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Polymer 47 (2006) 5259–5266

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Allyl functionalized telechelic linear polymer and star polymer via RAFT polymerization

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Received 17 October 2005; received in revised form 24 May 2006; accepted 25 May 2006

Abstract

Reversible addition-fragmentation chain transfer (RAFT) polymerization of styrene using bisallyl trithiocarbonate as a chain transfer agent (CTA) was studied. The polymerization exhibited first-order kinetics and the molecular weight increased linearly with increase of monomer conversion. Well defined allyl-functionalized telechelic polystyrene (PS), poly(*tert*-butyl acrylate) (P*t*BA) and corresponding triblock copolymers, polystyrene-*b*-poly(*n*-butyl acrylate)-*b*-polystyrene (PS-*b*-PnBA-*b*-PS) and poly(*tert*-butyl acrylate)-*b*-polystyrene-*b*-poly(*tert*-butyl acrylate) (P*t*BA-*b*-PS-*b*-P*t*BA) were prepared as characterized with GPC and NMR analysis. The allyl-end groups of the telechelic PS have been switched to 1,2-dibromopropyl groups quantitatively by bromine addition reaction, further substitution of the bromide with azide was also made. Furthermore, star PS with allyl-end-functionalized arms was synthesized by RAFT polymerization of divinyl benzene using allyl-functionalized PS as a macro-CTA via arm-first approach. Star polymer with a thiol-functionalized core was generated by aminolysis reaction of the star polymer and ethylenediamine. As a result, difunctionalized star polymer with allyl and thiol groups was obtained and was used as a stabilizer for the formation of gold nanoparticles.

Keywords: Allyl polymers; Telechelic polymers; Star polymers

1. Introduction

Telechelic polymers (α, ω-difunctional polymers) have been explored to a much extent in the past 20 years because they are precursors for preparing multi-block copolymers, grafted polymers, star polymers, and polymer networks [1–4]. A variety of telechelic polymers with terminals like hydroxy, carboxylic, epoxy groups and carbon–carbon double bond have been prepared by ionic polymerization, conventional radical polymerization, polycondensation and controlled radical polymerization (CRP) techniques [1–17]. Among these methods, CRP becomes an intriguing new technique that may generate polymers of controlled molecular weight and it may be carried out in the presence of many functional groups from monomers, initiators, or chain transfer agents (CTA) [4,9–17].

As early as CRP technique employed, nitroxide-mediated polymerization (NMP) and atom transfer radical polymerization (ATRP) have been used for preparing telechelic polymers [9–12]. However, it was generally done through two steps: polymer with one end being functionalized was synthesized firstly and then another end of polymer was functionalized by nucleophilic substitution, electrophilic addition, or radical addition. As an example of ATRP approach, hydroxyl telechelic polymers were prepared via ATRP of methyl methacrylate and butyl acrylate using 2-hydroxyethyl 2-bromoisobutyrate as initiator followed by nucleophilic substitution of the bromo-end group with 5-amino-1-pentanol [9]. As an example by NMP approach, α,ω-bisterpyridine-functionalized PS was prepared with a terpyridine initiator followed by a post-radical addition of terpyridinyl maleimide [13].

Furthermore, reversible addition-fragmentation chain transfer (RAFT) mediated radical polymerization, a typical type of CRP, has been used to prepare well-defined polymers with predetermined molecular weight and narrow polydispersity [14–19]. Trithiocarbonates, which can be synthesized with two good homolytic leaving groups, are effective RAFT agents to be applied to prepare telechelic polymers. In this case, the polymer chains grow in two directions and the leaving groups become the end groups inherently [14–17]. By this way, hydroxyl and carboxyl functionalized telechelic polymers have been

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doi:10.1016/j.polymer.2006.05.052

synthesized by RAFT mediated polymerization in one step with the functional trithiocarbonate as a CTA [14–17]. For example, Pan et al. have synthesized hydroxyl telechelic polymers and triblock copolymers by RAFT polymerization using *N*,*N*′-azobis(isobutyronitrile) (AIBN) as an initiator and *S*,*S*′-bis(2-hydroxylethyl-2′-butyrate) trithiocarbonate as a CTA [14].

Star or star-shaped polymers have been prepared by various living polymerizations. The research motivation is the morphology, physical properties and functions of star polymer may considerably differ from those of the linear analogues [20–27]. The star polymers with functionalized peripheries or cores may have important applications as supramolecular hosts, catalyst scaffolds, or substrates for nanoparticle formation [18,22–26]. Synthesis of core functionalized star polymers has been made by arm-first approach with a functionalized divinyl chemical [22–26] or by core-first approach with a functional initiator or CTA [27,28].

