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Synthesis, characterization and self-assembly behavior of six-armed star block copolymers with triphenylene core

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Abstract

Hexa-armed star block copolymers, s-[poly(L-lactide)-*b*-poly(styrene-*co*-*N*-acryloxysuccinimide)]$_6$ (s-[PLLA-*b*-poly(St-*co*-NAS)]$_6$) with triphenylene core have been successively prepared by the combination of ring-opening polymerization and atom transfer radical copolymerization, and they were used in the self-assembly in tetrahydrofuran, and the micelles with triphenylene core and PLLA as inner layer as well as poly(St-*co*-NAS) as shell were formed. After shell was cross-linked, PLLA was hydrolyzed in aqueous NaOH solution, the hollow spheres were formed. The structures, molecular weight and polydispersity index of the polymers were characterized by their ^{1}H NMR and FT-IR spectra, as well as GPC. Their morphologies were studied by TEM. The influence factors on the formation of various morphologies are under investigation.

Keywords: Hollow spheres; Self-assembly; Star block copolymer

1. Introduction

Among the supermolecular nanometer and micrometer-sized objects obtained from self-assembly of block and graft copolymers, hollow spheres on nanometer and submicrometer scales have been attracted much attention because of their academic interests and potential applications for serving as carries of catalysts and drugs, etc. [1–4]. Several methodologies for production of hollow polymer spheres have been developed. Self-assembly of rod-coil block copolymers in selective solvent [5] or nonselective solvent [6] produced hollow particles. Other methods include core removal of dendrimers [7]; calcinations or dissolution of the polymer core in the organic/inorganic composite particles obtained by layer-by-layer decomposition [8–10]. Another important method is to dissolve or decompose the polymeric cores of shell cross-linked polymer micelles via hydrolytic or ozonolytic degradation chemistry, which are prepared by self-assembly of block copolymers, following shell cross-linking reaction [11–14]. For example, the ABA triblock copolymers prepared by atom transfer radical polymerization (ATRP) [15] or di- and tri-block copolymers of poly(ethylene oxide) and poly(DL-valine-*co*-DL-leucine) [16] were self-assembled in selective solvents.

In this paper, we report the application of star shaped block copolymers to produce hollow polymer spheres. For easily determining whether the core is removed, the hexa-functional initiator containing triphenylene was used in the ATRP. In our previous report, hexa-armed star polymers with triphenylene discotic cores have been prepared by ATRP method [17]. Because of strong interaction between triphenylene groups, the star block copolymers can self-organize highly ordered films, such as ordered submicrometer porous film or ordered columns [18,19]. When 2, 3, 6, 7, 10, 11-hexakis[10′-(methylethacryloyloxy)decanyloxy] triphenylene in THF was polymerized under UV light at room temperature, polymers with oliver shape were formed [20]. For convenience cross-linking shell, *N*-acryloxysuccinimide (NAS) was copolymerized with styrene since substitution reaction of PNAS with amine compounds is very active. In order to hydrolyze the inner layer easily, poly(L-lactide) was selected as first block. Therefore, the hexa-armed star block copolymers, s-poly[L-lactid-*b*-(St-*co*-NAS)]$_6$, were prepared by combination of ring-opening polymerization and ATRP according to Scheme 1. Shell cross-linking micelles achieved by substitution reaction of NAS units with ethylenediamine, and after removing PLLA cores, the hollow spheres are obtained.

