7056 *Macromolecules* **2010**, *43*, 7056–7061
DOI: 10.1021/ma101460n

Macromolecules
ARTICLE

Stepwise Cleavable Star Polymers and Polymeric Gels Thereof

Xiubo Jiang, Yongming Chen,* and Fu Xi

Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100190, China

Received July 1, 2010; Revised Manuscript Received August 5, 2010

ABSTRACT: A multifunctional initiator 1 with chemically labile disulfide and ester groups bearing four bromoisobutyryl groups was prepared by esterification of bis(2-hydroxyethyl)disulfide with 2,2-bis(2-bromoisobutyroyloxymethyl)propionic acid. Then well-defined four-arm star polystyrenes, $(S_n)_4$, were synthesized by atom transfer radical polymerization of styrene initiated with 1. Owing to the presence of the −S−S− and the ester linkages in precisely controlled position of the $(S_n)_4$ core inherited from the initiator, such a star polystyrene demonstrated interesting stepwise cleavage properties dependent upon the applied conditions. When treating samples with tri-*n*-butylphosphine or dithiothreitol 2,3-dihydroxy-1,4-butanethiol, the disulfide linkage which located in the center of the star polymers was cleaved and, as a result, one star molecule $(S_n)_4$ was cut into two linear polystyrenes, $2(S_n)_2$, with a −SH group situated in the middle of chains. Then, the resulted $(S_n)_2$ could be further cleaved into two shorter polystyrenes, $2(S_n)_1$, by hydrolysis to cut two ester groups located in the middle of the PS chains with KOH in a solution of THF/EtOH. Moreover, the $(S_n)_4$ stars may also be decomposed into the shortest segment, $4(S_n)_1$, directly by applying the hydrolysis condition. Furthermore, a polymer organogel was obtained from the cleavable star polymers $(S_n)_4$ by subjecting atom transfer radical coupling reaction which occurred between their −Br arm ends that preserved during formation of the star polymers. This gel could be also decomposed into the linear polystyrene segments of different length by breaking disulfide and ester linkages, respectively.

Introduction

Star polymers are the simplest branched polymers, which contain only one central branching point, i.e., the core, and multiple emanating polymeric arms. During the past decade, star polymers have obtained much interest because of their interesting properties such as the low viscosity and the multiple terminals compared with those of linear polymers of the same molecular weights.[1] With the recent advances in living radical polymerization, the synthesis of well-defined star polymers has received much attention because the various functional monomers are available for the star polymer formation, which are impossible for living ionic polymerization routes. Star polymers have been mainly synthesized using "core-first" or "arm-first" methodology. In the "core-first" method, a multifunctional initiator, the core-to-be, is used to initiate the monomers to obtain multiarm star polymers.[2−6] For the "arm-first" method, the linear arms with reactive terminals are synthesized first and then the core is produced either via cross-linkable multifunctional monomers[1,7−13] or coupling agents.[14−18] Moreover, a one-pot approach has been reported, of which the cores were formed through an *in situ* process.[19−21]

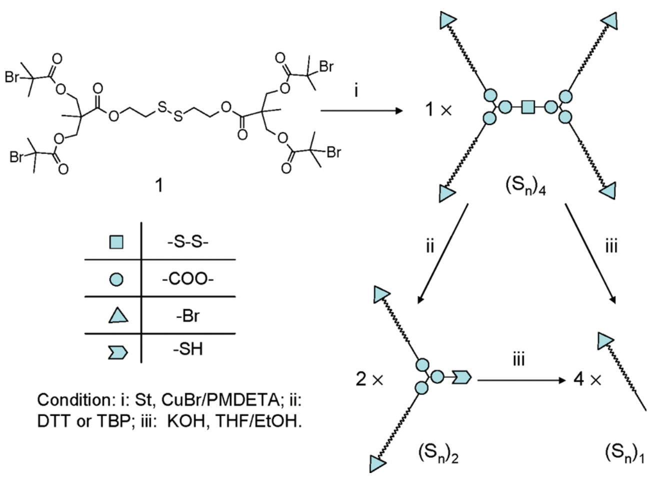
So far the research about star polymers mainly focuses on the synthetic methodology and structural control. Though many papers have been published on the synthesis of star polymers with various structures, only a few literatures have been found on the properties and functions of the well-defined star polymers. As the simplest branched polymers, the star/linear polymer blends were used to investigate stress relaxation dynamics[22] and the effect of miscibility.[23] Also star polymers of side-chain liquid crystalline polymers were investigated on thermotropic behavior in comparison with linear and comb polymers as well as the effect of the core of star polymers.[2,24,25] With the ability to encapsulate and isolate functional groups within the interior of the branched structure, star polymers containing different catalytic groups were used to catalyze cascade reactions.[26,27] Unimolecular micelles were also discussed based on amphiphilic star molecules,[28−30] which might have potential application in drug delivery. Amphiphilic star polymers were used as stabilizers to control formation of inorganic Pt nanoparticles.[31] It would be interesting if the star polymers could be switched into other forms of chain topology which may result in change of rheological properties because the chain dynamics of star polymer showed remarkable difference to the linear polymers.[32] Recently, a few reports involved the cleavage of well-defined star polymers and synthesis of new materials based on star polymers. For example, Qiao et al. have highlighted a particular focus on the degradation of a class of star polymers known as core cross-linked star polymers and application as potential drug delivery devices.[33] Davis and co-workers have reported synthesis of star polymers with degradable disulfide linkages by reversible addition−fragmentation chain transfer mediated radical polymerization using both "core-first" and "arm-first" methodologies.[6,34,35]