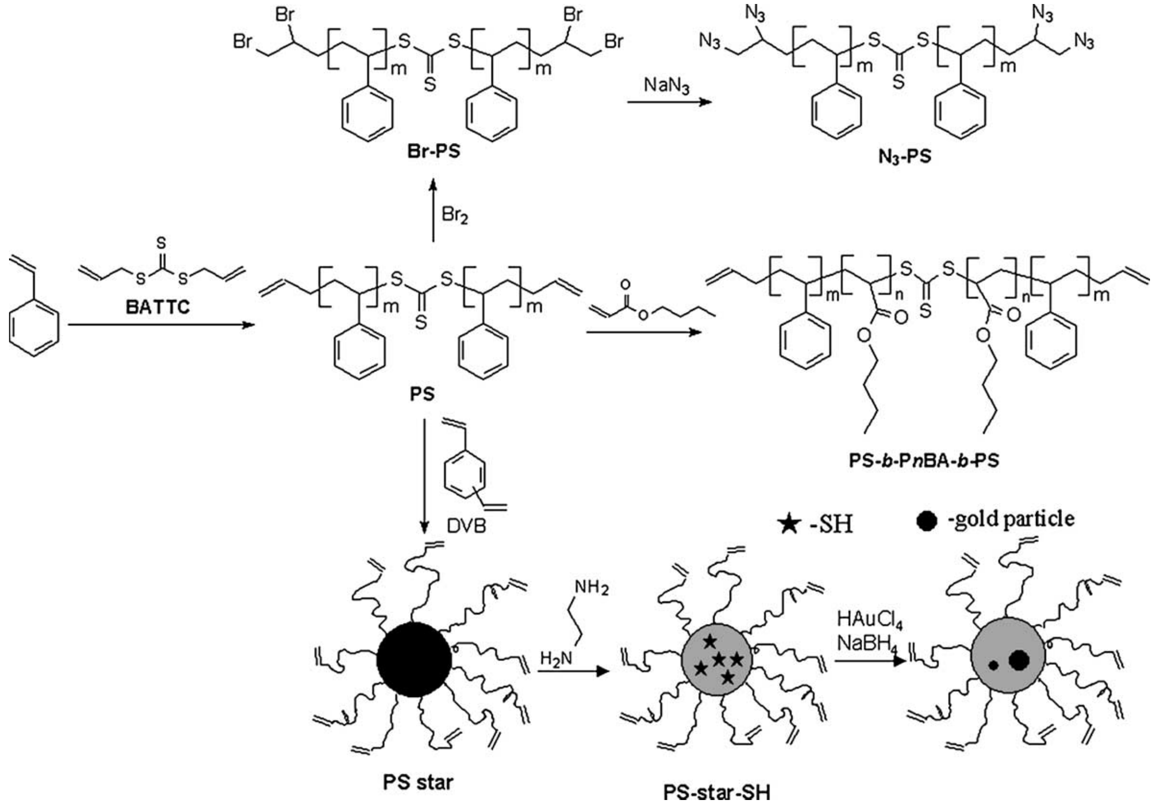
Allyl group is a reactive functional group, which can be used for various addition reactions. Therefore, allyls in polymer may be transformed into many functional groups [29,30]. Furthermore, allyl-terminated polymer is a kind of macromonomer being applied to prepare grafted copolymer [31]. Such reactive polymers have been synthesized by polymerizations using allyl-functionalized initiator or monomer, or by modifications with allyl compound [29–36]. Bisallyl functionalized telechelic polymer may be applied to prepare the well-defined gels with uniform cross-linking network if the polymer can be generated by controlled polymerization. However, to the best of our knowledge, there is no report on preparing such novel allyl polymers by CRP.

In this paper, a bisallyl trithiocarbonate (BATTC) was used as the CTA of a radical polymerization for synthesizing allyl-functionalized telechelic homopolymer and triblock copolymer. Allyl groups were also transformed into bromides, which further changed to azido groups by a reaction with NaN_3. Furthermore, when radical polymerization of divinyl benzene using the allyl-functionalized telechelic polystyrene as a macro-CTA was carried out, star polystyrene with allyl-end-functionalized arms was synthesized. Followed by aminolysis with ethylenediamine, star polymers with allyl-end-functionalized arms and a thiol-functionalized core were obtained. The synthetic rout is shown in Scheme 1.

2. Experimental

2.1. Materials

Styrene, *tert*-butyl acrylate (*t*BA) and *n*-butyl acrylate (*n*BA) were stirred with CaH_2 overnight and distilled under reduced pressure. Toluene was stirred with CaH_2 overnight and distilled. DVB (tech. ≥45%, Beijing Chemical Reagent) was passed through a basic alumina column before used. Allyl bromide was distilled before used. AIBN was recrystallized from ethanol. Other reagents were used as received.



Scheme 1. The synthesis route of bisallyl-functionalized telechelic polymers and star polymer and their properties thereof with BATTC mediated RAFT polymerization.

2.2. Measurement

Gel permeation chromatography (GPC) was performed by a set of a Waters 515 HPLC pump, a Waters 2414 refractive index detector, and combination of Styragel® HT-2, HT-3 and HT-4, effective molecular weight range is 100–10,000, 500–30,000 and 5000–600,000, respectively. THF was used as eluent at a flow rate of 1.0 mL/min at 35 °C. Polystyrene standards were used for the calibration. NMR spectra were recorded on a Varian 300 or 400 MHz spectrometer in $CDCl_3$ at room temperature. FT-IR spectra were obtained on a NICOLET AVATAR 300 infrared spectrometer. Elemental analyses were performed on Flash EA1112 elemental analysis instrument. UV–vis absorption spectroscope was recorded on a CARY 50 Conc UV–vis spectrum instrument. Transmission electron microscopy (TEM) was performed on a JEM-100CXII microscope. Specimen was prepared by dropping the colloid solution on a copper grid covered with a carbon film and then evaporating the solvent.