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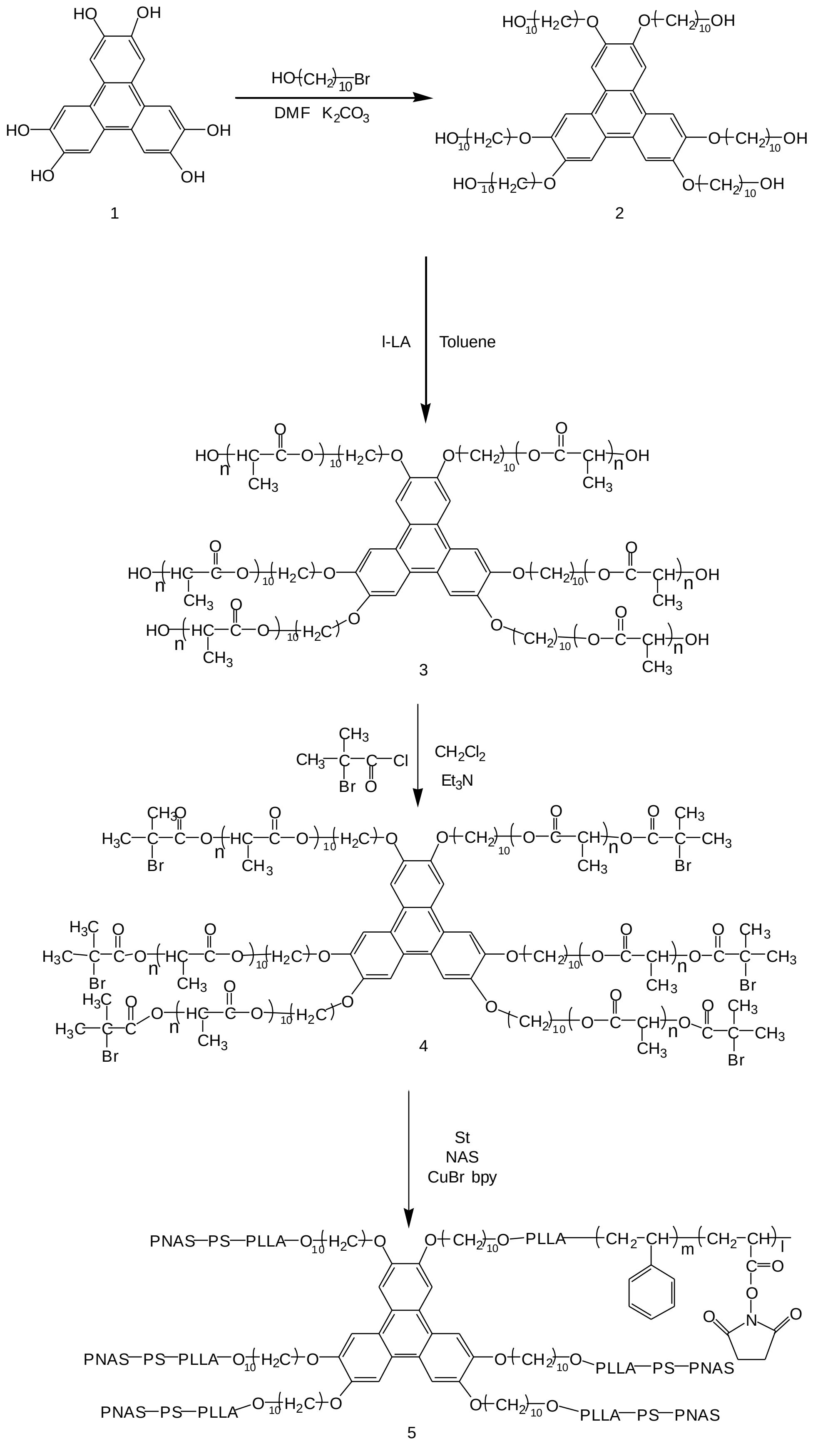
1
2
HO(CH2)10Br
DMF K2CO3
l-LA
Toluene
3
CH2Cl2
Et3N
4
St
NAS
CuBr bpy
PNAS—PS—PLLA
5

Scheme 1.

2. Experimental section

2.1. Materials

Dimethyl formamide (DMF) (A.R., Shanghai Reagent Co.) was treated with CaH_2 and distilled under reduced pressure before use. 10-Bromo-1-decanol was prepared according to the method described in Ref. [21]. Its ^1H NMR (300 MHz, $CDCl_3$), (TMS, δ, ppm): 1.33–2.00 (m, 16H, $-(CH_2)_8-$), 3.10 (s, 1H, OH), 3.37 (t, 2H, $BrCH_2$), 3.58 (t, 2H, OCH_2). K_2CO_3 (A.R., Shanghai Reagent Co.) was dried at 120 °C prior to use. α-Bromo-isobutyric chloride was prepared by the reaction of α-bromo-isobutyric acid (A.R., Shanghai Reagent Co.) with thionyl chloride (A.R., Shanghai Reagent Co.) at 80 °C. Its ^1H NMR (300 MHz, $CDCl_3$), (TMS, δ, ppm): 1.90 (s, 6H, $C(CH_3)_2$). Methylene dichloride (A.R., Shanghai Reagent Co.) was dried with CaH_2 and distilled prior to use. Trimethyl amine (A.R., Shanghai Reagent Co.) was distilled from KOH. Tetrahydrofuran (A.R. Shanghai Reagent Co.) was treated with Na and distilled before use. The L-lactide was crystallized in toluene prior to use. Styrene (St) was washed by NaOH and water, dried with anhydrous Na_2SO_4 and then distilled under reduced pressure before use. The compound, 2, 3, 6, 7, 10, 11-hexahydroxy triphenylene (HHTP) was prepared according to the method described in Ref. [22]. Its ^1H NMR (300 MHz, acetone-*d*), (TMS, δ, ppm): 7.83 (s, 6H; ArH), 3.32 (s, 6H; OH). *N*-Acryloxysuccinimide (NAS) was synthesized via the pathway describe in Ref. [23]. Its ^1H NMR (300 MHz, $CDCl_3$), (TMS, δ, ppm): 6.78, 6.18 (s, 2H; $C{=}CH_2$), 6.37–6.28 (s, 1H; $=CH$), 2.86 (s, 4H; $-CH_2CH_2-$). $Sn(Oct)_2$ (C.R., Sigma) was used as received.

