheme 1). Ethyl formate (4.0 mL, 50 mmol) was added dropwise to a solution of vinylmagnesium chloride solution (63 mL, 100 mmol, 1.6 M in THF) in dry THF (30 mL) at 0 °C under argon (Ar). After completion of the addition, the mixture was kept under stirring for further 1 h at room temperature. Then, the reaction was quenched with a saturated NH₄Cl solution (30 mL) and the mixture was extracted with ethyl acetate (20 mL \times 3). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated to give the crude 1,4-pentadien-3-ol.

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DCC (5.8 g, 28 mmol), DMAP (0.34 g, 2.8 mmol), and 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (4.9 g, 28 mmol) were added to a solution of crude 1,4-pentadien-3-ol (2.1 g, ~25 mmol) in THF (50 mL) at 0 °C under Ar. The mixture was stirred for 14 h at room temperature, followed by washing with brine. The organic extracts were dried over MgSO₄, filtered, and concentrated. The residue was purified by chromatography with silica gel (ethyl acetate/petroleum ether = 1:4) to give a colorless oil as the product (6.2 g, 52% yield). ¹H NMR (CDCl₃, 500 MHz, tetramethylsilane (TMS)): δ 1.24 (3H, s), 1.41 (3H, s), 1.45 (3H, s), 3.68 (2H, d, *J* = 10.0 Hz), 4.24 (2H, d, *J* = 10.0 Hz), 5.25 (2H, d, *J* = 10.0 Hz), 5.36 (2H, d, *J* = 10.0 Hz), 5.78 (dd, *J* = 10.0 Hz, 10.0 Hz), 5.83-5.90 (2H, m); mass spectrometry (MS) (electrospray ionization (ESI)) calcd. for C₁₃H₂₁O₄: [M + H]⁺ 241.1434; found: 241.1437.

Synthesis of (PM-OH)₂ (Scheme 1). A typical polyhomologation procedure is as follows. To a solution of 1,4-pentadien-3-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (1.08 g, 4.5 mmol) in THF (4.0 mL), freshly prepared thexylborane⁵³ (4.7 mL, ~0.89 M) was added dropwise at 0 °C under Ar, and the mixture was kept under stirring for 4 h at room temperature to give the organoborane solution.

To a 100 mL Schlenk flask charged with methylide solution (30 mL, 1.0 M in toluene), 2.0 mL of the above-prepared organoborane solution was added at 65 °C under Ar. After stirring at 65 °C for 10 min, 0.10 mL of the reaction solution was taken out and added to water containing phenolphthalein. The neutral solution (pH indicator) indicates the consumption of the ylide. Then, TAO-2H₂O (0.20 g) was added to the reaction mixture. After stirring at 90 °C for 4 h, the mixtures were poured into cold methanol (300 mL). The white solids were filtered, dried under vacuum, and characterized by ¹H NMR and HT-GPC [(PM₁₁₀-OH)₂, $M_{n, NMR}$ = 3400, PDI = 1.36].

Synthesis of (PM-alkyne)₂ (Scheme 2). A typical synthesis procedure is as follows. A solution of $(PM_{110}-OH)_2$ (1.36 g, 0.40 mmol), 4-pentynoic acid (400 mg, 4.0 mmol), N,N''-dicyclohexylcarbodiimide (DCC, 824 mg, 4.0 mmol), and N,N-dimethylpyridin-4-amine (DMAP, 49 mg, 0.40 mmol) in toluene (20 mL) was stirred at 90 °C overnight. The solution was cooled down, and the mixture was concentrated by a rotory evaporator and precipitated in methanol. The resulting white solid was filtered, dried under vacuum, and characterized by ¹H NMR and GPC [(PM₁₁₀-alkyne)₂, $M_{n, NMR}$ = 3600, PDI = 1.36].

Synthesis of (PM-alkyne)₂-(PCL-OH)₂ (Scheme 2). A typical synthesis procedure is as follows. A solution of $(PM_{110}-alkyne)_2$ (1.08)

g, 0.30 mmol) and Amberlyst-15 (wet) ion-exchange resin (300 mg) in toluene (20 mL) was stirred at 90 °C overnight. The solution was cooled down, and the mixture was concentrated by a rotory evaporator and precipitated in methanol. The white solid was filtered and dried under vacuum to give $(PM_{110}\text{-alkyne})_2$ - $(OH)_2$.

