

Synthesis and characterization of H-shaped copolymers by combination of RAFT polymerization and CROP

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Abstract

A novel trithiocarbonate, S,S' -bis(1-(((5-ethyl-2,2-dimethyl-1,3-dioxane-5-yl)methoxy)carbonyl)propyl) trithiocarbonate (CTA-H), was synthesized in the presence of the anion-exchange resin with OH^- form. And then it was used as the chain transfer agent in RAFT polymerizations of styrene (St), the polymers with controllable molecular weights and narrow molecular weight distributions were synthesized. After the terminal acetonide groups was deprotected in the presence of a cation-exchange resin with H^+ form, the polystyrene (PSt) with two hydroxyl groups in both chain ends was easily afforded. Then it was used as macro initiator in the cation ring open polymerization (CROP) of 1,3-dioxepane (DOP), and the well-defined H-shaped block copolymers, $(\text{PDOP})_2\text{PSt}(\text{PDOP})_2$, were successfully prepared. The H-shaped structure was characterized by its IR, GPC and ^1H NMR spectra, and also those of the hydrolysis products.

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Keywords: Trithiocarbonate; H-shaped copolymer; Reversible addition–fragmentation chain transfer polymerization

1. Introduction

AB_2 miktoarm star polymers represent the simplest example of branched copolymers. The next complex structure is the H-shaped copolymer, which can be considered as the connection of the A blocks in two AB_2 miktoarm star polymers. Due to their special structures, they show unique morphologies [1] and very interesting rheological properties of entangled polymer melts and solutions [2–6]. During the research in the relationship between the properties of H-shaped polymers and their structures, a synthetic method based on living anionic polymerization together with chlorosilane as a coupling agent have been developed since the early 1980s [1,2,7,8]. The first H-shaped polymer was synthesized from St by Roovers and Toporowski, successively H-shaped polyisoprene (PI) and polybutadiene (PBD), and H-shaped copolymer of PSt and PI were prepared with the similar method. However, because of the critical experiment condition and the limitation in monomers that can be applied in the living anionic polymerization, only a few kinds of polymers have been prepared successfully. In addition, the coupling reaction is

often time-consuming, and the troublesome purification is inevitable because the coupling reactions cannot go to completion and some byproducts will be generated.

The fast development of some living radical polymerization methods, such as atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT) polymerization offers a new route for the preparation of polymers with well-defined structures [9–11]. In our previous studies, we have synthesized a series of polymers with various structures, such as block copolymers [12–16], star-shaped polymers [17–20], comb-shaped polymers [21, 22] and hyperbranched polymers [23–26]. A kind of H-shaped copolymer of PSt and poly(ethylene glycol) (PEG), $(\text{PSt})_2\text{PEG}(\text{PSt})_2$ was also prepared by ATRP using multifunctional macro initiator [27]. In this paper, we report another method to prepare H-shaped copolymer of poly(1,3-dioxepane) (PDOP) and PSt, $(\text{PDOP})_2\text{PSt}(\text{PDOP})_2$ by the combination of RAFT polymerization and cationic ring-open polymerization (CROP). We synthesized a novel trithiocarbonate, CTA-H, which carries two terminal acetonide groups for protection of dihydroxyl groups, and the RAFT polymerization of St with CTA-H as the chain transfer agent was investigated. After deprotection of the terminal acetonide, PSt with two hydroxyl groups in each end was obtained and it was used as the macro initiator in the CROP of DOP to yield the H-shaped copolymer.

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2. Experimental

2.1. Materials

Tetrahydrofuran (THF) was distilled from a purple sodium ketyl solution. Dichloromethane was distilled from CaH_2 prior to use. Triethylamine was distilled after dehydrated by potassium hydroxide and refluxed with *p*-toluenesulfonyl chloride. The initiator, *N,N'*-azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. It was washed with an aqueous solution of sodium hydroxide (5 wt%) three times, and then washed with water until neutralization. After drying with anhydrous magnesium sulfate, it was distilled under reduced pressure. DOP was synthesized and purified according to the published method [28]. $\text{BF}_3 \cdot \text{OEt}_2$ was distilled before use. 1,1,1-Trihydroxymethyl propane (THMP), 2-bromobutyryl bromide and other reagents (analytical grade) were used as received without further purification.

