Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 6457–6462 **6457**
DOI: 10.1021/ma901041x

Macrocycle-Terminated Core-Cross-Linked Star Polymers: Synthesis and Characterization

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Received May 13, 2009; Revised Manuscript Received June 17, 2009

ABSTRACT: We have synthesized macrocyclic polystyrene- (PS-) terminated PS star polymers via a core-cross-linking approach in this work. A tadpole-shaped macrocyclic PS-*linear*-PS copolymer was synthesized at first via click chemistry and ATRP polymerization method. The "living" ATRP initiating chain-ends of the tadpole-shaped copolymers were linked together via ATRP polymerization with divinylbenzene to form a core-cross-linked macrocyclic star polymer. The number of arms attached to the macrocyclic star polymers was measured with NMR, and absolute molecular weights with gel permeation chromatography (GPC) with multiangle laser light scattering detector. These macrocyclic star polymers had a highly cross-linked core and many radiating arms. The shorter tadpole-shaped precursors caused core-cross-linked star polymers with higher molecular weights and more arm numbers. The macrocycle-terminated core-cross-linked star polymers showed two glass transition temperatures, one arising from the linear branches and another from the macrocycles.

Introduction

Due to the resulting unique topology and physical properties, the synthesis of macrocyclic polymers and the comprehensive polymer architecture based on macrocyclic units have attracted a great deal of interest in the past decades.[1,2] Many synthetic approaches to macrocyclic polymers have been developed; nevertheless, they can be mainly grouped into two strategies, the ring−chain equilibrium method and the end-linking method.[3,4] The end-linking strategy, specifically the intramolecular cyclization of linear precursors at high dilution, seems to be a more "classic" method compared with the ring−chain equilibrium method. The introduction of living free radical polymerization methods for linear precursors and new organic synthetic concepts for end-linking chemistry makes the end-linking method a robust and versatile way to form macrocyclic polymers. The so-called "click" chemistry, i.e. the Cu(I)-catalyzed cycloaddition of azides and alkynes to form 1,2,3-triazoles,[5] has become a reliable end-linking approach to macrocyclic polymers with high coupling efficiency. Grayson and co-workers recently reported an efficient route to well-defined macrocyclic polymers via "click" cyclization,[6] which has clearly showed the importance of the combination of the living radical polymerization and click reaction in the synthesis of macrocyclic polymers.

The structural design and property study of complex polymer architecture based on novel building units is always attractive to scientists. Macrocyclic polymers have also emerged as novel building blocks for the design of polymer structures recently. Three kinds of macrocycle-containing polymer structures are found in the literature, i.e., tadpole-shaped macrocyclic−linear copolymers,[7] macrocyclic copolymers bearing many linear branches,[8] and polymers with macrocycles embedded in the backbones that are synthesized by controlled cyclopolymerization of bis(vinyl) monomers with conformations favorable for ring-closing.[9] However, star polymers end-functionalized by macrocyclic blocks have not appeared in the literature yet, though the importance of star polymers has been generally acknowledged. Basically, star-like structures with many braches can "magnify" the functions of end-groups; however, they exhibit compact structures if compared with linear polymers. Star polymers end-functionalized by macrocyclic blocks may find applications in separation, molecule capturing or metal scavengers, etc.

In this work, we report on the synthesis of star polymers with macrocycles at the branch ends. We synthesize a tadpole-shaped linear−macrocyclic diblock polymer at first and then link the chain-ends of linear blocks together to form a star via a core-cross-linking method. Though many other approaches can be adopted for the synthesis of star-like polymers, however, the core-cross-linking method is characterized by its facility and fast formation of star-like polymers with many radiating arms. Many novel star polymers have been synthesized by the facile core-cross-linking method.[10]

Experimental Section

Materials. Diethanolamine (99%), 2-bromopropionyl bromide (98%), copper(I) bromide (CuBr, 98%) and sodium azide (98%) were purchased from Aldrich and used as received. *N*,*N*′,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA, 99%) and divinylbenzene (DVB, 80% mixture of isomers) were washed three times with 5% sodium hydroxide solution, once with distilled water, and then distilled over calcium hydride. Styrene (Aldrich, 99%) was stirred with CaH_2 overnight and distilled under reduced pressure prior to use. Triethylamine (Aldrich, 99%), tetrahyrofuran (THF), acetone and *N*,*N*-dimethylformamide (DMF) were distilled from CaH_2 under a dry nitrogen purge just before use.