2.3. Synthesis of bisallyl trithiocarbonate (BATTC)

Anion exchange resin (54 g, 180 mmol OH^-) was stirred with 4×200 mL of 1 mol/L NaOH aqueous solution in a day and washed with 4×200 mL water. After filtered under reduced pressure, the resin was added to carbon disulfide (400 mL) and stirred at room temperature for about 5 min. The color of the resin changed from light yellow to deep red. Then allyl bromide (3.02 g, 25.0 mmol) was added, and the reaction mixture was stirred under reflux for 6 h. After cooled to room temperature, the mixture was filtered and the resin was washed with tetrahydrofuran (THF). The solutions were combined and dried over anhydrous magnesium sulfate. Unreacted allyl bromide and solvent were removed under reduced pressure to give a yellow liquid (1.84 g, 77%). ^{1}H NMR ($CDCl_3$) δ (ppm): 5.85 (2H, m), 5.35 (2H, d), 5.22 (2H, d), 4.04 (4H, d). ^{13}C NMR ($CDCl_3$) δ (ppm): 222.2 (–S(*C*S)S–), 139.5 (CH_2*C*H), 119.6 (*C*H_2CH), 39.6 (*C*H_2S).

2.4. RAFT polymerization of styrene—a general procedure

BATTC (391 mg, 2.06 mmol) and styrene (11.39 g, 0.110 mol) were introduced into a 25 mL flask. After bubbling with argon for 30 min, the flask was placed in an oil bath at 110 °C under argon atmosphere with stirring for 19 h. The product was dissolved in THF and precipitated in methanol twice and then dried under vacuum at 40 °C to give the product (7.57 g).

2.5. Synthesis of bis(1,2-dibromopropyl)-polystyrene (Br-PS2)

Bromine (5%, volume ratio) in tetrachloromethane was dropped into a solution of PS2 (0.27 g) in tetrachloromethane (2 mL) until the solution turned to red. The solution was stirred at room temperature for 2 h and precipitated in methanol and then dried under vacuum at 40 °C. A powder (0.28 g) was obtained.

2.6. Synthesis of bis(1,2-diazidopropyl)-polystyrene (N_3-PS2)

Br-PS2 (0.21 g) was dissolved in DMF (1 mL) and NaN_3 (57.3 mg) was added. The solution was stirred at room temperature for 24 h and precipitated in methanol. The product was dried under vacuum at 40 °C. Yield: 0.16 g.

2.7. Synthesis of PS-b-PnBA-b-PS

PS2 (0.64 g, 0.2 mmol), AIBN (2.7 mg, 0.016 mmol) and *n*BA (12.78 g, 0.10 mol) were introduced into a 25 mL flask. After the mixture was bubbled with argon for 30 min, the flask was placed in an oil bath at 60 °C under argon atmosphere with stirring for 1 h. The product was dissolved in THF and precipitated in methanol/water (7/3, volume ratio) twice. The block copolymer was dried under vacuum at 40 °C. Yield: 8.33 g.

2.8. RAFT polymerization of t-butyl acrylate—a general procedure

BATTC (29.6 mg, 0.156 mmol), AIBN (5.1 mg, 0.031 mmol) and *t*BA (2.40 g, 18.8 mmol) were introduced into a 10 mL flask. After bubbling with argon for 30 min, the flask was placed in an oil bath at 60 °C under argon atmosphere with stirring for 10.5 h. The product was dissolved in THF and precipitated in methanol/water (5/5, volume ratio) twice. The product was then dried under vacuum at 40 °C. Yield: 1.16 g.

2.9. Synthesis of PtBA-b-PS-b-PtBA

P*t*BA (0.82 g, 0.11 mmol) was dissolved in styrene (3.55 g, 34.1 mmol). Then the solution was introduced into a 25 mL flask. After bubbling with argon for 30 min, the flask was placed in an oil bath at 110 °C under argon atmosphere with stirring for 12 h. The product was dissolved in THF and precipitated in methanol/water (7/3, volume ratio) twice, the block copolymer was then dried under vacuum at 40 °C. Yield: 2.62 g.

2.10. Synthesis of star polystyrene with allyl-functionalized arms (PS2-star)

PS2 (0.70 g, 0.22 mmol), AIBN (18.0 mg, 0.11 mmol) and DVB (0.57 g, 4.38 mmol) were dissolved in toluene (4 mL). The solution was introduced into a 10 mL flask. After bubbling with argon for 30 min, the flask was placed in an oil bath at 60 °C under argon atmosphere with stirring. Samples at different time intervals were taken to analyze by GPC. The product was precipitated in methanol and further dissolved in THF and precipitated in petroleum ether.

2.11. Aminolysis of star polystyrene (PS2-star-SH)

PS2-star (0.56 g) was dissolved in THF (4 mL). Ethylenediamine (0.5 mL) was added and the solution was stirred over night at room temperature. The product (PS2-star-SH) was precipitated in methanol twice and dried under vacuum at room temperature. Yield: 0.42 g.