2.2. Instruments and characterization

^1H NMR spectra were measured on a Bruker DMX-300 nuclear magnetic resonance (NMR) instrument using chloroform-d_6 ($CDCl_3$) as solvent and tetramethylsilane (TMS) as an internal standard. The measurements of molecular mass and molecular weight distribution of the polymer were carried out on a Waters 150C gel permeation chromatograph (GPC) equipped with micro-styragel columns (500, 10^3, and 10^4 Å) and a refractive-index detector at 30 °C. Narrowed polystyrene was used as calibration standard, and tetrahydrofuran (THF) was used an eluent at a flow rate of 1.0 mL/min. Fourier transform infrared (FT-IR) spectra were recorded on a Vectror-22 FT-IR instrument. The size measurement and morphology observation of micelles were performed on a JEM100-SX transmission electron microscopy (TEM). The UV absorbance spectra were recorded on a UV-2401 PC instrument.

2.3. Synthesis of 2, 3, 6, 7, 10, 11-hexa(10′-hydroxy decanoxyl) triphenylene (HHDTP)

Into a 100 mL, two necked round-bottom flask, dried powder K_2CO_3 (6.7 g, 50 mmol), 10-bromo-1-decanol (4.7 g, 20 mmol), 70 mL dried DMF and 2, 3, 6, 7, 10, 11-hexahydroxytriphenylene (HHTP, 1 g, 3 mmol) were added. The flask was degassed by evacuation-purging with high-purity N_2 three times. The reaction was carried out at 100 °C for 48 h under pure N_2 atmosphere. Then the reaction system was cooled down to room temperature while stirring. And the mixture was deposited in 500 mL water and a grey powder product was obtained. After washed with water for several times, the crude product was recrystallization in ethyl acetate to afford a brown powder product in 85% yield (3.2 g).

^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.81$ (s, 6H, ArH), 4.23 (t, 12H, $ArOCH_2$), $\delta = 3.63$ ppm (t, 12H, CH_2OH), $\delta = 1.94$ ppm (m, 18H, $OH + ArOCH_2CH_2$), $\delta = 1.55$–1.33 (m, 84H, $(CH_2)_7$).

2.4. Ring-opening polymerization of L-lactide with HHDTP as initiator

The hexa-armed star polymers, s-[poly(L-lactide)]$_6$, was synthesized using HHDTP and $Sn(Oct)_2$ as the initiator system. A typical polymerization procedure is as follows. Into a 5 mL dry glass tube equipped with a magnetic stirrer, HHDTP (50 mg, 0.04 mmol), L-LA (0.57 g, 4.0 mmol) and 2 mL dry toluene were added, the tube was connected to a vacuum pump, then an exhausting-refilling process was operated for three times. The tube was put into an oil bath at 115 °C while stirring for 10 min. $Sn(OCt)_2$ (35 mg) in 1 mL dry toluene was added into the mixture, and the exhausting-refilling process was carried out again to remove the toluene. The tube was put into an oil bath thermostated at 115 °C for 24 h, and then cooled down to room temperature rapidly. By adding polymer solution in CH_2Cl_2 into methanol, the product was precipitated and then collected by filtration. The product, s-[poly(L-lactide)]$_6$, [s-(PLLA–OH)$_6$], was dried in a vacuum oven at 40 °C overnight. The monomer conversion was determined gravimetrically.

2.5. Reaction of s-(PLLA–OH)$_6$ with α-bromo-isobutyric chloride

Into a 50 mL, two necked, round-bottom flask with a magnetic stirrer equipped with a constant-pressure dropping funnel, 0.5 g of s-(PLLA–OH)$_6$, 4 mL Et_3N and 10 mL dried CH_2Cl_2 were added. The flask was thermostated at 0 °C while stirring, a solution of α-bromo-isobutyric chloride (3 mL in CH_2Cl_2) was added dropwise. After 48 h reaction at 0 °C, the solution was dropped into CH_3OH and the precipitates were collected by filtration. The product, s-(PLLA-Br)$_6$ was purified by washing with methanol, and then dried in a vacuum oven at 40 °C overnight.

2.6. Preparation of s-[poly(LLA)-b-poly(St-co-NAS)]$_6$

A typical atom transfer radical copolymerization (ATRP) of St and *N*-acryloxysuccinimide (NAS) is as follows. Into a 20 mL glass tube equipped with a magnetic stirrer, s-(PLLA-Br)$_6$ (210 mg, 0.013 mmol), NAS (800 mg, 4.73 mmol), CuBr (12 mg, 0.083 mmol), bpy (40 mg, 0.250 mmol) and 5 mL St solution in 10 mL THF were added. The system was sealed under vacuum after three freeze-pump-thaw cycles, and then the tube was put into an oil bath maintained at 110 °C. After a prescribed time, the polymerization was quenched by putting the tube into an ice-water bath. Conversion was calculated by ^{1}H NMR and gravimetric methods. The mixture was dissolved in THF and the solution obtained was passed through a short column of neutral alumina for removing the copper salt. After precipitation by adding polymer solution in THF into methanol, the precipitate was collected by filtration, and the product, s-[poly(LLA)-*b*-poly(St-*co*-NAS)]$_6$, was dried in a vacuum oven at 40 °C overnight.