Methods. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer. ^{1}H NMR (300 MHz) spectra were recorded on a Bruker DMX-300 NMR spectrometer. Tetramethylsilane (TMS) was used as internal standard. The apparent molecular weight (M_{RI}) and molecular weight distribution were determined by gel permeation chromatography (GPC) using a series of three linear Styragel columns. Waters 1515 pump and Waters 2414 differential refractive index

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Published on Web 07/08/2009

(RI) detector (set at 40 °C) were used. The eluent was THF at a flow rate of 1.0 mL/min. The measurement of absolute molecular weight was performed by GPC (Waters 1515 Isocratic HPLC Pump) equipped with a DAWN EOS (Wyatt Technology) multiangle laser light scattering detector (MALLS) operating with a He−Ne laser (633 nm wavelength). DSC was performed on a Perkin-Elmer Diamond DSC instrument at a heating rate of 10 K/min. MALDI−TOF mass spectrum was acquired using an Applied Biosystems Voyager Elite spectrometer with delayed extraction using the reflection positive iron mode. Dithranol was used as the matrix, and silver trifluoroacetate as the cation source, in a 50/5/2 Matrix/Ag^+/polymer ration. The relaxation delay was set to 500 ns, with an acceleration voltage of 20 KV, a grid voltage of 70%, without guide wire, and low mass gate at 1000 AMU.

Preparation of 2,2′-(Prop-2-ynylazanediyl)diethanol (1). According to a similar procedure reported previously by our group and others, compound **1** was synthesized.[11] To a mixture of propargyl bromide (5.95 g, 50 mmol) and anhydrous K_2CO_3 (13.8 g, 100 mmol) in dry acetone (250 mL) was charged diethanol amine (5.25 g, 50 mmol). The reaction mixture was refluxed for 24 h with good stirring. The reaction mixture was then cooled, and the potassium salts were filtered off. The reaction mixture was concentrated, and was extracted with chloroform and washed with water. The organic layer was further washed well with water, dried over $MgSO_4$, filtered, and concentrated to give 6.8 g carmine viscous oil. The crude product was purified by passing through a silica gel column (ethyl acetate: methanol = 2:1) to give pure product **1** (5.9 g) as yellow viscous oil. Yield: 83%. ^{1}H NMR (δ, ppm, $CDCl_3$): 3.66 (m, 4H, $N(CH_2CH_2OH)_2$), 3.49 (m, 2H, $NCH_2C{\equiv}CH$), 3.39 (broad, s, 2H, $(CH_2OH)_2$), 2.75 (m, 4H, $N(CH_2CH_2OH)_2$), 2.16 (m, 1H, $NCH_2C{\equiv}CH$).

Preparation of Initiator (3). 2-Bromoisobutyryl bromide (4.58 g, 20 mmol) was added dropwise to a solution of **1** (2.86 g, 20 mmol) and triethylamine (2.02 g, 20 mmol) in dry THF at 0 °C. The solution was stirred for 24 h and allowed to reach room temperature slowly. The mixture was then transferred to a separation funnel with 350 mL of dichloromethane and rinsed successively with 10% HCl, 5% $NaHCO_3$, and deionized water. The organic phase was dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The crude extract was further purified on a silica gel column (dichloromethane: methanol = 3:1) to give the pure product (4.2 g, 14.4 mmol). Yield: 72%. ^{1}H NMR (δ, ppm, $CDCl_3$): 4.28 (m, 2H, NCH_2CH_2OCO), 3.66 (m, 2H, NCH_2CH_2OH), 3.49 (m, 2H, $NCH_2C{\equiv}CH$), 2.90 (m, 2H, NCH_2CH_2OCO), 2.75 (m, 2H, NCH_2CH_2OH), 2.16 (m, 1H, $NCH_2C{\equiv}CH$), 1.95 (m, 6H, $OCOC(CH_3)_2Br$).