2.12. Preparation of gold nanoparticles

PS2-star-SH (20 mg, 8.9×10^{-6} mol SH) was dissolved in THF (4 mL) and $HAuCl_4$ (42 μL, 0.03 mol/L) in methanol was added. After stirred at room temperature for 3 h, an excess of $NaBH_4$ in methanol was added. The solution changed into purple immediately. After 2 h, the solution was concentrated and a drop of solution was taken for preparing TEM sample.

3. Results and discussion

3.1. Synthesis of bisallyl functionalized telechelic homopolymer and triblock copolymer

An allyl-functionalized CTA, BATTC, was prepared by a simple way according to a general method [37]. The formation of BATTC was confirmed by ^{13}C and ^{1}H NMR measurements, which are shown in Figs. 1 and 2(a), respectively. In particularly, the shift at 222.2 ppm in ^{13}C NMR spectrum is attributed to the carbon of carbon–sulfur double bond [38].

Firstly, the performance of BATTC as a RAFT agent of a radical polymerization was explored. Styrene was polymerized thermally in the presence of BATTC at 110 °C and *t*BA was polymerized using AIBN as the initiator and BATTC as the CTA at 60 °C. As shown in Fig. 3(a), the semilogarithmic plot of $\ln([M]_0/[M])$ vs reaction time of the RAFT thermal polymerization of styrene at 110 °C was linearly in the region studied (up to ca. 68% conversion), indicating that the radical concentration remained constant. It is of note that there is no inhibition that observed commonly in RAFT mediated polymerization. However, this phenomenon has also been observed in some researches [14,38–45]. Some factors, like higher temperature, the structure of RAFT agent and the feeding ratio, can eliminate the inhibition period. In terms of RAFT agent, it seems that trithiocarbonates sometimes eliminate the inhibition period during the polymerization [14,38–42]. The trithiocarbonate might be consumed gradually before the equivalent was acquired, as a result, the radical concentration during the initialization period could be higher than that during propagation.

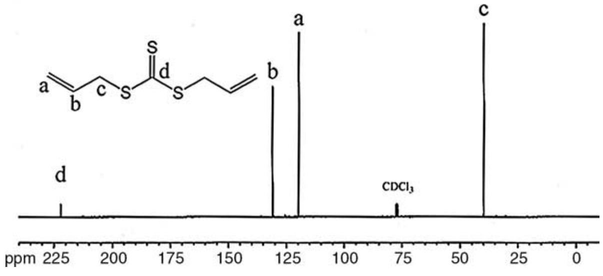


Fig. 1. The ^{13}C NMR spectrum of bisallyl trithiocarbonate.

The number average molecular weights given by GPC, $M_{n,GPC}$, increased linearly with increase of monomer conversion and they agreed well with that estimated by monomer conversion (Fig. 3(b)). Furthermore, the polydispersity decreased from 1.35 to 1.19 and narrow distributed polymers were thus generated. This result suggested that no side reactions occurred during the polymerization from the allyl groups and indicated that BATTC was an efficient CTA for CRP of styrene. The presence of α,ω-bisallyl end groups was characterized as shown in following section.