^tBu-P₂ (0.625 mL, 2 M, 1.25 mmol) was added to the solution of $(PM_{110}\text{-}alkyne)_2\text{-}(OH)_2$ (900 mg, 0.25 mmol) in toluene (10 mL), then caprolactone (5.70 g, 50 mmol) was added to the mixture. The resulting solution was stirred in a preheated oil bath at 90 °C for 14 h. Then, the reaction was quenched by adding CH₃COOH/MeOH (10 vol %) and cooled to room temperature. The mixture was concentrated by a rotory evaporator and precipitated in methanol. The white solid was filtered, dried under vacuum, and characterized by ¹H NMR and GPC [(PM₁₁₀-alkyne)₂-(PCL₁₅-OH)₂, 2.2 g, *M*_{n, NMR} = 7.0 × 10³, PDI = 1.39].

Synthesis of (PM-alkyne)₂-(PCL-N₃)₂ (Scheme 2). A typical synthesis procedure is as follows. A solution of $(PM_{110}-alkyne)_2$ -(PCL₁₅-OH)₂ (1.16 g, 0.10 mmol), 2-azidoacetic acid⁵⁷ (200 mg, 2.0 mmol), DCC (412 mg, 2.0 mmol), and DMAP (25 mg, 0.20 mmol) in toluene (10 mL) was stirred at 90 °C overnight. The solution was cooled down, and the mixture was concentrated by a rotory evaporator and precipitated in methanol. The resulting white solid was filtered, dried under vacuum, and characterized by ¹H NMR and GPC [(PM₁₁₀-alkyne)₂-(PCL₁₅-N₃)₂, $M_{n, NMR} = 7.1 \times 10^3$, PDI = 1.39].

Synthesis of [*c*-(**PM**-*b*-**PCL**)]₂ (**Scheme 2**). A typical synthesis procedure is as follows. Copper(I) bromide (CuBr, 29 mg, 0.2 mmol) and PMDETA (35 mg, 0.20 mmol) were dissolved in toluene (250 mL). The mixture was degassed by three freeze–pump–thaw (FTP) cycles and then put in a preheated oil bath at 90 °C; then, (PM₁₁₀-alkyne)₂-(PCL₁₅-N₃)₂ (116 mg, 0.01 mmol) in toluene (150 mL) was added to the CuBr/PMDETA solution via a peristaltic pump at a rate of 1.4 mL/h. After completion of the addition, the reaction solution was concentrated, purified by passing through a neutral alumina column using toluene as eluent to remove the copper, and precipitated in methanol three times. The white solid was filtered, dried under vacuum, and characterized by ¹H NMR and GPC. {[(*c*-(PM₁₁₀-*b*-PCL₁₅))]₂, *M*_{n, NMR} = 7.1 × 10³, PDI = 1.39}.

RESULTS AND DISCUSSION

As shown in Scheme 1B, 1,4-pentadien-3-ol was converted to 1,4-pentadien-3-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate by esterification with 2,2,5-trimethyl-1,3-dioxane-5-carboxylate acid. The cyclic hydroboration of 1,4-pentadiene-3-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate with thexylborane afforded the B-thexyl-boracyclic compound, which was used as initiator for polyhomologation of dimethylsulfoxonium methylide in the next step. After oxidation-hydrolysis with TAO·2H₂O, 2,2,5-trimethyl-1,3-dioxane-functionalized α,ω -dihydroxyl polymethylene (PM-OH)₂ was obtained. Two samples with different molecular weights were synthesized, and their molecular characteristics are listed in Table 1. The molecular weights were determined by the ¹H NMR end-group analysis ($M_{n, NMR} = 3.4/11.3 \times 10^3$), and the polydispersity index by HT-GPC with polystyrene standards (polydispersity index:

Tal	ole	1.	Mol	lecula	ar C	harac	terist	ics	of	(PM	-OH)	$)_2$
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entry	Sample	$M_{\rm n, NMR}^{a}$	$M_{\rm n, \ GPC.}^{b}$	DPa	Ð
1	$(PM_{110}-OH)_2$	3400	4500	110	1.36
2	$(PM_{396}-OH)_2$	11 300	12 000	396	1.27

 ${}^{a}M_{n, NMR}$ and DP were calculated from ¹H NMR spectra (600 MHz, C₂D₂Cl₄, 90 °C) using the area ratio of protons of terminal CH₂OH at $\delta = \sim 3.7$ ppm to the backbone. ${}^{b}D(M_{w}/M_{n})$ and $M_{n, GPC}$ determined by HT-GPC (1,2,4-trichlorobenzene, 150 °C, PS standards).