Preparation of Linear PS Precursors (4). A Schlenk flask was flame-dried under vacuum and charged with copper(I) bromide (72 mg, 0.50 mmol), PMDETA (86.5 mg, 0.50 mmol), and styrene (5.2 g, 50 mmol) under a N_2 atmosphere. The reaction mixture was degassed by three freeze−pump−thaw cycles. Initiator **3** (146 mg, 0.50 mmol) was added via syringe. The reaction mixture was placed in a preheated 80 °C oil bath and allowed to stir under nitrogen for 1.5 h.

The Schlenk flask was then dipped into liquid nitrogen to stop the polymerization. Subsequently, the solution was diluted with THF followed by passing through a column of neutral alumina to remove the copper salts. The product was precipitated from an excess of methanol twice, filtered, and vacuum-dried at 40 °C to give a white solid of 1.96 g. Yield: 38%. Calcd M_{NMR} = 3460. GPC: $M_{n,RI}$ = 3600, PDI = 1.10.

Preparation of 4-N_3 (5). A 100 mL round bottomed flask was filled with **4** (1.08 g, 0.30 mmol), sodium azide (117 mg, 1.8 mmol), and DMF (15 mL). The solution was allowed to stir at room temperature for 24 h before purification by precipitation into methanol to give a white solid. Yield: 95%. Calcd M_{NMR} = 3280. GPC: $M_{n,RI}$ = 3700, PDI = 1.09.

Cyclization of 5 To Form Macrocycle 6 by "Click" Reaction. We carried out the cyclization reaction according to a similar procedure described by Grayson et al.[6] To a round-bottomed flask (1 L) was added DMF (700 mL), which was saturated by pure N_2. Sodium ascorbate (392 mg, 1.98 mmol) was added to the DMF solution followed by dropwise addition of $CuSO_4$ (158.4 mg, 0.99 mmol) in 1 mL of water, yielding a turbid brown suspension. A separate flask containing compound **5** (0.120 g, 0.033 mmol) dissolved in 5 mL DMF was degassed through three freeze/thaw cycles, the contents of which was then added to the $CuSO_4$/sodium ascorbate reaction mixture via a syringe pump at a rate of 1.5 mL/h. The reaction was carried out at 30 °C under N_2 atmosphere. The reaction was allowed to proceed at 30 °C for an additional 1 h followed by concentration to remove most solvents. Then, the mixture was extracted with dichloromethane. The organic layer was passed through a column of neutral alumina to remove the copper salts. The product was precipitated from an excess of methanol twice, filtered, and vacuum-dried at 40 °C to give a white solid of 0.106 g. Yield: 88%. Calcd M_{NMR} = 3160. GPC: $M_{n,RI}$ = 2800, PDI = 1.10. MALDI−TOF MS: M_n ($M + Ag^+$) = 3040.5, PDI = 1.03.

Preparation of Macrocyclic Initiator (7) from 6. Compound **6** (100 mg, 0.028 mmol) and triethylamine (84.8 mg, 0.84 mmol) were dissolved in dry THF (20 mL) and cooled to 0 °C. 2-Bromoisobutyryl bromide (192.4 mg, 0.84 mmol) was added dropwise to the reaction mixture. It was then stirred for 24 h at room temperature. After filtration, the solution was repeatedly precipitated in cold methanol to give a white solid (product 7) of 0.96 g. Yield: 92%. GPC: $M_{n,RI}$ = 2900, PDI = 1.11.

General Procedure for Producing the Tadpole-Shaped Linear−Macrocyclic Copolymer (8) from 7 and Styrene. A mixture of styrene (485 mg, 4.8 mmol), CuBr (3.43 mg, 0.024 mmol), PMDETA (9.62 μL, 0.048 mmol), anisole (2 mL), and macrocyclic initiator (**7**) (90 mg, 0.024 mmol) was added to a Schlenk flask and was degassed by three freeze−pump−thaw cycles. The flask was then immersed in an oil bath at 100 °C to conduct the polymerization. During the procedure, some of resulting polymers were taken out from the reaction mixture by syringe at several interval times for analysis. Each sample was diluted with THF, and then was passed through a column of neutral alumina to remove the copper salts. The products were precipitated from an excess of methanol twice, filtered, and vacuum-dried at 40 °C and analyzed by GPC. Three tadpole-shaped linear−macrocyclic copolymers from the same macrocyclic PS but different linear PS were synthesized.