2.7. Preparation of the shell cross-linked stable nanospheres

The star block copolymer, s-[poly(LLA)-*b*-poly(St-*co*-NAS)]$_6$ (30 mg, 6.54×10^{-4} mmol) (sample 4 in Table 2) was dissolved in 15 mL THF. Into this solution, ethylenediamine (3 mg, 0.05 mmol) in 60 μL THF was added. The cross-linking reaction was carried out at ambient temperature for 2 days. Shell cross-linked micelles were obtained by precipitating the solutions into methanol, followed by filtration. The product obtained was dried at 40 °C under vacuum overnight.

2.8. Hydrolyzation of PLLA segments and preparation of the hollow nanospheres

To the shell cross-linked micelles solution in THF, 4 mL of aqueous 2% NaOH was added dropwise at room temperature, and the solution was stirred at 55 °C for 24 h. Then the solution was dialyzed against THF for 2 days.

3. Results and discussion

3.1. Ring-opening polymerization of LLA with HHDTP as initiator

As we know, alkyl alcohol is an initiator of LLA, HHDTP with six hydroxyl groups was prepared by the reaction of HHTP with 10-bromo-1-decanol, and its structure was confirmed by ^{1}H NMR spectrum. Then this compound and Sn(Oct)$_2$ were used as initiating system in the ring-opening polymerization of LLA. The conditions and results are listed in Table 1. In all cases, higher conversions (>96%) were obtained. For verifying the formation of six armed star polymers, their ^{1}H NMR spectra were measured, and Fig. 1(A) shows a typical ^{1}H NMR spectrum (No. 1 in Table 1). The signals *a*, *b*, *c*, *d* and *e*, respectively, at $\delta=7.83$, 4.23, 4.12, 1.94 and 1.33 ppm are assigned to the protons in HHDTP. The signals *f* and *g* at $\delta=5.17$ and 1.58 ppm are ascribed to the methine and methyl protons in LLA units, respectively. The methine proton next to terminal hydroxyl group is sited at $\delta=4.36$ ppm (*h*). The signal of methylene protons next to hydroxyl group in HHDTP at $\delta=3.63$ ppm was completely disappeared in Fig. 1(A), indicating the complete esterification reaction. The further evidence for the formation of six-armed star PLLA is the integration ratio = 1:1 of the signals *a* to *h*. Assuming that each macromolecule contains six PLLA chains, the number-average molecular weight, $M_{n,PLLA}$ (NMR) can be calculated based on ^{1}H NMR data, and the calculated results are listed in Table 1. The agreement between M_n (NMR) and M_n (th) indicates that the molecular weight of s-(PLLA–OH)$_6$ can be controlled by the molar ratio of LLA to HHDTP and conversion.

3.2. Copolymerization of St and NAS with s-(PLLA-Br)$_6$/CuBr/bpy as initiation system

For preparation of the well-defined star block copolymers, s-[poly(LLA)-*b*-poly(St-*co*-NAS)]$_6$, complete esterification of s-(PLLA–OH)$_6$ with α-bromoisobutyric chloride is important. Thus, we estimated the esterification degree of s-(PLLA–OH)$_6$ from their ^{1}H NMR spectra. Fig. 1(B) is the ^{1}H NMR spectrum of the esterification product of No. 1 in Table 1. The complete disappearance of the terminal methine signal at $\delta=4.36$ ppm (*h*) in Fig. 1(B) must result from complete conversion of terminal CH$_2$OH into ester group. The signals *g* at $\delta=1.98$ and 1.95 ppm are ascribed to the methyl protons in terminal butyryl units. The integration ratio of peak *a* to *g* is 1:6, which demonstrates the complete transformation of terminal CH$_2$OH groups to ester groups, and the hexa-functional macrointiator s-(PLLA-Br)$_6$ was successfully synthesized.

The star block copolymers, s-[poly(LLA)-*b*-poly(St-*co*-NAS)]$_6$s were achieved by solution copolymerization of St and NAS at 110 °C using s-(PLLA-Br)$_6$/CuBr/bpy as initiating system. The conditions and results are listed in Table 2. Fig. 1(C) is a typical ^{1}H NMR spectrum of sample 4 in Table 2.

Table 1
Conditions and results of ring-opening polymerization of LLA

No[a]	[HHDTP]$_0$: [LLA]$_0$ (molar ratio)	Conversion[b] (%)	M_n (th)[c]	M_n (NMR)[d]	M_n (GPC)[e]	M_w/M_n[e]
1	1:100	98	15,400	16,800	25,500	1.07
2	1:200	96	28,900	27,800	49,900	1.05
3	1:300	97	43,200	45,100	64,600	1.12

[a] The polymerization was carried out at 115 °C for 24 h. [Sn(Oct)$_2$]$_0$:[LLA]$_0$ = 1:300 (molar ratio).

[b] Determined by gravimetric method.

[c] Calculated according to $M_n\ (\text{th})=[\text{LLA}]_0/[\text{HHDTP}]_0\times72\times2\times\text{conversion}+M_{\text{HHDTP}}$, where [LLA]$_0$ and [HHDTP]$_0$ are the molar quantities of monomer and HHDTP, respectively, and M_{HHDTP} is the molar mass of HHDTP.