2.2. Synthesis of *S,S'*-bis(1-(((5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methoxy)carbonyl) propyl) trithiocarbonate (CTA-H)

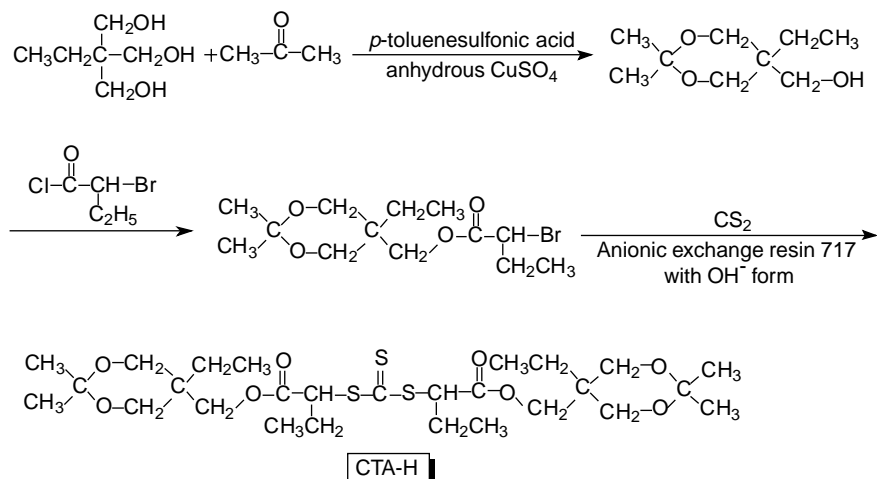
CTA-H was synthesized according to Scheme 1. The typical procedure is as follows. THMP (13.4 g, 0.10 mol) dissolved in 30 ml of THF, acetone (6.4 g, 0.11 mol), *p*-toluenesulfonic acid (2.0 g) and anhydrous CuSO_4 (8.0 g, 0.05 mol) were added into a 100 ml round-bottom flask equipped with a magnetic bar. The mixture was stirred under reflux for 6 h, and the solution turned into blue. The solution obtained from filtration was passed through a short alumina column to remove the copper salt completely. After removal of THF and acetone, 13.2 g 5-ethyl-2,2-dimethyl-5-hydroxymethyl-1,3-dioxane (EDHD) was obtained as a colorless liquid by distillation at 72 °C/mmHg (yield: 75.9%). $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (TMS, ppm): 0.84 (t, 3H, $\text{CH}_3\text{CH}_2\text{C}$), 1.32 (q, 2H, $\text{CH}_3\text{CH}_2\text{C}$), 1.41 (d, 6H, $(\text{CH}_3)_2\text{C}$), 3.65 (s, 4H, $\text{C}(\text{CH}_2\text{O})_2\text{C}$), 3.73 (s, HOCH_2C).

EDHD obtained (12.2 g, 0.07 mol), triethyl amine (8.1 g, 0.08 mol) and 80 ml of CH_2Cl_2 were added into a 250 ml