It is known that the core-first approach has been applied to prepare the star polymers with well-defined arm number. Moreover, when a multifunctional initiator is used, the obtained star polymers will have a functional core inherited from the initiator. Herein, we reported well-define four-arm star polystyrenes, $(S_n)_4$, with stepwise cleavable properties by atom transfer radical polymerization (ATRP) using a functional initiator 1, which contains disulfide and ester linkages that can be cleaved in the presence of tri-*n*-butylphosphine (TBP) or dithiothreitol 2,3-dihydroxy-1,4-butanethiol (DTT) and hydrolysis, respectively. As shown in Scheme 1, one four-arm star polystyrene $(S_n)_4$ may be decomposed into two linear $(S_n)_2$ whose molecular weight is half of its precursor by breaking the disulfide bond. Then the obtained $(S_n)_2$ can further

---

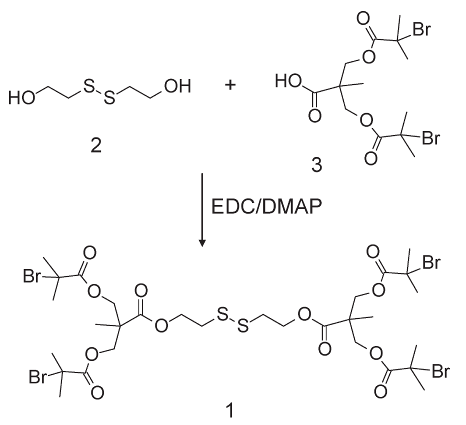
*Corresponding author. Telephone: +0086-10-62659906. Fax: +0086-10-62559373. E-mail: ymchen@iccas.ac.cn.

Scheme 1. Synthesis of Four-Arm Star Polystyrene $(S_n)_4$ and Its Degradation Products by Different Cleavage Strategies



Condition: i: St, CuBr/PMDETA; ii: DTT or TBP; iii: KOH, THF/EtOH.

Scheme 2. Synthesis of Cleavable Initiator 1 for Cleavable Star Polymers



be halved to two shorter linear $(S_n)_1$ by hydrolysis of ester groups. Also the $(S_n)_4$ could be decomposed straightway to the $(S_n)_1$ whose molecular weight is one-fourth of the starting polymer $(S_n)_4$ by cleaving ester groups through hydrolysis (Scheme 1). Therefore, this research supplies a smart star polymer that can be degraded to form the well-defined linear polymers composed of the arm segments. Furthermore, the star polymer $(S_n)_4$ has four bromide end groups which can be used to form polymer organogels by radical coupling reaction between the bromide terminals. As a result, the polymer organogels composed of star polymers as building blocks can be obtained and may also show a stepwise degradation by breaking disulfide and ester linkages, respectively.

Experimental Section

Materials. Styrene (St; Beijing Chemical Factory) and dichloromethane (DCM) were dried over CaH_2 and distilled prior to use. 2-Bromoisobutyryl bromide (98%, Aldrich), 4-(dimethylamino)pyridine (DMAP; 99%, Alfa Aesar), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA; 99%, Aldrich), *N*-(3-(dimethylamino)propyl)-*N*′-ethylcarbodiimide hydrochloride (EDC; Aldrich), bis(2-hydroxyethyl) disulfide (**2**; technical grade, Aldrich), TBP (95%, Alfa Aesar), DTT (99%, Aldrich) were used as received. Other reagents were commercialized chemicals and used as received. 2,2-Bis(2-bromoisobutyroyloxymethyl)propionic acid (**3**) (Scheme 2) was synthesized according to a previous procedure and its structure was confirmed by an ^{1}H NMR spectrum.[36]

Measurements. ^{1}H NMR spectra were recorded with a Bruker 400-MHz spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. The average molecular weights and polydispersity indices of all the samples were measured with a size exclusion chromatography (SEC) system equipped with a Waters 515 HPLC pump, three Waters Styragel columns (HT2, HT3, and HT4), a Rheodyne 7725i sampler, and a Waters 2414 refractive-index (RI) detector. Polystyrene standards were used to calibrate the SEC system. THF was used as the eluent at a flow rate of 1 mL/min at 35 °C.

Synthesis of Initiator 1. 2 (0.46 g, ca. 3.0 mmol), **3** (2.85 g, 6.6 mmol), and DMAP (0.40 g, 3.3 mmol) were dissolved in 15 mL of CH_2Cl_2. Then EDC (1.03 g, 6.6 mmol) was added upon stirring. After 12 h, 100 mL of CH_2Cl_2 was added to the solution, which was extracted with water three times. The combined CH_2Cl_2 phase was dried over $MgSO_4$, and then the solvent was evaporated to give a viscous liquid. The product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 5:1). The liquid **1** was dried at 25 °C under vacuum, giving 2.42 g of product (82%). ^{1}H NMR ($CDCl_3$, δ, ppm): 4.5−4.3 (m, 12H, $-CH_2O-$), 3.0−2.9 (t, 4H, $-CH_2S-$), 2.0−1.9 (s, 24H, $-C(CH_3)_2-$), 1.4−1.3 (s, 6H, $-CCH_3-$). ^{13}C NMR ($CDCl_3$, δ ppm): 172.1 ($-CO-O-CH_2CH_2S-$), 170.9 ($-CO-CBr(CH_3)_2$), 66.2 (CH_2CH_2-S-), 62.9 ($-CH_2-O-C(=O)-C(CH_3)_2Br$), 55.4 ($-C(CH_3)_2Br$), 46.8 ($(-O-CH_2)_2-CCH_3$), 36.7 ($-CH_2-S-$), 30.6 ($(CH_3)_2-C-$), 17.9 ($CH_3C-$). Anal. Calcd for $C_{30}H_{46}Br_4O_{12}S_2$: C, 36.67; H, 4.72; S, 6.52. Found: C, 37.11; H, 4.77; S, 6.25.