 $D(M_w/M_n) = 1.36/1.27)$. All HT-GPC traces were monomodal with narrow molecular weight distributions (Figure 1).

The proof of the successful synthesis of (PM-OH)₂ came from ¹H NMR spectra. As shown in Figure 2a,b, the characteristic chemical shift due to vinyl protons in 1,4pentadiene-3-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate at δ = 5.9-5.8 ppm (m, H_b), δ = 5.3, 5.4 ppm (d, H_a) disappeared after the hydroboration/polyhomologation/oxidation/hydrolysis reaction, and a new peak at $\delta = 3.65$ ppm of the $-CH_2$ connected to the hydroxyl group $(H_{a'})$ appeared, an indication of polymerization initiation from the two vinyl groups initiating sites. The signals (H_e) at δ = 3.65 and 4.21 ppm, assigned to protons of the $-CH_2$ - from the dioxane group, indicate that the 2,2,5-trimethyl-1,3-dioxane-5-carboxylate group remained intact during the polyhomologation. The observed integration area ratio of aliphatic protons at $\delta = 1.1 - 1$ 1.5 ppm ($H_{b\&e}$, two protons for each methylene unit, two PM chains) $[S_{b\&\sigma}/4H]$ to that of protons assigned to $-CH_2$ connected to the hydroxyl group and -CH2- from the dioxane group at δ = 3.65 ppm (H_{a'&e'} four protons from two PM chains and two protons from the dioxane group) $[S_{a'\&e'}]$ 6H] was derived by the following formula: $m = (S_{b,g}/4H)$: $(S_{a',e}/6H)$, which is the degree of polymerization of each PM chain. This integrated ratio was used to determine the numberaverage molecular weight of the macroinitiator (PM-OH)₂.

Synthesis and Characterization of 4-Miktoarm Star Copolymers, (PM-alkyne)₂-(PCL-N₃)₂. The 4-miktoarm star copolymer, (PM-alkyne)₂-(PCL-N₃)₂, precursor of eightshaped cyclic, was synthesized according to the following general steps (Scheme 2): (a) introduction of an alkynyl group on both PM chain ends to get (PM-alkyne)₂; (b) removal of the OH-protective group to afford (PM-alkyne)₂-(OH)₂; (c) ROP of ε -caprolactone with the difunctional initiator to obtain the 4-arm star copolymers (PM-alkyne)₂-(PCL-OH)₂; and (d) introduction of azido groups on both PCL chain ends to afford (PM-alkyne)₂-(PCL-N₃)₂.

And more specifically, the -OH groups of the synthesized (PM-OH)₂ was reacted with 4-pentynoic acid, in the presence of DMAP and DCC, to give (PM-alkyne)₂. To ensure the complete esterification of -OH groups, a 10-fold excess of 4pentynoic acid was used. The ¹H NMR spectrum of polymer $(PM-alkyne)_2$ is shown in Figure 3a. A comparison to that of $(PM-OH)_2$ (Figure 2b) shows that the signal of the methylene protons adjacent to the -OH groups shifted from $\delta = 3.67$ ppm(a') to 4.14 ppm(a''), and new signals (g), (h), and (i) appeared at δ = 2.02 and 2.56 ppm, attributed to the terminal proton of the alkyne functional group and to the methylene protons adjacent to the triple bond, respectively. The esterification was further verified by FT-IR analysis. A comparison of the spectrum of (PM-alkyne)₂ to that of (PM-OH)₂, shows that a characteristic signal of alkyne groups appeared at 3314 cm^{-1} (Figure 4b).

For polymer (PM-alkyne)₂, the protective group was cleaved under mildly acidic conditions to give two free –OH groups in the middle of the polymethylene chain. The two –OH groups were utilized to initiate the ROP of ε -caprolactone with the phosphazene superbase ^tBu-P₂ as a catalyst in toluene at 90 °C. The successful ROP was confirmed by ¹H NMR, FT-IR, and HT-GPC techniques. Comparing the ¹H NMR spectra of (PM-alkyne)₂-(PCL-OH)₂ with the corresponding (PMalkyne)₂ (Figure 3b,a), the fingerprints of PCL block appeared at δ = 1.40, 1.71, 2.34, and 4.12 ppm. Also, the signal of the methylene protons adjacent to the –OH groups from the end



Figure 1. GPC traces of linear PMs and the corresponding 4-miktoarm star copolymers (TCB at 150 °C).