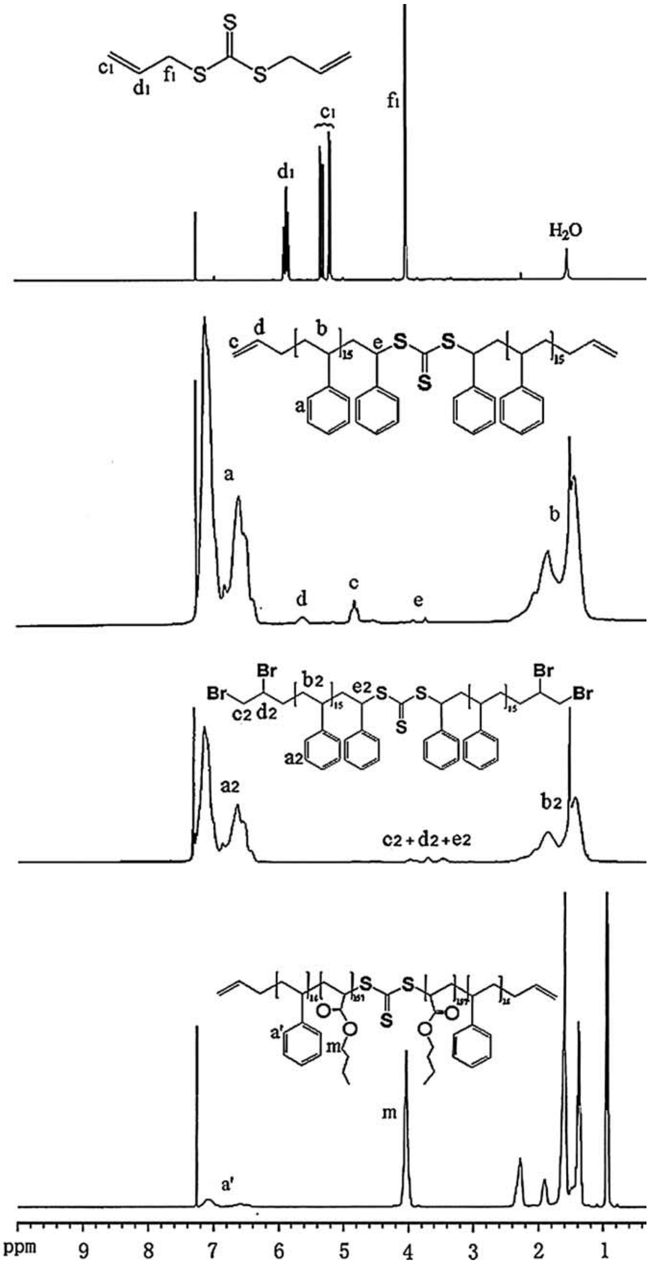


Fig. 2. The ^{1}H NMR spectrum of the RAFT agent BATTC, bisallyl functionalized polystyrene (PS2), bis(1,2-dibromopropyl) polystyrene (Br-PS2) and triblock copolymer PS2-*b*-P*n*BA2-*b*-PS2.

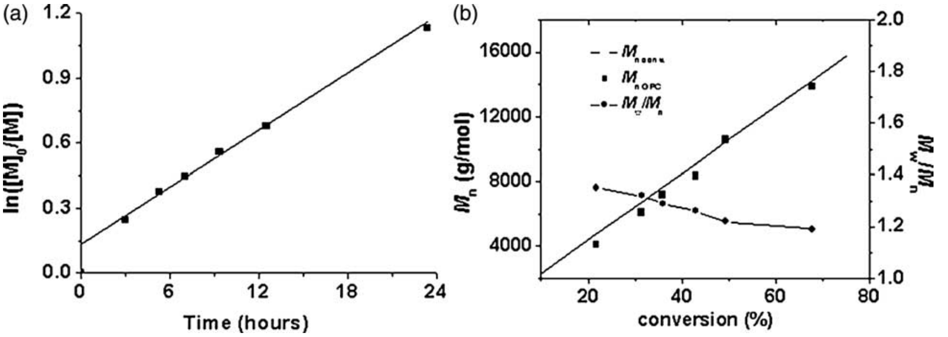


Fig. 3. (a) Dependence of $\ln([M]_0/[M])$ on time, (b) evolution of the molecular weights and M_w/M_n with monomer conversion for thermal polymerization of styrene at 110 °C in bulk using BATTC as CTA. [styrene]/[BATTC] = 200/1.

Since PS was synthesized by RAFT polymerization with BATTC as a CTA, in principle, every polymer chain had two allyl groups located at the chain ends and had a trithiocarbonate group at the middle. In order to confirm thus produced PS does have a trithiocarbonate group located in its center, chain cleavage was made by using ethylenediamine in THF at room temperature. The GPC traces of PS4 before and after dealt with ethylenediamine are shown in Fig. 4. The molecular weight of the cleaved PS was half that of PS4 and the polydispersity still remained narrow. This result clearly indicates that each polymer consisted of two PS segments of equal length. The protons of allyl end group in PS2 can be found at 5.56–5.74 and 4.84–4.94 ppm by comparing the ^{1}H NMR spectra of BATTC and PS2 (Fig. 2(a) and (b)). In addition, the molecular weight of the PS evaluated by comparing the integrated area of aromatic protons of PS at 6.39–7.26 ppm with that of the allyl end at 4.84–4.94 ppm agreed well with that given by GPC using polystyrene as standards (Table 1), demonstrating the existence of two allyls in each polymer chain.

Therefore, allyl groups were not consumed during the reaction and they were positioned in the polymer chain ends as expected. Although allyl group is also reactive for radical addition and for chain transfer reaction by hydrogen abstraction, the chain transfer to allyl group should be much low than that to the thiocarbonate for chain propagation. This corresponds to the results from other controlled radical polymerization initiated with allyl compounds [35,36]. In addition, the research results from several groups also revealed that the allyl side reactions have been restricted during ATRP of allyl methacrylate [32–34].

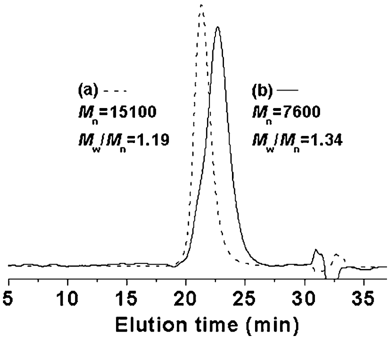


Fig. 4. GPC curves of (a) PS4 in Table 1 and (b) PS4 treated with ethylenediamine in THF at room temperature.