Preparation of Macrocycle-Terminated Core-Cross-Linked Star Polymers (9). In a typical procedure, a mixture of precursor **8** ($M_{n,RI}$ = 6200, PDI = 1.12, 100 mg, 0.016 mmol), DVB (70 μL, 0.48 mmol), CuBr (2.3 mg, 0.016 mmol), and PMDETA (6.4 μL, 0.032 mmol) in anisole (1.6 mL) was added to a Schlenk flask and degassed by three freeze−pump−thaw cycles. The flask was then immersed in an oil bath at 110 °C and heated for 48 h. Samples were taken from the reaction mixture and analyzed directly by GPC. Finally, the mixture was diluted with THF, and was purified by passing through a column of neutral alumina to remove the copper salts. The product was precipitated from an excess of methanol twice, filtered, and vacuum-dried at 40 °C to give a crude product (0.091 g).

Unreacted precursor **8** was removed from the crude product by precipitation fractionation. The crude product (91 mg) was dissolved in 10 mL of THF. Methanol (8 mL) was added dropwise to the solution while a precipitate was observed. The solid was allowed settling and then filtered. This procedure was repeated several times to obtain comparatively pure core-cross-linked star polymers (product 9, 48 mg). Yield: 53%. GPC: $M_{n,RI}$ = 357800, PDI = 1.37.

Results and Discussion

The synthesis of macrocyclic star polymers is outlined in Scheme 1. A linear PS with three functional groups, i.e., a hydroxyl group, an alkyne and an azide group is synthesized at

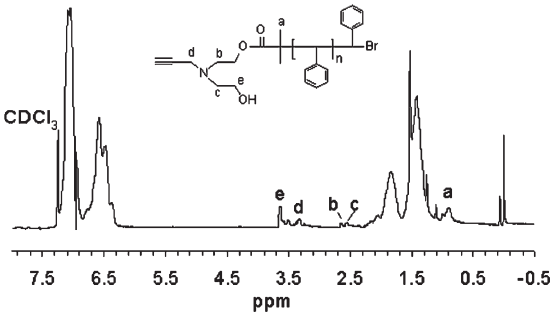
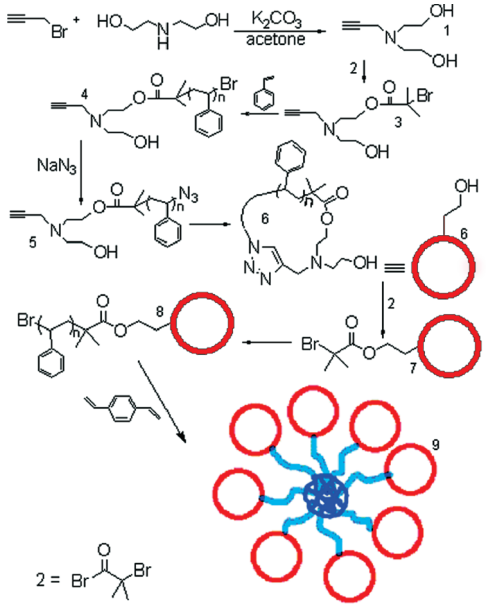


Figure 1. ^{1}H NMR of compound **4**.

Scheme 1. Synthesis of Macrocyclic Star Polymer



first. The alkyne and azide groups at chain-ends are linked to form a macrocyclic polymer via "click" reaction, leaving a pendant hydroxyl group for further growth of a linear PS branch via ATRP polymerization. The "living" chain-ends of the linear branches stemming from the macrocyclic PS moieties are chemically anchored to a cross-linked core to form a core-cross-linked macrocyclic star polymer.

Synthesis of a Linear Precursor. The purpose of this step is to synthesize a linear PS with a side hydroxyl group, and terminal alkyne and azide groups. 2, 2′-(Prop-2-ynylazanediyl) diethanol (compound 1) is synthesized at first, and the structure is characterized by NMR (Figure 1S in the Supporting Information). Compound **3** is obtained by esterification of compound 1 with 2-bromoisobutyryl bromide and careful separation by silica gel column chromatography. The ^{1}H NMR of compound **3** is illustrated in Figure 2S (Supporting Information). The NMR and thin-layer chromatography analysis show that pure compound **3** is obtained. The ATRP polymerization of styrene is then started from the 2-bromo-2-methylpropionic ester to obtain a linear precursor (compound **4** in Scheme 1). Figure 1 is the ^{1}H NMR of compound **4**. The resonance peaks appeared in Figure 1 are assigned to relevant protons. The number average molecular weight (M_n) of compound 4 is 3600 with a polydispersity index of 1.10 measured by GPC. The M_n calculated from the NMR spectrum is about 3460, which is quite close to the M_n measured by GPC.