Figure 2. ¹H NMR spectra of (a) 1,4-pentadien-3-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate in chloroform-*d* at 25 °C and (b) $(PM_{110}-OH)_2$ in $C_2D_2Cl_4$ at 90 °C.

of the PCL chain appeared at δ = 3.67 ppm (j). In the FT-IR spectrum of (PM-alkyne)₂-(PCL-OH)₂ (Figure 4c), a strong band at 1723 cm⁻¹, attributed to the polycaprolactone, appeared after ROP. The GPC curves in Figure 1a,b show the variation of molecular weights and molecular weight distributions of the 4-miktoarm star copolymers prepared from the linear PM precursors. A slight shift of the elution peak of $(PM_{110}-alkyne)_2-(PCL_{15}-OH)_2$ to the lower-molecular-weight side, compared to the linear PM precursor (PM₁₁₀-OH)₂, was observed. In the case of $(PM_{396}\text{-}alkyne)_2\text{-}(PCL_8\text{-}OH)_2$, a shift to a slightly higher-molecular-weight side occurred, compared to the corresponding linear one. There was no significant shift between the GPC traces of 4-miktoarm copolymers and the linear precursors, and this should be attributed to the branched structure of the star polymer.⁵⁸ The hydrodynamic volume increases with molecular weight and decrease when the architecture is changed from the linear (2-arm star) to 4-arm star (same-arm molecular weight). Therefore, it does not change much in this case. Similar results were also observed in our previous work.53

Finally, the 4-miktoarm star copolymer (PM-alkyne)₂-(PCL-N₃)₂ was obtained by esterification of the –OH groups of the PCL chain ends with 2-azidoacetic acid. This signal (j) of the methylene protons adjacent to the –OH groups shifted to δ = 4.12 ppm (j') after esterification. At the same time, a new signal (k) appeared at δ = 3.89 ppm, attributed to the methylene protons adjacent to the azido group (Figure 3c). From the FT-IR spectra (Figure 4d), the characteristic absorption of the azido group around 2110 cm⁻¹ can be observed.

Synthesis and Characterization of Eight-Shaped Copolymers $[c-(PM-b-PCL)]_2$. The intramolecular cyclization by "click" reaction was carried out by a slow and continuous addition of the star copolymer $(PM-alkyne)_2-(PCL-N_3)_2$ solution into the catalyst solution. To avoid the formation of a byproduct from intermolecular condensation, cyclization was carried out under high-dilution conditions. The GPC traces and molecular characteristics of the precursors and the final products are shown in Figure 5 and Table 2. $M_{n, NMR}$ was determined by the ¹H NMR end-group analysis; $M_{n, GPC}$ and

Scheme 2. Synthesis of [c-(PM-b-PCL)]₂ from (PM-OH)₂



 $D(M_w/M_n)$ were determined by HT-GPC with polystyrene standards (Table 2). The hydrodynamic volume of cyclic polymer is smaller than that of their linear precursors, and this feature could be described by using R, the ratio of the peak value of molecular weight $(M_{p, GPC})$ of the cyclic polymer to that of the linear precursor.⁵⁹ The *R* values are 0.90 and 0.91, respectively. Comparing the GPC traces in Figure 5, it is obvious that GPC trace of [c-(PM₁₁₀-b-PCL₁₅)]₂ shifted to longer elution time, meaning smaller hydrodynamic volume compared to the star precursor. For the GPC trace of [c- $(PM_{396}-b-PCL_8)]_2$, there is a rather big shoulder observed, indicating the existing of byproduct. This byproduct is possibly due to the intermolecular click reaction (linear polycondensates or bigger cyclics). The increasing distance of the terminal groups of polymer chain favors rather intermolecular than intramolecular reaction. The $D(M_w/M_p)$ values of the cyclic products are 1.35 and 1.39 (Table 2). All cyclic polymers were characterized by ¹H NMR and FT-IR spectroscopy after precipitation in methanol and drying.