Synthesis of $(S_n)_4$ by ATRP of St with 1 as Initiator. A mixture of St (25.4 g, 0.244 mol), anisole (13.9 mL), PMDETA (20.8 mg, 0.12 mmol), and **1** (0.60 g, 0.61 mmol) was charged into a Schlenk flask and degassed by three freeze−pump−thaw cycles. The flask was then filled with nitrogen, and CuBr (17.3 mg, 0.12 mmol) was quickly added to the frozen mixture. After sealing the flask, it was evacuated and backfilled with nitrogen three times. The flask was then immersed in an oil bath and heated to 80 °C. After the predetermined time, the final reaction mixture was terminated by exposing to air and diluted with THF. The solution was filtered through a column filled with basic alumina, and the polymer was precipitated in a large amount of methanol and dried in a vacuum at 50−60 °C.

Preparation of PS Gel Using Atom Transfer Radical Coupling (ATRC) Procedure. Four-arm star $(S_{35})_4$ (3.1 g, 0.2 mmol) and PMDETA (138.6 mg, 0.8 mmol) were dissolved in 4 mL of toluene in a Schlenk flask and the mixture was degassed by three freeze−pump−thaw cycles. The flask was then filled with nitrogen, and CuBr (114.8 mg, 0.8 mmol) was quickly added to the frozen mixture. After the flask was closed, it was evacuated and backfilled with nitrogen three times. After reaction for 15 h at 70 °C, the polymer gel was prepared. The white dried gel (3.05 g, 98%) was obtained by extracting with mixture of THF/CH_3OH (1/1 to 3/1 to 5/1 v/v) in Soxhlet extractor for 5 days and then dried in a vacuum at 50−60 °C.

General Procedure of Cleavage of Four-Arm Star Polystyrene.

Breaking Disulfide Llinkages. (A) By TBP: Four-arm star polystyrene $(S_{35})_4$ (0.2 g, 0.013 mmol) was dissolved in 4 mL of the mixture of THF/H_2O (10/1), followed by a 20 μL of TBP solution. After 3 h, the polymer was precipitated with CH_3OH and analyzed by SEC.

(B) By DTT: Four-arm star polystyrene $(S_{15})_4$ (0.2 g, 0.027 mmol) was dissolved in 4 mL of deoxygenated THF, followed by DTT (0.41 g, 2.7 mmol). The mixture was stirred under nitrogen for 48 h at 60 °C. The polymer was precipitated with CH_3OH and analyzed by SEC.

Breaking Ester Linkages by Hydrolysis. Four-arm star polystyrene $(S_{35})_4$ (0.2 g, 0.013 mmol) was dissolved in 10 mL of THF/CH_3OH (v/v, 1/1), followed by KOH (0.36 g, 6.5 mmol). The mixture was stirred overnight under reflux. The polymer was precipitated with CH_3OH and analyzed by SEC.

General Procedure of Decomposition of Polystyrene Gels.

Breaking Disulfide Linkages. The polystyrene gel (0.2 g) was put in a flask, followed by 4 mL of the mixture of THF/

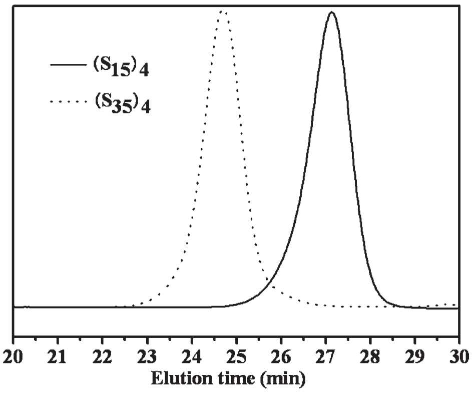


Figure 1. SEC curves of four-arm star polystyrenes from different time. Conditions: [St]/[**1**]/[CuBr]/[PMDETA] = 400:1:0.2:0.2; V_{St}:V_{anisole} = 2:1, 80 °C.

H_2O (10/1). A 40 μL of TBP solution was added in the flask. After 24 h, the mixture became a transparent solution. The mixture was precipitated with CH_3OH and analyzed by SEC.

Breaking Ester Linkages by Hydrolysis. The polystyrene gel (0.5 g) was put in a flask, followed by 10 mL of THF/CH_3OH (v/v, 1/1). Then KOH (0.5 g) was added in the flask. After refluxed 12 h, the mixture was precipitated with CH_3OH and analyzed by SEC.