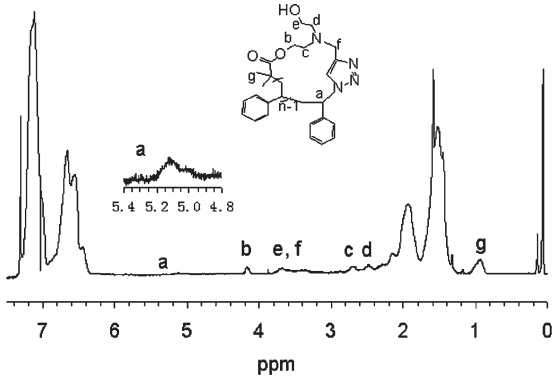


Figure 2. ^{1}H NMR of macrocyclic compound **6**.

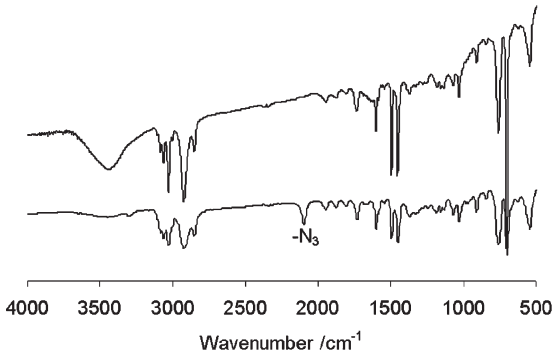


Figure 3. FTIR of compound **5** (bottom) and macrocyclic PS **6** (top).

Synthesis of a Macrocyclic Precursor. After azidation of the end −Br groups with sodium azide, the linear PS precursor (compound **4**) is then transformed into a macrocyclic PS with a pendant hydroxyl group (compound **6**) via click reaction in a dilute solution. Besides the high efficiency and quantitative yield of click reactions under the current conditions, a highly dilute condition is also an important factor in determining whether an α,ω-functionalized polymer will prefer cyclization or condensation.[1−4] The macocyclic product (compound 6) is isolated by extraction and precipitation as described by Grayson et al.[6]

The structure of the macrocyclic polystyrene is characterized by using ^{1}H NMR and FTIR. Figure 2 shows the ^{1}H NMR spectra of the macrocyclic precursor (compound **6**). Compared to the linear PS precursors, a new resonance peak at about 5.1 ppm appears after "click" cyclization, which is ascribed to the proton of CH_2CH(Ph)N due to the formation of 1,2,3-trazole. The other resonance peaks are assigned well to relevant protons as tagged in Figure 2. The "click" cyclization is also monitored by using the FTIR spectra (Figure 3). After click reactions, both the signals of the azide (2090 cm^{-1}) and terminal alkyne (3280 cm^{-1}) disappear as expected. GPC comparison between the linear precursor and the macrocyclic sample is usually a strong support for cyclization. In contrast to linear PS precursors, the macrocyclic precursor exhibits a longer size exclusion time indicating a decrease of hydrodynamic volume (Figure 4), which is consistent with the results of Grayson.[6] Due to the smaller hydrodynamic volume of a macrocyclic polymer compared with its linear precursor, the M_n of **6** measured with GPC is only 2800 and PDI 1.10. The ratio of the molecular weight (GPC) of macrocyclic PS **6** to that of the linear precursor **5** is 2800/3700 = 0.76. The value is in good agreement with the experimental value (0.70) obtained in macrocyclic PS prepared by living bifunctional anionic polymerization and by

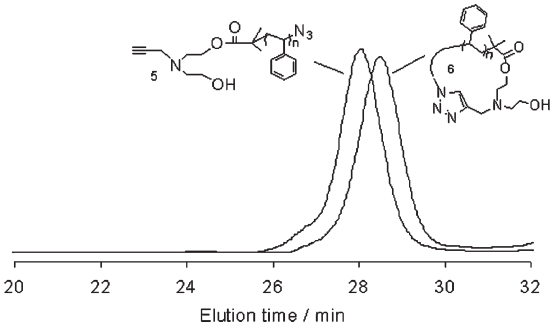


Figure 4. GPC of linear compound **5** and macrocyclic PS **6**.