[d] Calculated by ^{1}H NMR according to $M_n=(I_{5.17}/I_{7.83})\times72\times6+M_{\text{HHDTP}}$, where $I_{5.17}$ and $I_{7.83}$ are the integral values of the signals at 5.17 and 7.83 ppm, 72 and M_{HHDTP} are the molecular weights of LLA unit and HHDTP, respectively.

[e] Measured by GPC and the narrow polydispersity polystyrene standards were used in the calibration of molecular weight.

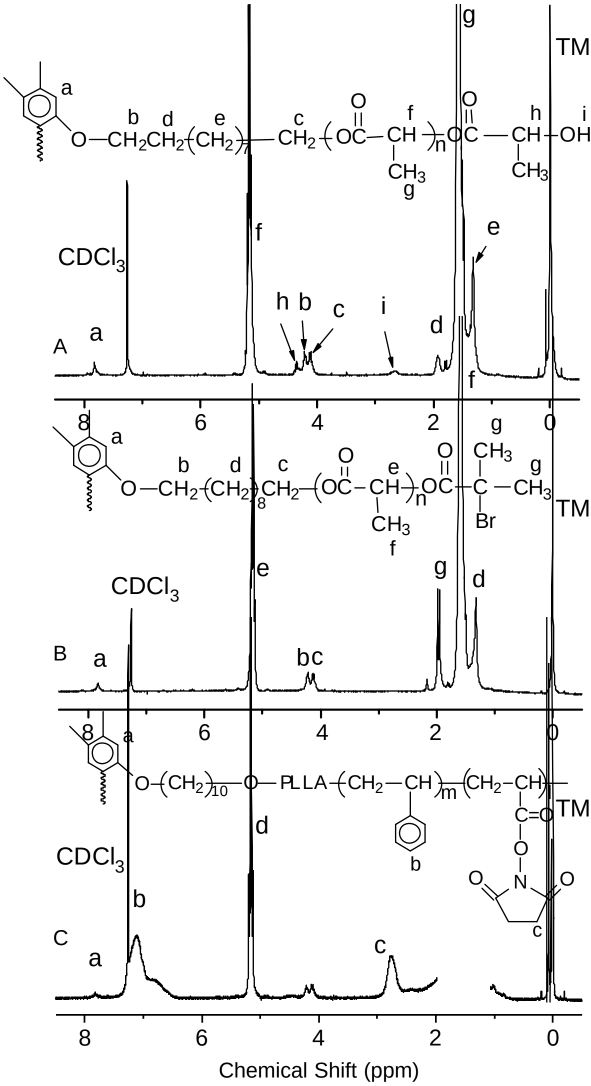

Fig. 1. ^{1}H NMR spectra of polymers: (A) s-(PLLA–OH)$_6$ (No. 1 in Table 1); (B) s-(PLLA-Br)$_6$ obtained from estarification reaction of s-(PLLA–OH)$_6$ (No. 1 in Table 1) with BrC(CH$_3$)$_2$COCl; (C) s-[polyLLA-*b*-poly(St-*co*-NAS)]$_6$ (No. 4 in Table 2).

The signals of the phenyl protons in PSt blocks appear at 7.08–6.60 ppm; the signals of methylene and methine protons in the backbone of poly(St-*co*-NAS) at 1.06–2.00 ppm are partially overlapped with the methyl signals in PLLA. Signal *c* at 2.75 ppm is ascribed to methylene protons in the NAS units. The signal of methine proton in LLA units appeared at $\delta = 5.17$ ppm. Based on the integration ratio of the signals at 7.08–6.60 to that at 5.17 and 2.75 ppm, the number-average molecular weights of star shaped polymers and poly(St-*co*-NAS), $M_{\mathrm{n,PLLA,P(S/NAS)}}$ (NMR) and $M_{\mathrm{n,P(S/NAS)}}$ (NMR), can be calculated, and the results are listed in Table 2. The macroinitiator, s-(PLLA-Br)$_6$ remained in the copolymer was not detected from a single GPC curve of the sample 4 in Table 2 in Fig. 2(B).

3.3. Fabrication of hollow spheres with a cross-linked shell

The solvent is one of the important factors to influence the assembly behavior of triphenylene derivatives in solution. For example, hexaalkoxyl triphenylenes can assemble in hydrocarbon solvent [24], but cannot observe congeries in CH$_2$Cl$_2$ [25]. The self-assembly behavior is decided by energy competition. The interaction between macromolecules and solvent prevents the assembly of triphenylene core; but the attraction between discotic molecules boosts the assembly. Solution concentration of the triphenylene derivatives also affects self-assembly results, such as their lower concentration in hydrocarbon solvent led to random shapes of aggregates. When the concentration increased to an appropriate value, the random shapes changed into regular congeries [26]. THF is not a good solvent for PLLA segments, but is a good solvent for PSt segments. Thus aggregation of the six-star block copolymer macromolecules will occur as shown in Fig. 3(A). Due to the strong interaction between triphenylene cores, theoretically the star block copolymers, s-[poly(LLA)-*b*-poly(St-*co*-NAS)]$_6$ can form micelles with triphenylene core, PLLA as inner layer and PSt-*co*-PNAS as shell. As a result, the micelles are larger than one single macromolecule of the star block copolymer. After the self-assembly of No. 4 in Table 2 was carried out in 0.2 wt% solution in THF, the ethylenediamine was used as the cross-linker. After 2 days reaction at room temperature, the product was analyzed by ^{1}H NMR, FT-IR and UV spectra, and the results are shown in Figs. 4–6, respectively. For comparison, the FT-IR and UV spectra of the sample before cross-linking reaction are also shown in Figs. 5(A) and 6(A), respectively. In comparison with Fig. 1(C), the signal *c* at 2.75 ppm ascribed to methylene protons in NAS unit decreased greatly, and the signal *a* at 7.83 ppm disappeared completely in Fig. 4, which demonstrates the occurrence of