By using the bisallyl functionalized telechelic PS as a macro-CTA, bisallyl functionalized PS-*b*-P*n*BA-*b*-PS triblock telechelic copolymers were also prepared through the RAFT polymerization of monomer *n*BA. The conditions and results of polymerizations are listed in Table 1. The GPC curve shifts toward shorter elution time completely and a single narrow peak, signed to PS2-*b*-P*n*BA2-*b*-PS2 triblock copolymer, may be observed (Fig. 5), demonstrating the high efficiency of the RAFT polymerization with the macro-CTA. Compared with the ^{1}H NMR spectra of PS2 in Fig. 2(b), the characteristic signals of butyl group of P*n*BA block at 3.95–4.20 and 0.91–0.95 ppm are found in Fig. 2(d) besides the signals of aromatic protons of PS. The above results demonstrate the formation of the block copolymer. As expected from the polymerization mechanism, the bisallyl functions were located at two ends of the triblock copolymer.

The characterization data of P*t*BA listed in Table 1 further confirmed the effectiveness of BATTC in controlling radical polymerization of acrylate. Moreover, well-defined P*t*BA-*b*-PS-*b*-P*t*BA triblock copolymer was synthesized with the P*t*BA as a macro-CTA in RAFT polymerization of styrene at 110 °C in bulk (Table 1). This polymer can be transformed into amphiphilic triblock copolymer of poly(acrylic acid) with allyl ends by hydrolysis of *t*BA units.

3.2. Synthesis of bis(1,2-dibromopropyl) and bis (1,2-diazidopropyl) capped telechelic PS

In order to illustrate the reactivity of the allyl groups, the bisallyl-terminated PS was treated with bromine. When bromine solution in tetrachloromethane was added dropwise into the polymer solution, the red color disappeared quickly, indicating the presence of carbon–carbon double bonds. The appearance of the characteristic absorption of carbon–bromine bond at 786.85 cm^{-1} in the FT-IR spectra of product (Br-PS2) shown in Fig. 6(b) confirmed the occurrence of the addition reaction. From the ^{1}H NMR spectrum of the addition product shown in Fig. 2(c), the resonance of the methylene protons close to the bromine could be found at 3.41–4.09 ppm, while that of the allyl

Table 1
Experimental conditions and characterization data for preparing bisallyl-functionalized homopolymers and triblock copolymers via RAFT polymerization mediated with BATTC

Sample	Monomer/CTA/AIBN[a]	CTA	Time (h)	Conv. (%)[b]	M_n[c] (conv.)	M_n[d] (NMR)	M_n[e] (GPC)	M_w/M_n[e] (GPC)
PS1	102/1/0	BATTC	14	51.6	5660	5590	5940	1.24
PS2	52/1/0	BATTC	19	63.0	3600	3500	3190	1.28
PS3	200/1/0	BATTC	8	42.2	8290	–	8970	1.29
PS4	200/1/0	BATTC	25	69.7	14,700	–	15,100	1.19
PS2-*b*-P*n*BA1-*b*-PS2	400/1/0.1	PS2	2.5	91.6	50,500	–	97,200	1.22
PS2-*b*-P*n*BA2-*b*-PS2	500/1/0.1	PS2	1	60.1	42,100	43,700	54,700	1.23
P*t*BA	120/1/0.2	BATTC	10.5	47.1	7420	–	10,870	1.34
P*t*BA-*b*-PS-*b*-P*t*BA	308/1/0	P*t*BA	12	50.7	27,400	–	38,500	1.19

[a] Polymerizations of styrene were carried out at 110 °C and polymerizations of *n*BA and *t*BA were carried out at 60 °C in bulk.

[b] Evaluated by $(W_{(\text{product})} - W_{(\text{CTA})})/W_{(\text{monomer})} \times 100\%$, $W_{(\text{product})}$, $W_{(\text{CTA})}$ and $W_{(\text{monomer})}$ are weight of product, CTA and monomer.

[c] Calculated by $([\text{monomer}]/[\text{CTA}]) \times (\text{Conv.}) \times M_{n(\text{monomer})} + M_{n(\text{CTA})}$, $M_{n(\text{monomer})}$ and $M_{n(\text{CTA})}$ are molecular weight of monomer and CTA.

[d] Evaluated by ^{1}H NMR spectrum: for polystyrene series, $[(A_{6.39-7.26}/5)/(A_{4.84-4.94}/4)] \times 104 + 190$; $A_{6.39-7.26}$ and $A_{4.84-4.94}$ are integral areas at the region indicated; for triblock copolymers, comparison of the integrated area of peaks at 6.39–7.26 ppm with that at 3.9 ppm was made by using the molecular weight of corresponding macro-CTA. The ascriptions of various protons were labeled in Fig. 2.

[e] Given by GPC with linear polystyrene as calibration.

protons at 5.56–5.74 and 4.84–4.94 ppm disappeared completely. A quantitative conversion of the allyl terminals into the bromide was indicated. Therefore, the allyls located in the polymer chain ends can be used for further polymer functionalization.

The nucleophilic substitution of the halogen atom at a polymer chain end by an azide anion is very efficient and the organic azides can be used for a variety of chemical transformations by the reaction like ‘click reaction’ [4]. Switching resultant bromo-terminated PS into azido-terminated PS was tested by reacting with NaN_3. FT-IR spectra of the azido-terminated PS was shown in Fig. 6(c). A typical absorption of the azido group at 2100.20 cm^{-1} was found while that of carbon–bromine bond at 786.85 cm^{-1} disappeared. This means that the bromo-end groups have been changed into azido-end groups efficiently and the azido-terminated PS was produced.