Results and Discussion

Synthesis of Cleavable Four-Arm Star Polystyrene. Functional initiator **1** was prepared by esterification of bis(2-hydroxyethyl)disulfide **2** with **3** (Scheme 2) in the presence of EDC and DMAP. The characterization of **1** by ^{1}H NMR, ^{13}C NMR and elemental analysis shown in experimental demonstrated that the preparation was successful. This initiator contains four bromoisobutyryl groups for growth of polymer arms, one disulfide for reduction cleavage of the expected four-arm star polymers into half, and six ester linkages for hydrolysis cleavage of each arm.

In order to make the study of cleavage clearer, inert polystyrene was considered. The reason was that the polystyrene was stable under the conditions of either reduction of the disulfides or hydrolysis of the esters. Also polystyrene standards were used as calibration of the SEC system, so the molecular weight (M_n) of cleaved linear polystyrenes determined by SEC was actual value. The ATRP of St initiated by 1 was conducted in anisole at a molar feed ratio of [St]/[**1**]/[CuBr]/[PMDETA] = 400:1:0.2:0.2. Two samples were obtained by terminating the reaction at different reaction time, i.e., different monomer conversion. The SEC traces of two star samples are shown in Figure 1 and it was indicated that the polymerization was controlled and no radical coupling was detected although the monomer conversion reached 35% for a star polymer formation. The degree of polymerization (DP), and also the molecular weight M_n, was determined by the area ratio between the characteristic peaks of phenyl protons (peak a in 6.8−7.1 ppm) and the methyl protons of isobutyryl unit from the **1** unit (peak b in 0.9 ppm) from ^{1}H NMR (Figure 2). Thus, obtained DPs of two samples matched that evaluated from the monomer conversion by weighing products after precipitation. The properties of cleavable four-arm star polystyrenes were collected in Table 1. It may be found that the molecular weight of star polystyrene $(S_{35})_4$ (M_n = 15400) determined by ^{1}H NMR was higher than that (M_n =11800) determined by SEC, which accorded to that the star polymer has a more compact structure and less hydrodynamic volume compared to those of linear polymers of the same molecular weight.

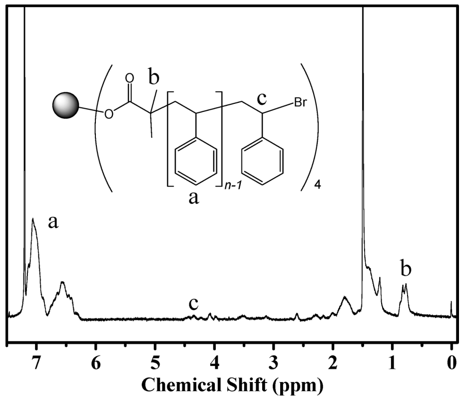


Figure 2. ^{1}H NMR spectrum of four-arm star polystyrene $(S_{35})_4$.

Table 1. Properties of the Four-Arm Star Polystyrenes in Figure 1[a]

products	reaction time (h)	monomer conversion (%)	M_n[b]	M_n[c]	PDI[c]
$(S_{35})_4$	36	35	15 400	11 800	1.05
$(S_{15})_4$	12	15	7200	6100	1.08

[a] Conditions: [St]/[**1**]/[CuBr]/[PMDETA] = 400:1:0.2:0.2; V_{St}:V_{anisole} = 2:1, 80 °C. [b] Determined by ^{1}H NMR. [c] Determined by SEC.

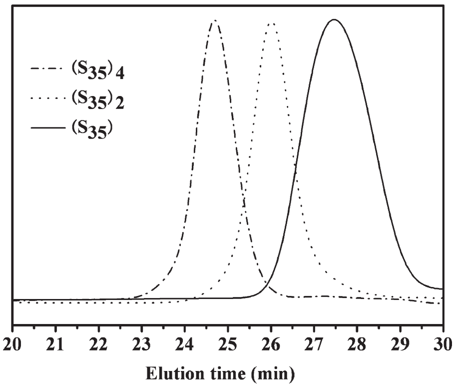


Figure 3. SEC curves of four-arm star polystyrenes $(S_{35})_4$ and its degraded segments by sequent cleavage of disulfide and ester groups, respectively.