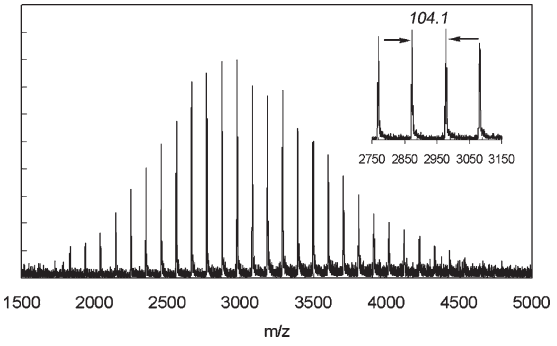


Figure 5. MALDI−TOF MS of macrocyclic PS **6** (Ag^+).

coupling with α,α′-dichloro-*p*-xylene, and the theoretical value (0.66) predicted by Bloomfield and Zimm via viscosity analysis.[12] Meanwhile, unimodal and symmetrical trace of macrocyclic precursors reveals the absence of condensation products and high efficiency of click reactions.

MALDI−TOF MS of macrocyclic compound **6** is illustrated in Figure 5. According to the MALDI−TOF MS, the accurate M_n of **6** with an Ag cation ($M_n + Ag^+$) is 3040.5, and PDI 1.03. Thus the M_n of **6** is 2932.8. The MALDI−TOF MS also shows the absence of impurities of linear PS with different end groups or with higher molecular weights due to the formation of dimer, etc. The structural characteristics evidenced by GPC, MALDI−TOF MS, NMR, and FTIR verify the successful cyclization.

Synthesis of Macrocyclic Star Polymers. The macrocyclic ATRP initiator (**7**) is synthesized through the reaction of macrocyclic precursor (**6**) and 2-bromoisobutyryl bromide. And then, a series of linear−macrocyclic copolymers (**8**) with different molecule weights are synthesized. The kinetics of styrene polymerization initiated by the macrocyclic initiator is studied using CuBr/PMDETA as the catalytic system at 100 °C. Figure 6 demonstrates the dependence of molecular weight and distribution index on monomer conversion. M_n is linearly increased with the increase of conversion, and the PDI is narrow (between 1.1 and 1.2) as expected. The first-order kinetic plot of polymerization demonstrates that the reaction processes in a controlled fashion with the monomer consumption increasing.

Core-cross-linking method is used to form macrocyclic star polymers from the linear−macrocyclic copolymers (compound **8**), and DVB is used as the cross-linking reagent. To optimize the molar ratio of DVB to compound **8**, different reaction systems with different [DVB]/[**8**]$_0$ are tested, and monitored by GPC. GPC traces of macrocyclic star polymers formed at different [DVB]/[**8**]$_0$ are showed in Figure 7. The elution peaks due to the residual linear−macrocyclic copolymers exist in all traces of crude

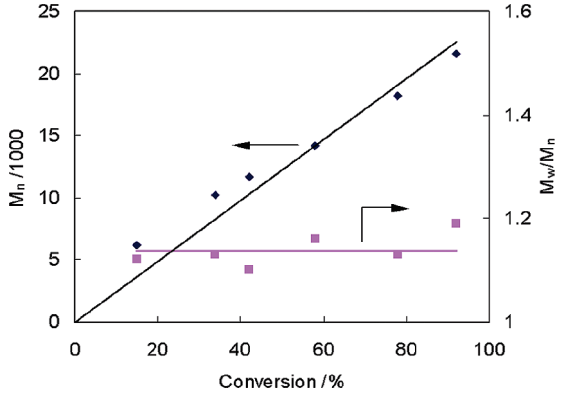


Figure 6. Dependence of number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) on monomer conversion.