3.3. Synthesis of star PS with allyl-end-functionalized arms

So called arm-first approach has been applied for star polymer preparation. Pan et al. have applied a macro-CTA to prepare star polymer via arm-first approach [46]. However, there is no report on star polymer formation based on the macro-CTA produced by the trithiocarbonate mediated radical polymerization. Herein, when the allyl telechelic PS was used as the macro-CTA, RAFT polymerization of DVB was started from the middle of the macro-CTA chains and the star polymers with arm ends being functionalized with allyls were prepared. It has been discovered that the formation of PS star by arm-first approach was affected by molecular weight of macro-CTA or macro-initiator, feed ratios and polymerization time [23,24,46]. Increase of the molar ratio of DVB to macro-CTA would produce a larger cross-linked core with more PS arms, but too high ratio would result in gelation. The RAFT polymerization of DVB with PS2 as a macro-CTA was studied by using the molar feed ratio of DVB/PS2/AIBN at 20/1/0.5.

GPC traces shown in Fig. 7 indicated that the peak moved gradually to shorter elution time and the polydispersity became broader due to appearance of shoulder with proceeding of the polymerization. This implies the occurrence of polymerization of DVB [24,46]. Indeed, the GPC curve at 6 h displayed a peak with an obviously shoulder, which was ascribed the formation of the block copolymers. The areas of the slow fraction decreased while that of the shorter fraction increased, suggesting that more and more linear polymers changed to

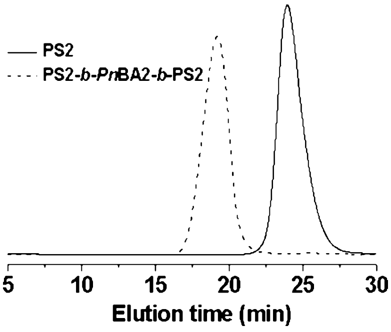


Fig. 5. GPC curves of PS2 and PS2-*b*-P*n*BA2-*b*-PS2 in Table 1.

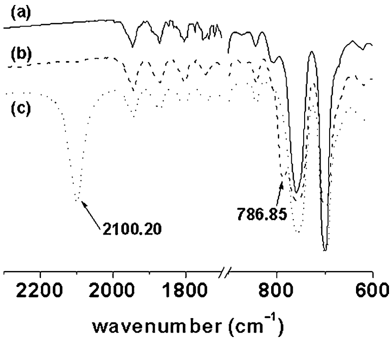


Fig. 6. FT-IR spectra of (a) bisallyl polystyrene (PS2), (b) bis(1,2-bromopropyl) polystyrene (Br-PS2) and (c) bis(1,2-diazidopropyl) polystyrene (N_3-PS2).

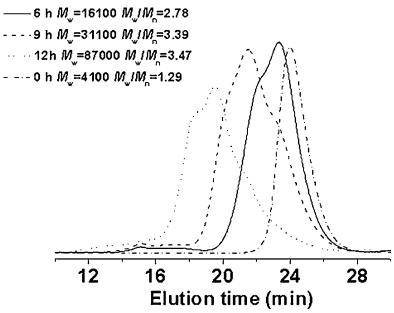


Fig. 7. GPC traces of the RAFT polymerization of DVB in toluene at 60 °C with PS2 as CTA. DVB:PS2:AIBN was 20:1:0.5 and the DVB concentration in toluene was 1.10 mol/L.

star polymers. A small third fraction appeared, which could be owing to star–star coupling reaction with evolution of polymerization.

The star polymer, PS2-star, was further characterized with NMR analysis (Fig. 8). A peak ascribed to those protons of unreacted vinyl groups of DVB was found at 4.98–5.38 ppm, indicating the DVB was introduced. The methylene protons (3.85–3.96 ppm) near to the trithiocarbonate group disappeared, revealing that the resonance of the methylene protons was restricted by the cross-linked DVB core. However, the signals of allyl groups at 5.56–5.74 and 4.84–4.94 ppm were also observed, demonstrating that the allyl functional groups remained during the star polymer formation. Therefore, the star polymer of its periphery being functionalized with allyls was prepared.

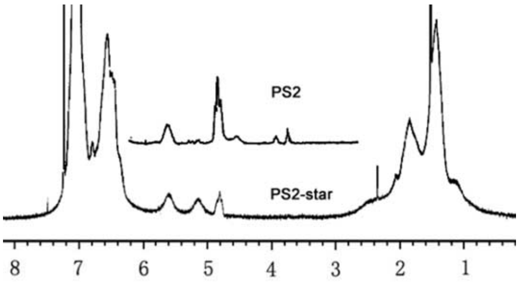


Fig. 8. The ^{1}H NMR spectrum of PS2-star and a part of PS2.

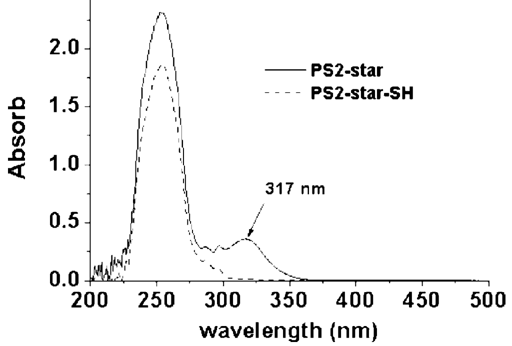


Fig. 9. The UV–vis spectrum of PS2-star before and after aminolysis.