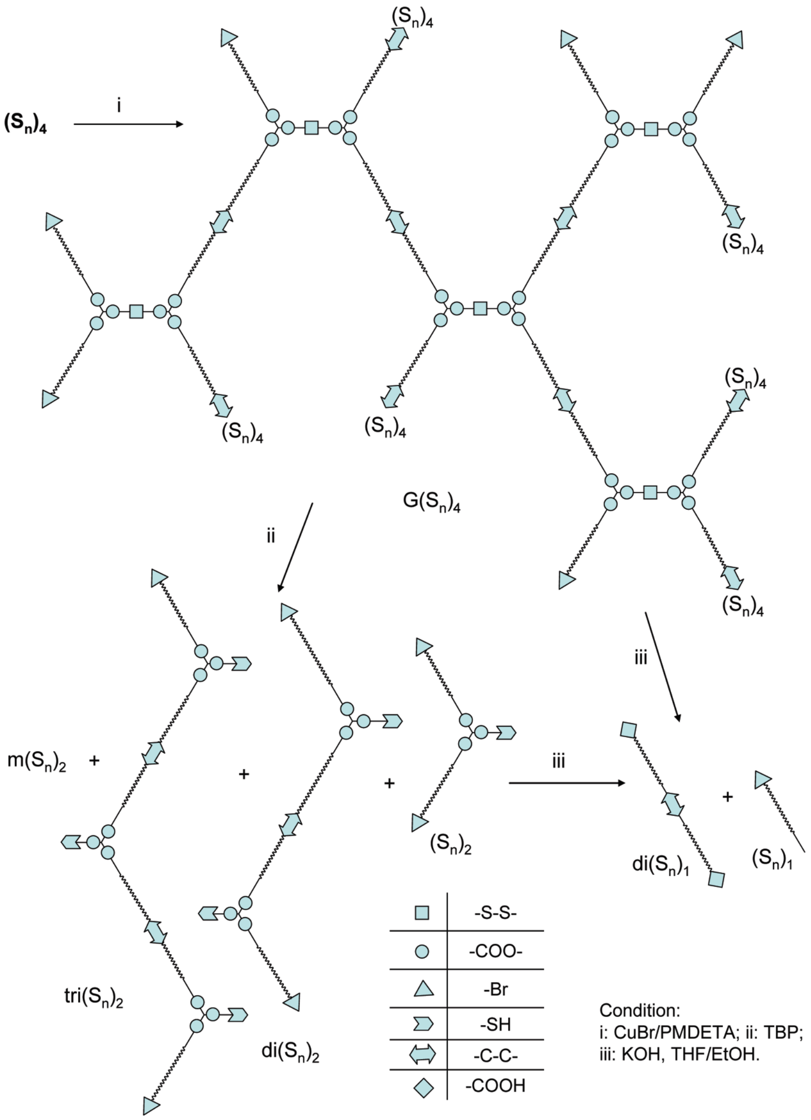
Table 2. Characterization of Cleaved Products of the Star Polystyrenes

star polystyrenes	M_n[a]	M_n (PDI)[b]	M_n (PDI)[c]	M_n (PDI)[d]
$(S_{35})_4$	15 400	6800 (1.05)	3300 (1.10)	3300 (1.10)
$(S_{15})_4$	7200	3000 (1.08)	1400 (1.14)	1400 (1.15)

[a] Determined by ^{1}H NMR. [b] Reductive products of $(S_n)_4$ with TBP. Data were determined by SEC. [c] Hydrolytic products of $(S_n)_2$ with KOH. Data were determined by SEC. [d] Hydrolytic products of $(S_n)_4$ with KOH. Data were determined by SEC.

Arm Cleavage of Star Polymers. Inherited from the initiator used, the product of the ATRP of St initiated by 1 (Scheme 1) contains an internal disulfide bond located in the center of $(S_n)_4$, which can be cleaved in the presence of reducing agents. As shown in Scheme 1, one star, $(S_n)_4$, would be cleaved into two linear polystyrenes, $(S_n)_2$, who was a dimer of the arms and their molecular weights were half of that of the star polymers. Furthermore, the disulfide would be split into two −SH groups which located in the middle of the cleaved dimer chains, respectively. A variety of reagents for this type of reduction have been described in the literature, due to its application in protein chemistry and biochemistry.[37,38] In the current study, TBP and DTT were

Scheme 3. Formation of Polymer Organogel G(S_n)$_4$ by ATRC of (S_n)$_4$ and Its Degradation Products by Different Cleavage Strategies



used to cleave the disulfide-containing star polystyrenes. TBP was added in a THF solution of the star polymer (S_{35})$_4$ and the reaction was conducted at room temperature. After 3 h, the reactant was analyzed by SEC with the (S_{35})$_4$ as a comparison. As shown in Figure 3, a monomodal peak (dot line) was observed at a long elution time and no any starting polymers were found, indicating that the cleavage was complete. Since the cleaved products were the linear polystyrenes, their molecular weights measured by the SEC calibrated with standard PS were absolute values. It is noteworthy that the number-averaged molecular weight of the degraded products (S_{35})$_2$ (M_n = 6800, PDI = 1.05) given by SEC was about half of that of the starting materials (S_{35})$_4$ (M_n = 15400, PDI = 1.05) evaluated by ^{1}H NMR, demonstrating that the star PS was cleaved into two parts from the disulfide bond. Also the same cleavage of star polystyrenes occurred when the disulfide linkages were reduced with DTT. Cleavage of the different star polymer (S_{15})$_4$ showed a similar behavior as that of the (S_{35})$_4$ and Table 2 collected the properties of the cleaved star polymers.

From the structure of the cleaved product, (S_n)$_2$, by the above-mentioned chemistry (Scheme 1), two arm segments were linked by two ester groups located at the molecular center, indicating the capability to degrade further. The second step of cleavage was occurred at the ester bonds by hydrolysis with KOH. As a result, one (S_{35})$_2$ would degrade into two pieces of linear polystyrenes, (S_{35})$_1$, which were the cleaved arms from the star polymer. After refluxing for 12 h, the products were characterized by SEC which was included into Figure 3 (solid line). Obviously, the second cleavage reaction underwent completely, and the number-averaged molecular weight of the hydrolyzed product (S_{35})$_1$ (M_n = 3300, PDI = 1.10) was half of that of the (S_{35})$_2$ (M_n = 6800, PDI = 1.05). The properties of hydrolysis cleaved product, including that of (S_{15})$_2$, are shown in Table 2. The above results indicated that the present star polymers with four arms could be degraded step-by-step by different chemistry. Furthermore, since the arms were linked onto the core of the star polymers through ester groups, the four-arm star polymers (S_{35})$_4$ could be cleaved straightway into the individual arms (S_{35})$_1$ whose number-averaged molecular weight were about one-fourth of that of (S_{35})$_4$ (data shown in Table 2).