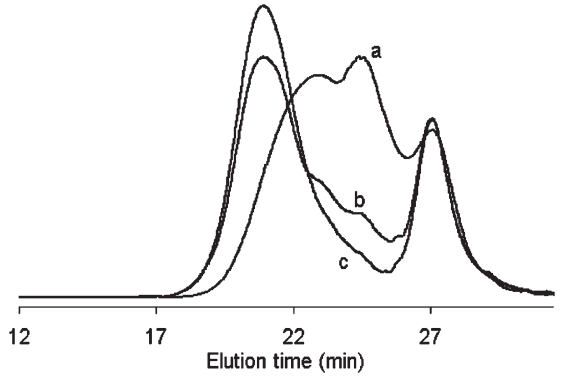


Figure 7. GPC traces of star-forming reactions at different [DVB]/[**8**]$_0$ of 15 (a); 25 (b) and 30 (c). A sample of compound **8** with M_n of 6200 and PDI of 1.12 is used.

products. An elution peak at lower elution time is assigned to the macrocyclic star polymer. A symmetrical elution peak due to a macrocyclic star polymer is found at [DVB]/[**8**]$_0$ of 30. According to the comparison illustrated in Figure 7, a molar ratio [DVB]/[**8**]$_0$ of 30 is chosen as an optimum condition for the preparation of unimodal macrocyclic star polymers. Because of the big differences in molecular weights, the residual linear−macrocyclic copolymers (compound **8**) are easily removed from the crude products by precipitation fractionation. The purification efficiency can be monitored by GPC. Figure 8 illustrates the GPC traces of the samples before and after purification, taken from the reaction system of a linear−macrocyclic copolymer with M_n of 6200. After purification, a unimodal macrocyclic star polymer is obtained ($M_{n,RI} = 357800$, PDI = 1.37). Three core-cross-linked macrocyclic star polymers from three linear−macrocyclic precursors have been synthesized as listed in Table 1.

Because star polymers, especially core-cross-linked star polymers, have very compact structures and smaller hydrodynamic volumes compared with linear standards, the absolute molecular weights of the core-cross-linked star polymers are analyzed by GPC with MALLS detector. The light scattering detector is more sensitive to high molecular weight polymers. The absolute molecular weights are listed in Table 1. Comparison between the molecular weight data obtained with RI detector and MALLS detector supports that core-cross-linked star polymers have a very compact structure.

We can estimate the arm number per star polymer via NMR spectra using TMS with exact concentration as the

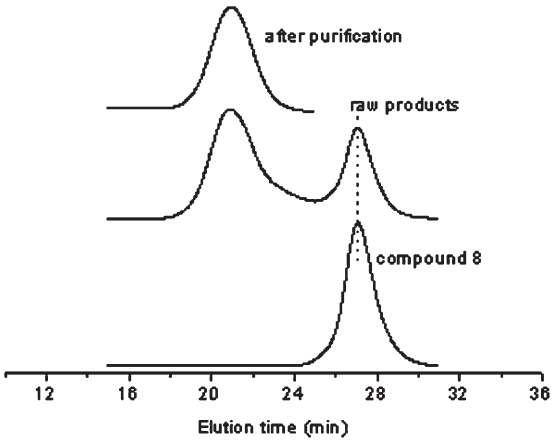


Figure 8. .GPC traces of linear−macrocyclic copolymers (compound **8**), the reaction mixture ([DVB]/[**8**]$_0$ = 30) and finally macrocyclic star polymers isolated by precipitation fractionation. A sample of compound 8 with M_n of 6200 and PDI of 1.12 is used.

Table 1. Synthesis of Macrocyclic Star Polymer 9 from Linear−Macrocyclic Precursor 8 at Molar Ratio [DVB]/[8]$_0$ of 30

	precursors **8**		products **9**				
run	M_n[a]	[**8**]$_0$	M_n[b]	PDI[b]	M_n[c]	PDI[c]	n[d]
1	6.2	10	357.8	1.37	571.0	1.37	63
2	11.7	10	436.5	1.36	1394.6	1.32	77
3	18.3	10	242.7	1.28	431.6	1.32	17

[a] The unit is mM for [**8**]$_0$, and kg/mol for M_n, respectively. [b] Data were measured by GPC with RI detector. [c] Absolute GPC with MALLS detector. [d] Number of arms calculated from NMR using TMS as a standard.