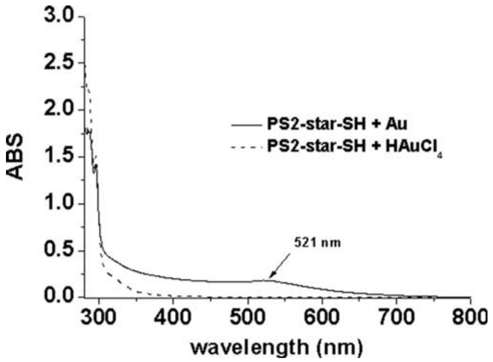


Fig. 10. The UV–vis spectrum of PS2-star-SH with $HAuCl_4$ introduced and the corresponding gold nanoparticles prepared by reduction with $NaBH_4$.

3.4. Synthesis of star PS with allyl-end-functionalized arms and a thiol-functionalized core

After aminolysis with ethylenediamine, THF solution of PS2-star changed from yellow into colorless. As indicated by UV–vis spectrum shown in Fig. 9, the peak ascribed to the trithiocarbonate at 317 nm disappeared. In addition, sulfur content by elemental analysis decreased from 1.96 to 1.43% after reaction. Therefore, the cleavage of the trithiocarbonates in the star core was successfully. As a result, the thiol was produced when the trithiocarbonate group was destroyed. Since the trithiocarbonate groups were enwrapped in the core of star polymer, the star PS with allyl-end-functionalized arms and a thiol-functionalized core (PS2-star-SH) was obtained. As expected, the structure of star polymer was remained after the aminolysis since the DVB was inserted into C–SC(S) and cross-linked, the cleavage of trithioester did not influence the C–C linkages between the PS arms and PDVB core.

It was known that thiol groups bind gold strongly due to the soft character of both Au and sulfur. To explore the function of thiols in the core of star PS, PS2-star-SH was used as a

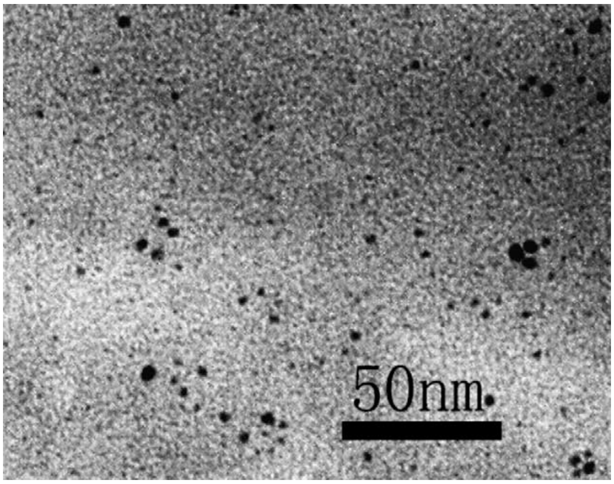


Fig. 11. The TEM micrograph of gold nanoparticles according to the sample in Fig. 10.

stabilizer for preparation of gold nanoparticles. $HAuCl_4$, which may interact with thiol functionality, was introduced into the solution of PS2-star-SH and gold nanoparticles were produced by the reduction of $NaBH_4$. After an excess of $NaBH_4$ was introduced, the solution changed into purple immediately. The appearance of the peak at 521 nm in UV–vis spectra (Fig. 10) proved the formation of gold nanoparticles [47]. TEM was used to observe the morphology of gold nanoparticles stabilized by PS2-star-SH. Dark gold particles with diameters in range of 2–5 nm were found as indicated in Fig. 11.

4. Conclusions

In conclusion, a symmetric allyl-functionalized trithiocarbonate was used as a CTA in RAFT polymerization of styrene and *t*BA. It has been proved that the radical polymerization mediated by BATTC was a controlled reaction. As a result, well-defined homopolymers and triblock copolymers of styrene, *n*BA and *t*BA with narrow distribution have been prepared. PS chains growing in two directions was proved by cleaving the polymer chains at the trithiocarbonate conjunction by ethylenediamine. Allyl groups have been located at the two ends of polymers as characterized by ^1H NMR analysis. By bromine addition reaction, the allyl groups were translated into 1,2-dibromopropyl groups and further into 1,2-diazidopropyl groups by end group modifications. Furthermore, star PSs with allyl functionalized arms were synthesized by the radical polymerization of divinyl benzene using the telechelic PS as a macro-CTA. The trithiocarbonate groups in the star core have been transformed into the thiols by aminolysis with ethylenediamine. Therefore, di-functional star PS with allyl-end-functionalized arms and a thiol-functionalized core was obtained, which was used as the stabilizer for preparing gold nanoparticles.

Acknowledgements

Financial support from NSF China (20534010) and the Directional Innovation Project (KJCX2-SW-H07) of the CAS is greatly acknowledged.

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