Formation and Cleavage of Polymer Gels with Star Polymer. It was reported that, in the presence of CuBr/PMDETA and reducing agents such as Cu(0), the radical−radical coupling reaction between the bromide terminated polymers may be occurred highly efficiently, which was called as ATRC.[39,40] Since the star polymers (S_n)$_4$ had four bromide

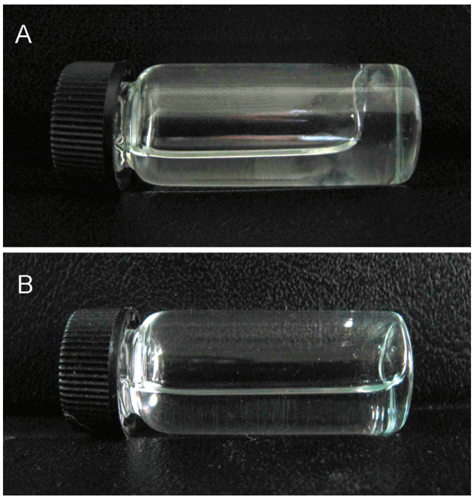


Figure 4. Reduction of polystyrene gel G(S_{35})$_4$ by TBP: (A) swollen polystyrene gel in THF; (B) sample A after adding TBP, 24 h.

terminals during ATRP process, the ATRC reaction of the (S_n)$_4$ was conducted in a solution to generate a polymer gel, G(S_n)$_4$, with the star polymers as building blocks. As shown in Scheme 3, such a gel, with a similar structure to the "model network" with a fixed length between the cross-linked points,[41,42] was also expected to show the stepwise cleavage properties.

We chose the four arm star polystyrene (S_{35})$_4$ to explore the gelation and the degradation. The coupling reaction of (S_{35})$_4$ was proceeded in the presence of CuBr/PMDETA and the gelation of the mixture finished in ca. 10 h. To remove CuBr/PMDETA and those uncoupled star polymers, Soxhlet extraction was subjected by changing the solvent ratio of THF/CH_3OH from 1:1 to 3:1 to 5:1 for 5 days. As shown in Figure 4A, a complete colorless transparent organogel, G(S_{35})$_4$, was obtained and the mass of the dried gel was equaled to that of the charged polystyrene (S_{35})$_4$, meaning that almost all four-arm star polymer (S_{35})$_4$ was transformed into the star polystyrene gel during the ATRC. The swelling degree of this gel G(S_{35})$_4$ in THF was ca. 900%.

Before to show the results, it is necessarily to analyze the structure of degraded products from the gel G(S_n)$_4$ by two cleavage strategies. The radical coupling forms the stable −C−C− linkages between the star polymer blocks and the cleavage of either −S−S− or ester linkages cannot influence the new linkage formed by ATRC. Therefore, by cleavage of −S−S−, a series of linear polymers composed of the (S_{35})$_2$ segments linked by −C−C− could be obtained. The number of the (S_{35})$_2$ segments depends upon the ATRC reaction efficiency. In the ideal case of a complete coupling, a linear polymer (it is also possible to form cyclic polymers) with many (S_{35})$_2$ segments should be produced. However, it is impossible to conduct a highly efficient coupling in a cross-linked networks and those uncoupling ends would become the terminals of the linear polymers, which composed multi-, tri-, di- and single (S_{35})$_2$, i.e., m(S_{35})$_2$, tri(S_{35})$_2$, di(S_{35})$_2$, and (S_{35})$_2$. For the case of hydrolysis by KOH, all the ester groups can be broken and, as a result, much simpler products are expected. Cleavage of the coupling between two arms produces a dimer of the polystyrene arms, di(S_{35})$_1$. If there is the uncoupling point, only (S_{35})$_1$ should be obtained. All the linear polymer segments by two cleavages are summarized in Scheme 3.

Figure 4 shows the physical state of the polystyrene gel G(S_{35})$_4$ in THF before and after the addition of TBP. When the gel was treated with TBP for 24 h, the swollen gel in THF disappeared completely and became a solution (Figure 4B), demonstrating the quantitative cleavage at the −S−S− linkages. The produced solution of THF was analyzed by SEC and the trace is shown in Figure 5, compared with that of the precursor star polymer (S_{35})$_4$. It was found that a broad trace (solid line) composed of several overlapped peaks was obtained. The main peak at 23 min (peak a in Figure 5) gave a peak molecular weight of 19800, which was about three times as that of (S_{35})$_2$ (M_n = 6800 in Table 2). It should be the tri(S_{35})$_2$ cleaved from the gel. The shoulder peak at 24 min (peak b in Figure 5) is close to that of the precursor (S_{35})$_4$. Since the gel had been extracted thoroughly with a good solvent of the star polymers, this peak had to be attributed to the cleaved products. The peak gave a molecular weight of 12500 which doubled to that of (S_{35})$_2$, demonstrating that the components should be the di(S_{35})$_2$. The peak at 25.5 min (peak c in Figure 5) has a peak value of 6900, which well agreed to that of (S_{35})$_2$. The product was cleaved from the half of the star blocks that had not been coupled. Then, those shoulder peaks at the shorter eluent time should be attributed to those linear polymers with more (S_{35})$_2$ segments.