Table 2
Conditions and results for ATRP of St and NAS with s-(PLLA-Br)$_6$/CuBr/bpy as initiation system

No[a]	s-(PLLA-Br)$_6$	Conv. (%)[b]	$M_{\mathrm{n,PLLA,P(S/NAS)}}$[c]	$M_{\mathrm{n,P(S/NAS)}}$ (NMR)[c]	M_{n} (GPC)[d]	$M_{\mathrm{w}}/M_{\mathrm{n}}$[d]	Molar ratio of St/NAS
4	No. 1	7.8	45,900	29,100	38,300	1.10	1:0.41
5	No. 2	12.8	75,400	47,600	59,800	1.26	1:0.44
6	No. 3	16.3	105,700	60,600	155,500	1.42	1:0.43

[a] The polymerization was carried out at 110 °C, [s-(PLLA-Br)$_6$]:[CuBr]:[bpy]:[NAS]:[St] = 1:6:18:350:3000 (molar ratio).

[b] Conversion was calculated based on ^{1}H NMR data.

[c] Calculated according to $M_{\mathrm{n,PLLA,P(S/NAS)}} = M_{\mathrm{n,P(S/NAS)}} + M_{\mathrm{n,PLLA}}$, where $M_{\mathrm{n,PLLA}}$ is the molecular weight of 6-arm macroinitiator, and $M_{\mathrm{n,P(S/NAS)}}$ is the molecular weight of P(S/NAS) segment. $M_{\mathrm{n,P(S/NAS)}} = (M_{\mathrm{n,PLLA}}/(72 \times I_{5.17}))(((I_{7.08-6.60} \times 104)/5) + (I_{2.75}/4) \times 169)$, where $I_{7.08-6.60}$ and $I_{2.75}$ are the integral values of the signals of the phenyl protons in PSt and methylene protons in the NAS units, respectively.

[d] Measured by GPC and the narrow polydispersity polystyrene standards were used in the calibration of molecular weight.

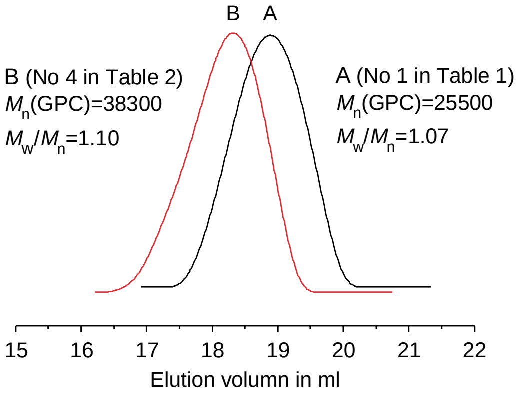

Fig. 2. Typical GPC traces of s-(PLLA–OH)$_6$ (A, No. 1 in Table 1) and s-[poly(LLA)-*b*-poly(St-*co*-NAS)]$_6$ (B, No. 4 in Table 2).

cross-linking reaction. From the integration ratio of signals at 7.08–6.60 and 2.75 ppm, we can calculate that 85% NAS units were taken part in the cross-linking reaction. Thus the cross-linkage of shell is 0.25. Fig. 5(A) and (B) show FT-IR spectra of the samples before and after cross-linking reaction of s-[PLLA-*b*-poly(St-*co*-NAS)]$_6$ (No. 4 in Table 2), respectively. The two new absorption bands of characteristic amide group at $\nu = 1670.5$ and 1517.0 cm^{-1} appeared in Fig. 5(B) verify the occurrence of cross-linking reaction. The UV spectra of the samples before and after cross-linking reaction shown, respectively, in Fig. 6(A) and (B) demonstrate that the characteristic absorption band of triphenylene cores at $\lambda =$ 306 nm became much stronger after cross-linking reaction, which may be resulted from the overlapping of π electrons due to tight stack of triphenylene cores. All the facts confirmed that the shell is cross-linked as shown in Fig. 3(B).