calibration standard. The masses of samples and TMS for NMR analysis are carefully weighted. The ^{1}H NMR of the macrocyclic star PS obtained in run 3 is illustrated in Figure 9. The peak "a" is due to the methyl groups of 2-bromopropionyl esters located on the arms of the star (12 protons in each arm). According to the integration values of peak "a" and TMS, we obtain the moles of arms per gram of star sample, which multiplied by the absolute molecular weight makes the arm number of a star. The data of arm numbers are listed in Table 1. Possibly because of higher concentrations of active centers, the shorter arm precursors cause core-cross-linked star polymers with higher molecular weights and more arm numbers. These results indicate that starlike polymers with compact structures are obtained. These macrocyclic star polymers have a highly cross-linked core and many radiating arms.

DSC Analysis of Macrocyclic Star Polymers. A macrocyclic polymer is a polymer without chain-ends. According to chain-end free volume theory, a macrocyclic polymer may have a higher glass transition temperature than its linear analogue,[13] thus may exhibit a more rigid conformation. We have studied the glass transition behaviors of these macrocyclic star polymers. Figure 10 shows the DSC plots. In the conditions of this study, the linear PS shows a glass transition at about 82 °C, while the macrocyclic PS at 90 °C (Figure 10). According to Figure 10, the macrocyclic star polymers show clearly two glass transition temperatures at about 82 and 90 °C, respectively. The former T_g arises from the linear PS, and the latter one from the macrocyclic PS. It is very interesting that the macrocyclic star PS shows two distinct T_g, which may imply phase-separation between linear PS and macrocyclic PS. Miscible polymer mixtures often show only one T_g.[14] The macrocyclic star PS may have very interesting

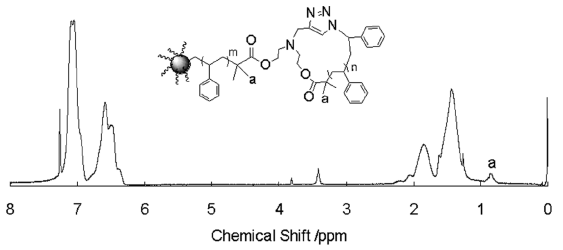


Figure 9. ^{1}H NMR of macrocyclic star PS **9**.

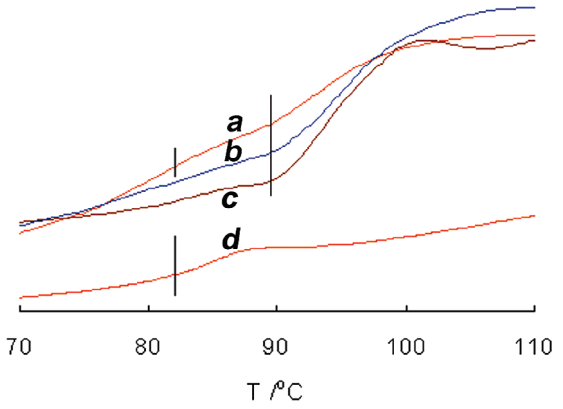


Figure 10. DSC plots of macrocyclic star polymers with M_n of 242700 (a), 357800 (b), and 436500 (c) compared with the linear precursor (d).

properties that worth further study in the future. The ideal macrocyclic star polymer may have an interesting core−shell structure with a loose but rigid shell.

Conclusions

We have synthesized macrocyclic star polymers via a core-cross-linking approach. The combination of ATRP and click chemistry supplies a robust way to synthesize tadpole-shaped linear−macrocyclic copolymers. The "active" centers of the linear−macrocyclic polystyrene from the ATRP reactions are joined together via a core-cross-linking method to form macrocyclic star polystyrenes. NMR and GPC with MALLS results show that these macrocyclic star polymers have a compact structure and many radiating arms. DSC analysis demonstrates that the macrocycle star polystyrene with low molecular weights show two glass transition temperatures of linear branches and macrocycles. Phase-separation between linear PS and macrocyclic PS may occur in the macrocyclic star PS. The macrocyclic star PS may have very interesting properties that worth further study in the future.

Acknowledgment. The National Natural Science Foundation of China (Project No. 50773076)is acknowledged for support.

Supporting Information Available: ^{1}H NMR spectra of **1** (Figure 1S) and **3** (Figure 2S). This material is available free of charge via the Internet at http://pubs.acs.org.

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