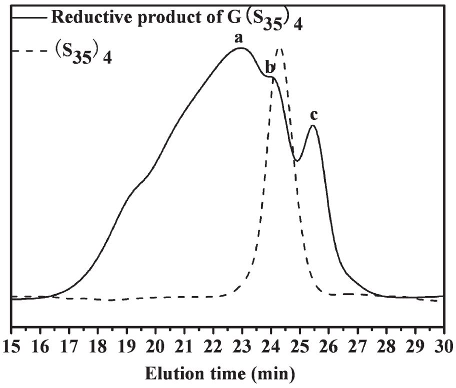


Figure 5. SEC curves of the reductive degraded products from the organogel G(S_{35})$_4$ and starting star polymer (S_{35})$_4$ for comparison.

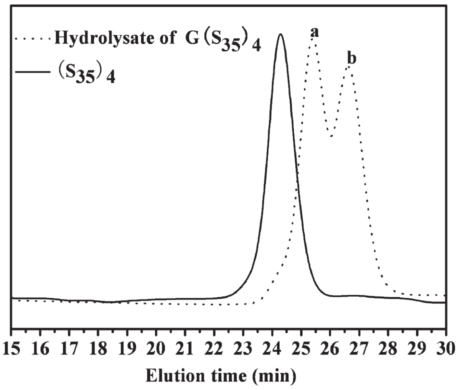


Figure 6. SEC curves of the hydrolysate of the cleaved G(S_{35})$_4$ by TBP and the starting star polymer (S_{35})$_4$ for comparison.

Then the reductive product of G(S_{35})$_4$ treated with TBP was decomposed by hydrolysis with KOH, only two polymers were shown in SEC (the dot line in Figure 6). Thought two peaks were overlapped, each polymer had a pretty low polydispersity index. One cleaved polymer (peak a in Figure 6) had a similar molecular weight of the (S_{35})$_2$ that obtained by cleavage of the star polymer (S_{35})$_4$ at the −S−S− point and it was assigned to the coupled arms being cut at the ester linkage to the star core. The peak at longer eluent time (peak b in Figure 6) had a similar molecular weight of the (S_{35})$_1$. From the Scheme 3, this peak was of the cleaved arm segments that had not been coupled with other arms. Above results nicely matched the analysis of the cleaved structures shown in Scheme 3. By comparing the area of the peaks a and b in Figure 6, the coupling ratio of the end bromide of star polystyrenes was about 51%. Also the $G(S_{35})_4$ can directly be decomposed with KOH, a similar SEC curve was obtained as shown in the case of the final products of $G(S_{35})_4$ being decomposed by two steps.

Conclusions

We have prepared a kind of well-defined smart star polystyrenes with four arms. By designing the initiator of ATRP, the disulfide and ester linkages had been precisely positioned in the core of the star polymers. By applying the different chemistry to cleave the disulfide and ester linkages respectively, such a four-arm star polymer may be cut into two halves that composed of two arms and then into four parts that are the cleaved individual arms. Using such a star polymer as the building block, novel polymer organogels have been obtained by applying ATRC to couple the bromide ends of the arms. This gel also showed interesting properties of degradation into the solutions of linear polymers composed of the arm segments by conducting cleavage at disulfide and ester linkages, respectively.

Since the star polymers can be degraded into the linear arm segments of different number in each step, this concept may be applied to tune the properties of star polymer materials. For example, it is known that the instinct viscosity of a polymer solution is proportion to its molecular weight. If the polymers with a well-defined architecture may be degraded into a controlled number of polymer segments, the viscosity of a polymer solution should be decreased in a stepwise way, implying that the change of materials properties follows a stepwise manner by the controlled cleavage strategy. This point differs to the conventional degradable polymers whose chain cleavage occurs randomly in an uncontrolled way. Moreover, the fission properties of star polymers may be applied to design the functional molecular cargos which may be cleaved under a certain condition and then release the guest species.

Acknowledgment. Financial support from NSF China (Nos. 20534010 and 20625412) is gratefully acknowledged.