The morphology of the shell cross-linked micelles was examined on TEM. A typical TEM image is shown in Fig. 7. Spherical micelles with 110 nm in average diameter can be clearly seen. The micelles' size is much larger than one single macromolecule (∼35 nm), indicating that they are aggregates of the star block copolymer macromolecules. After cross-linked reaction, the micelles became stable. The preparation of hollow spheres is possible by removal of PLLA cores, and separation of the micelles from cross-linking reaction solution is not needed. The decomposition of inner layer, PLLA was performed by dropping 2% NaOH aqueous solution into the reaction solution at room temperature, and then the solution was stirred at 55 °C for about 24 h. The hydrolysis solution was dialyzed against THF for 2 days for removal of the small molecules formed in hydrolysis.

To confirm the removal of the triphenylene and PLLA, the FT-IR and UV spectra of the hydrolyzed products were measured. Figs. 5(C) and 6(C) show the typical FT-IR and UV spectra of the hollow spheres obtained, respectively. From Fig. 5(C), we can see that the absorption band of ester carbonyl groups at $\nu = 1763.5$ cm^{-1} disappears almost completely. The characteristic absorption band of triphenylene cores at

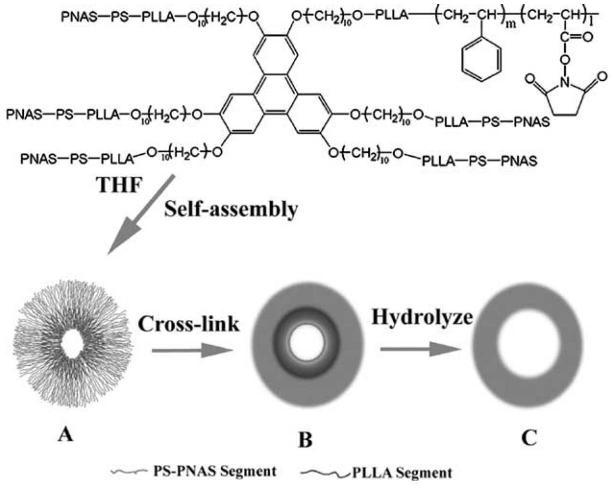

Fig. 3. A schematic illustration of the formation of the hollow spheres.

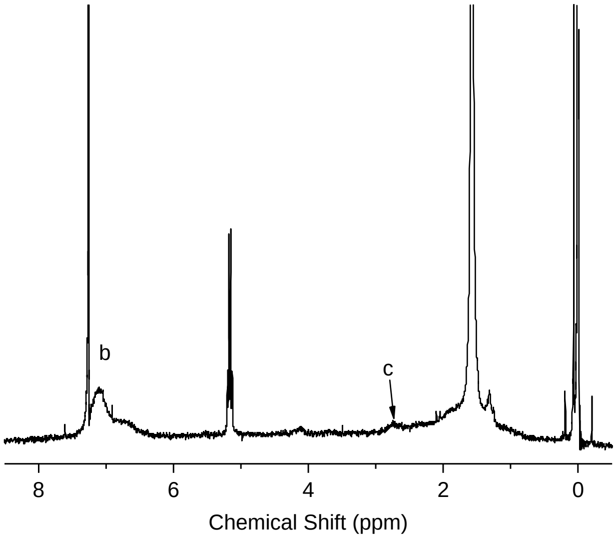

Fig. 4. Typical ^{1}H NMR spectrum of cross-linked nano-spheres prepared from No. 4 in Table 2.

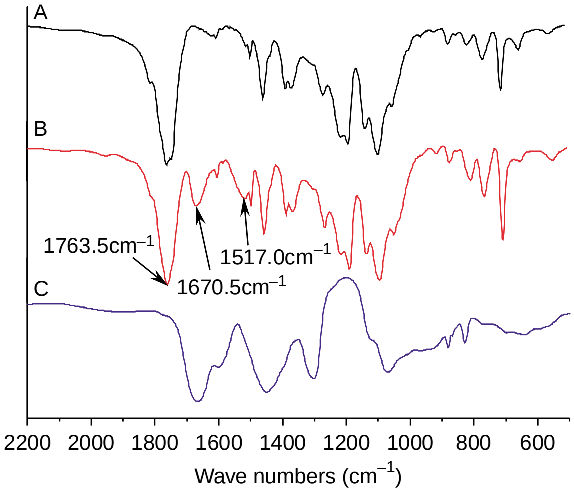

Fig. 5. Typical FT-IR spectra of (A) s-[poly(LLA)-*b*-poly(St-*co*-NAS)]$_6$ (No. 4 in Table 2); (B) cross-linked nanospheres; (C) hollow spheres obtained from hydrolytic reaction.

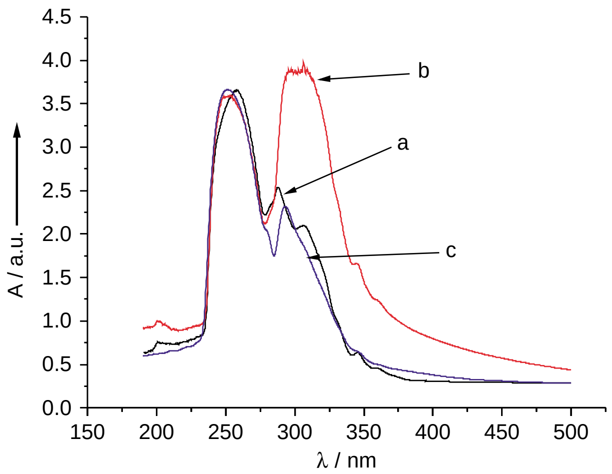

Fig. 6. Typical UV spectra of (A) s-[poly(LLA)-*b*-poly(St-*co*-NAS)]$_6$ (No. 4 in Table 2); (B) cross-linked nanospheres; (C) hollow spheres obtained from hydrolytic reaction.