As shown in Figure 3d, a comparison with the corresponding $(PM-alkyne)_2-(PCL-N_3)_2$ (Figure 3c) shows that the signal (i) belonging to the terminal proton of the alkyne disappeared, and a new signal at 7.42 ppm (i') appeared, assigned to proton of triazole ring formed from the alkyne and azido groups. A new signal (g'+h') between 2.90 and 3.10 ppm also appeared, due to the transformation of alkyne to triazole, similar to our previous report.²³ And there is still a weak signal at 2.56 ppm assigned to the methylene protons adjacent to the triple bond, meaning that not all of the alkyne group was transferred to triazole. This might be from the trace amount of unreacted 4arm precursor or the intermolecular condensation byproduct. It is very difficult to separate the unreacted or bimolecular byproduct from the eight-shaped product because of its poor solubility, but the high yield of the eight-shaped cyclic product is still confirmed by comparing the integration area of these two peaks (g+h, g'+h') in Figure 3d (see details in Figure S6, ESI[†]). From the FT-IR spectra (Figure 4e), it could be observed that the characteristic absorption of the azido group

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Figure 3. ¹H NMR spectra of (a) $(PM_{396}-alkyne)_{2'}$ (b) $(PM_{396}-alkyne)_{2'}(PCL_8-OH)_{2'}$ (c) $(PM_{396}-alkyne)_{2'}(PCL_8-N_3)_{2'}$ and (d) $[c-(PM_{396}-b-PCL_8)]_2$ in $C_2D_2Cl_4$ at 90 °C.



Figure 4. FT-IR spectra of (a) $(PM_{110}-OH)_{2^{\prime}}$ (b) $(PM_{110}-alkyne)_{2^{\prime}}$ (c) $(PM_{110}-alkyne)_{2^{\prime}}(PCL_{15}-OH)_{2^{\prime}}$ (d) $(PM_{110}-alkyne)_{2^{\prime}}(PCL_{15}-N_{3})_{2^{\prime}}$ and (e) $[c-(PM_{110}-b-PCL_{15})]_{2^{\prime}}$.

around 2110 cm^{-1} and the alkyne group around 3314 cm^{-1} disappeared after click cyclization. From all of the above, it can be concluded that the intramolecular cyclization was successful.

Triple-detection GPC (refractometry, light scattering at λ = 670 nm and viscometry) was also used to compare the linear to

the corresponding cyclic polymers. Unfortunately, due to the weak signals of the light scattering and viscometer responses (Figure S3, Supporting Information), it was impossible to extract conclusions.

Actually, we first tried to synthesize this PM-based eightshaped copolymer according to another strategy (Scheme S1; see details in the Supporting Information) from a linear precursor with two alkyne groups at the chain ends and two azido groups in the middle of the chain, followed by intramolecular click chemistry. The ¹H NMR results showed the absence of cyclization due to the steric hindrance of azido groups in the middle of the chain, so we improve the strategy by using 4-miktoarm star-type precursor instead of the linear one.

The thermal behavior of the cyclic copolymers and their corresponding precursors, studied by differential scanning calorimetry (DSC), are shown in Figure 6. The 4-miktoarm star copolymer (PM₁₁₀-alkyne)₂-(PCL₁₅-N₃)₂ with $M_n = 7100$ exhibited two relatively melting peaks at 106.5 and 44.6 °C, attributed to the PM and PCL blocks, respectively (Figure 6a). For the corresponding cyclic [c-(PM₁₁₀-b-PCL₁₅)]₂, the melting point (T_m) of PM slightly decreased (100.8 °C) while the T_m of PCL slightly increased to 45.3 °C (Figure 6b). A similar trend was observed in the case of [c-(PM₃₉₆-b-PCL₈)]₂ (Figure 6d) compared to the corresponding precursors (Figure 6c), at significantly lower melting temperatures of the PM block. The melting temperatures of the PCL block were present with a very small peak at around 37 °C,



Figure 5. GPC traces of eight-shaped cyclic copolymers and the corresponding 4-miktoarm star precursors (TCB at 150 °C).

Table 2. Molecular Characteristics of 4-Miktoarm Star Copolymers $(PM-alkyne)_2$ - $(PCL-N_3)_2$ and the Corresponding Eight-Shaped Cyclic Products $[c-(PM-b-PCL)]_2$

entry	sample	$M_{\rm n, NMR}^{a}$	$M_{\rm p, \ GPC}^{b}$	\overline{D}^{b}	R ^c
1	$(PM_{110}-alkyne)_2-(PCL_{15}-N_3)_2$	7100	5400	1.39	0.91
	$[c-(PM_{110}-b-PCL_{15})]_2$	7100	4900	1.39	
2	(PM ₃₉₆ -alkyne) ₂ -(PCL ₈ -N ₃) ₂	13 400	13 100	1.26	0.90
	$[c-(PM_{396}-b-PCL_8)]_2$	13 400	11 900	1.35	

^{*a*} $M_{\rm n, NMR}$ was calculated from ¹H NMR spectra (600 MHz, C₂D₂Cl₄) at 90 °C. ^{*b*} $D(M_{\rm w}/M_{\rm n})$ and $M_{\rm p, GPC}$ determined by HT-GPC (1,2,4-trichlorobenzene, 150 °C, PS standards). ^{*c*}R is the ratio of the $M_{\rm p, GPC}$ of cyclic polymers to their linear precursors.