References and Notes

(1) Gao, H. F.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317–350.
(2) Kasko, A. M.; Heintz, A. M.; Pugh, C. *Macromolecules* **1998**, *31*, 256–271.
(3) Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. *Macromolecules* **2003**, *36*, 1505–1513.
(4) Matyjaszewski, K.; Qin, S.; Boyce, J. R.; Shirvanyants, D.; Sheiko, S. S. *Macromolecules* **2003**, *36*, 1843–1849.
(5) Heise, A.; Hedrick, J. L.; Frank, C. W.; Miller, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 8647–8648.
(6) Liu, J. Q.; Tao, L.; Xu, J. T.; Jia, Z. F.; Boyer, C.; Davis, T. P. *Polymer* **2009**, *50*, 4455–4463.
(7) Fukukawa, K.-I.; Rossin, R.; Hagooly, A.; Pressly, E. D.; Hunt, J. N.; Messmore, B. W.; Wooley, K. L.; Welch, M. J.; Hawker, C. J. *Biomacromolecules* **2008**, *9*, 1329–1339.
(8) Gao, H. F.; Matyjaszewski, K. *Macromolecules* **2008**, *41*, 1118–1125.
(9) Du, J.; Chen, Y. M. *Macromolecules* **2004**, *37*, 3588–3594.
(10) Du, J.; Chen, Y. M. *J. Polym. Sci., Part. A: Polym. Chem.* **2004**, *42*, 2263–2271.
(11) Gao, H. F.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 3154–3160.
(12) Gao, H. F.; Ohno, S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2006**, *128*, 15111–15113.
(13) Gao, H. F.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 399–401.
(14) Altintas, O.; Yankul, B.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part. A: Polym. Chem.* **2006**, *44*, 6458–6465.
(15) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599.
(16) Fournier, D.; Hoogenboom, R.; Schubert, U. S. *Chem. Soc. Rev.* **2007**, *36*, 1369–1380.
(17) Parrish, B.; Breitenkamp, R. B.; Emrick, T. *J. Am. Chem. Soc.* **2005**, *127*, 7404–7410.
(18) Englert, B. C.; Bakbak, S.; Bunz, U. H. F. *Macromolecules* **2005**, *38*, 5868–5877.
(19) Ishizu, K.; Park, J.; Shibuya, T.; Sogabe, A. *Macromolecules* **2003**, *36*, 2990–2993.
(20) Deng, G. H.; Chen, Y. M. *Macromolecules* **2004**, *37*, 18–26.
(21) Deng, G. H.; Cao, M.; Huang, J.; He, L. H.; Chen, Y. M. *Polymer* **2005**, *46*, 5698–5701.
(22) Lee, J. H.; Archer, L. A. *Macromolecules* **2002**, *35*, 6687–6696.
(23) Avgeropoulos, A.; Freire, J. J.; Kosmas, M.; Vlahos, C. *J. Chem. Phys.* **2007**, *126*, 174904.
(24) Kasko, A. M.; Pugh, C. *Macromolecules* **2006**, *39*, 6800–6810.
(25) Pugh, C.; Kasko, A. M.; Grunwald, S. R. *J. Polym. Sci., Part. A: Polym. Chem.* **2008**, *46*, 4363–4382.
(26) Helms, B.; Guillaudeu, S. J.; Xie, Y.; McMurdo, M.; Hawker, C. J.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6384–6387.
(27) Chi, Y.; Scroggins, S. T.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2008**, *130*, 6322–6323.
(28) Heise, A.; Hedrick, J. L.; Frank, C. W.; Miller, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 8647–8649.
(29) Kreutzer, G.; Ternat, C.; Nguyen, T. Q.; Plummer, C. J. G.; Manson, J. E.; Castelletto, V.; Hamley, J. W.; Sun, F.; Sheiko, S. S.; Herrmann, A.; Ouali, L.; Sommer, H.; Fieber, W.; Velazco, M. I.; Klok, H. A. *Macromolecules* **2006**, *39*, 4507–4516.
(30) Schramm, O. G.; Pavlov, G. M.; van Erp, H. P.; Meier, M. A. R.; Hoogenboom, R.; Schubert, U. S. *Macromolecules* **2009**, *42*, 1808–1816.
(31) Zhang, L. W.; Niu, H. J.; Chen, Y. M.; Liu, H. F.; Gao, M. Y. *J. Colloid Interface Sci.* **2006**, *298*, 177–182.
(32) Zamponi, M.; Pyckhout-Hintzen, W.; Wischnewski, A.; Monkenbusch, M.; Willner, L.; Kali, G.; Richter, D. *Macromolecules* **2010**, *43*, 518–524.
(33) Wiltshire, J. T.; Qiao, G. G. *Aust. J. Chem.* **2007**, *60*, 699–705.
(34) Setijadi, E.; Tao, L.; Liu, J. Q.; Jia, Z. F.; Boyer, C.; Davis, T. P. *Biomacromolecules* **2009**, *10*, 2699–2707.
(35) Liu, J. Q.; Liu, H. Y.; Jia, Z. F.; Bulmus, V.; Davis, T. P. *Chem. Commun.* **2008**, 6582–6587.
(36) Heise, A.; Nguyen, C.; Malek, R.; Hedrick, J. L.; Frank, C. W.; Miller, R. D. *Macromolecules* **2000**, *33*, 2346–2354.
(37) Sun, H. L.; Guo, B. G.; Cheng, R.; Meng, F. H.; Liu, H. Y.; Zhong, Z. Y. *Biomaterials* **2009**, *30*, 6358–6366.
(38) Hou, X. D.; Li, Q. B.; Jia, L.; Li, Y.; Zhu, Y. D.; Cao, A. M. *Macromol. Biosci.* **2009**, *9*, 551–562.
(39) (a) Yurteri, S.; Cianga, I.; Yagci, Y. *Macromol. Chem. Phys.* **2003**, *204*, 1771–83. (b) Sarbu, T.; Lin, K. Y.; Spanswick, J.; Gil, R. R.; Siegwart, D. J.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 9694–9700.
(40) Sarbu, T.; Lin, K. Y.; Ell, J.; Siegwart, D. J.; Spanswick, J.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 3120–3127.
(41) Johnson, J. A.; Lewis, D. R.; Diaz, D. D.; Finn, M. G.; Koberstein, J. T.; Turro, N. J. *J. Am. Chem. Soc.* **2006**, *128*, 6564–6565.
(42) Johnson, J. A.; Finn, M. G.; Koberstein, J. T.; Turro, N. J. *Macromolecules* **2007**, *40*, 3589–3598.