$\lambda=306$ nm disappears completely in Fig. 6(C). All these facts evidenced the removal of triphenylene cores as shown in Fig. 3(C).

The TEM images of the hollow spheres were measured, and Fig. 8 is a typical image. The nano-spheres with dark shells and light cores are observed obviously, demonstrating the formation of hollow particles. The diameter of the particles in Fig. 8 is between 120 and 140 nm, and the diameter of hollows and the thickness of shell are about 60–80 and 10–25 nm, respectively. The cavities shown in this figure are not regular spheroid. This reflects the aggregation of PLLA with triphenylene core because PLLA and triphenylene are removed and poly(St-*co*-NAS) shell remains. The exact reason is not clear at present, probably the interaction between triphenylene groups affects their self-assembly.

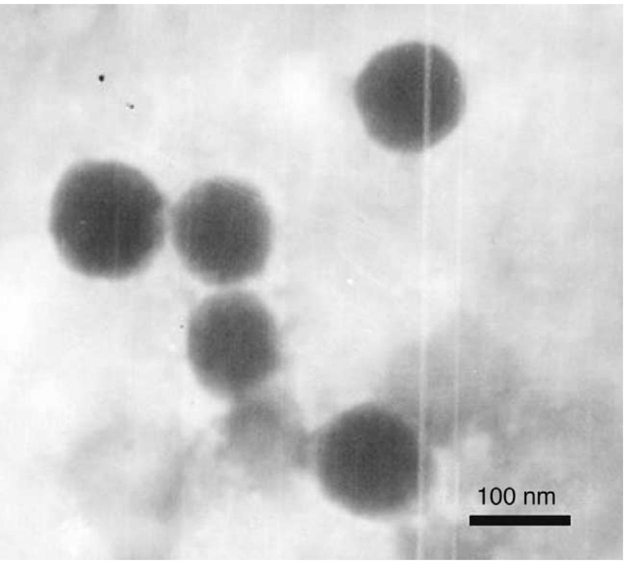

Fig. 7. TEM image of the cross-linked nanospheres prepared from No. 4 in Table 2, scale bar = 100 nm.

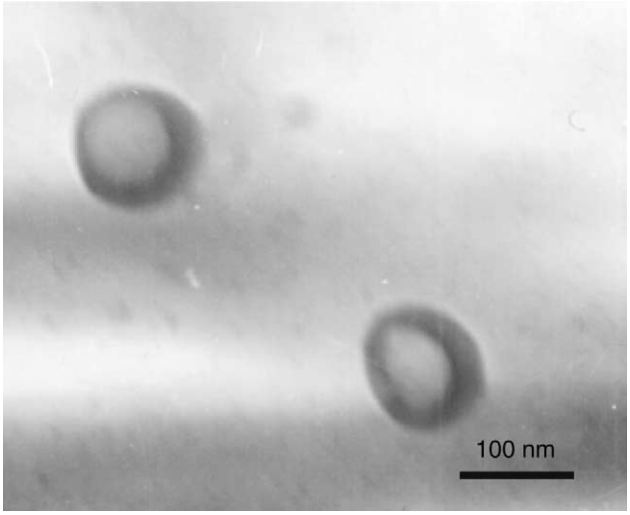

Fig. 8. TEM image of hollow spheres obtained after hydrolysis of shell cross-linked micelles, scale bar = 100 nm.

4. Conclusion

Hollow nanospheres with hydrophilic inner walls have been successfully prepared via two steps, the preparation of shell cross-linked micelles and the alkaline hydrolysis of inner layer PLLA in the shell cross-linked micelles. A hexa-armed star polymer, s-[PLLA]$_6$ can be prepared by ring-opening polymerization of LLA with Sn(Oct)$_2$ and HHDTP having 6 hydroxyl groups as catalyst and initiator. After the s-(PLLA–OH)$_6$ obtained is transformed to s-(PLLA-Br)$_6$ by the reaction with α-bromoisobutyric chloride, the hexa-armed star block copolymer, s-[PLLA-*b*-poly(St-*co*-NAS)]$_6$ has been successively prepared by the ATRP of St and NAS. The self-assembly of this star shaped block copolymer in THF forms micelles with triphenylene core, inner layer PLLA and poly(St-*co*-NAS) shell due to strong interaction between triphenylene groups. The shell cross-linked micelles can be achieved by the substitution reaction of ethylenediamine with NAS. The hydrolysis of the inner layer PLLA of micelles in aqueous NaOH solution produces the hollow nanospheres.

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