Figure 6. DSC traces for copolymers: (a) $(PM_{110}\text{-}alkyne)_2$ - $(PCL_{15}\text{-}N_3)_2$; (b) $[c-(PM_{110}\text{-}b-PCL_{15})]_2$; (c) $(PM_{396}\text{-}alkyne)_2$ - $(PCL_8\text{-}N_3)_2$; and (d) $[c-(PM_{396}\text{-}b-PCL_8)]_2$.

probably due to its low composition. The more complex the structure, the higher the influence on $T_{\rm m}$ and $X_{\rm c}$, due to the reduced mobility of the chains.

Finally, the self-assembly behaviors of $(PM_{110}\text{-}alkyne)_2$ - $(PCL_{15}\text{-}N_3)_2$ and $[c-(PM_{110}\text{-}b\text{-}PCL_{15})]_2$ copolymers, as an example, were investigated and compared. PM-based block copolymers in selective solvents for one block self-assemble to form micellar structures. The morphology and size of the selfassembled micelles are affected by different architectures. In this case, DMF was chosen as a selective solvent for PCL, and therefore, the DMF-phobic PM block could form the core. Solutions of $[c-(PM_{110}-b-PCL_{15})]_2$ and their corresponding precursors $(PM_{110}-alkyne)_2-(PCL_{15}-N_3)_2$ in DMF were prepared with the same concentration. The size distribution of the formed nanoparticles in all DMF solutions was measured by dynamic light scattering (DLS) at room temperature (Figure 7). The size of the nanoparticles formed by $[c-(PM_{110}-b-PCL_{15})]_2$.



Figure 7. Size distribution of the formed micelles in DMF: (a) $(PM_{110}\text{-}alkyne)_2$ - $(PCL_{15}\text{-}N_3)_2$ and (b) $[c-(PM_{110}\text{-}b-PCL_{15})]_2$.

 PCL_{15})]₂ was smaller than that of $(PM_{110}\text{-}alkyne)_2\text{-}(PCL_{15}\text{-}N_3)_2$ (Figure 7: 414 nm for a; 251 nm for b). The smaller peak in Figure 7b around 25 nm must be contributed to the unimolecular chain which does not self-assemble. The decrease of the micelle size may be attributed to the formed cyclic topology, which will restrict the aggregation of polymethylene block. The PDI of the $(PM_{110}\text{-}alkyne)_2\text{-}(PCL_{15}\text{-}N_3)_2$ solution is 0.048 according to the DLS, indicating a monodisperse particle system. A higher value of 0.706 was observed for $[c-(PM_{110}\text{-}b\text{-}PCL_{15})]_2$ solutions because of the byproducts and the unimolecular chains.

CONCLUSIONS

A novel synthetic strategy toward well-defined eight-shaped cyclic block copolymers consisting of PM and PCL blocks was

developed by combining the novel thexylborane chemistry with polyhomologation, ROP, and click reaction. 1,4-Pentadien-3-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate underwent cyclic hydroboration to afford a boracyclic initiator, which was used for the polyhomologation of dimethylsulfoxonium methylide to give α, ω -dihydroxyl polymethylene. Subsequent esterification, deprotection, and ROP resulted in 4-miktoarm star copolymers, followed by intramolecular click cyclization. Although it is difficult to further purify the obtained product, the eight-shaped structure can be confirmed by HT-GPC, ¹H NMR, and FT-IR spectroscopy. The difference in the thermal properties and the self-assembly behavior was observed by DSC and DLS, also indicating the successful synthesis of eight-shaped cyclic block copolymers. This general strategy expands the applicability of the difunctional borane initiator and opens new horizons toward PM/cyclic-based complex polymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b02571.

¹H NMR spectra (Figures S1 and S2); triple-detection GPC traces (Figure S3); FT-IR spectra (Figure S4); NMR spectra (Figures S5 and S6); and synthetic strategy of [c-(PM-b-PCL)]₂ (Scheme S1) (PDF)

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Notes

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