round-bottom flask equipped with a magnetic bar. The mixture was cooled at 0 °C in the ice-water bath, then 2-bromobutyryl bromide (17.2 g, 0.075 mol) diluted with 20 ml CH_2Cl_2 was dropped in slowly within 2 h. After stirring for 6 h, the reaction mixture was washed with 100 ml 5% NaHCO_3 solution for three times and then with 100 ml distilled water. The organic phase was diluted with CH_2Cl_2 , and then dried with anhydrous magnesium sulfate overnight. After filtration from the magnesium salt, the filtrate was distilled under reduced pressure and 17.3 g (5-ethyl-2,2-dimethyl-1,3-dioxane-5-yl) methyl 2'-bromobutyrate (EDMB) was collected at 172 °C/1 mmHg (yield: 76.5%). $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (TMS, ppm): 0.84 (t, 3H, $\text{CH}_3\text{CH}_2\text{C}$), 1.03 (t, 3H, $\text{CH}_3\text{CH}_2\text{CHBr}$), 1.34 (q, 2H, $\text{CH}_3\text{CH}_2\text{C}$), 1.41 (d, 6H, $(\text{CH}_3)_2\text{C}$), 2.08 (q, 2H, $\text{CH}_3\text{CH}_2\text{CHBr}$), 3.67 (s, 4H, $\text{C}(\text{CH}_2\text{O})_2\text{C}$), 4.20 (t, 1H, $\text{CH}_3\text{CH}_2\text{CHBr}$), 4.31 (s, 2H, COOCH_2C).

Anionic exchange resin 717×7 with Cl^- form (3 mM/g) in a column was continuously washed with 5% NaOH aqueous solution at a flow rate of 5 ml/min for 12 h, and then washed with deionized water until neutralization. The resin was dried at 60 °C in vacuum oven until constant weight. The dried resin (15 g) was added into carbon disulfide (50 ml), which acts as both solvent and reactant, and then the suspension was stirred at room temperature for about 5 min. The color of resin turned from yellow to blood red due to the formation of CS_3^{2-} on the polymeric support. Into this suspension, EDMB (6.46 g, 0.02 mol) was added. The mixture was then stirred under reflux for 16 h, and the color of the solution turned gradually into yellow. After completion of the reaction, the resin was filtered and washed with carbon disulfide. The filtrate was dried over anhydrous magnesium sulfate. After the solvent was evaporated under reduced pressure, the product obtained was purified through silica column chromatography with petroleum ether/ethyl acetate (4:1 v/v) as eluent. After the solvent was removed under reduced pressure, 1.52 g CTA-H was obtained as a pale yellow powder (yield: 25.6%).

$^1\text{H NMR}$ (300 MHz, CDCl_3), δ (TMS, ppm): 0.85 (t, 6H, $2\text{CH}_3\text{CH}_2\text{C}$), 1.03 (t, 6H, $2\text{CH}_3\text{CH}_2\text{CHS}$), 1.34 (q, 4H,



Scheme 1. Synthesis of the chain transfer agent, CTA-H.

2CH₃CH₂C), 1.41 (d, 12H, 2(CH₃)₂C), 2.06 (q, 4H, 2CH₃-CH₂CHS), 3.67 (s, 8H, 2C(CH₂O)₂C), 4.31 (s, 4H, 2COOCH₂-C), 4.73 (t, 2H, 2CH₃CH₂CHS). IR (neat, cm⁻¹): ν = 1734 (C=O), 1064(C=S).

2.3. Polymerization with CTA-H

Into a 5 ml sealed polymerization tube with magnetic stirring bar, CTA-H, AIBN, St and THF were added, and the tube was closed with three-way stopcocks. After being degassed by freeze-vacuum-thaw three times, the tube was sealed under vacuum, and the sealed tube was immersed in an oil bath thermostated at 100 °C while stirring. After a prescribed time, the polymerization tube was cooled down to room temperature rapidly, and the polymer was precipitated by pouring the polymer solution in THF into methanol. After dried in a vacuum oven at 40 °C for 24 h, PSt with dihydroxymethyl groups protected by acetonide in both ends was obtained.

2.4. Removal of the acetonide protected group at chain end

Cationic exchange resin 732×7 with Na⁺ form (2 mM/g) in a column was continuously washed with 5% HCl solution at a flow rate of about 5 ml/min for 12 h, and then washed with deionized water until neutralization. The resin was dried at 60 °C in vacuum oven until constant weight. For the preparation of sample PSt1 in Table 1, into the solution of PSt with acetonide protection group (1.2 g, ~0.18 mmol) in 20 ml THF, the dried resin (6.0 g) and methanol (10 ml) were added, and the reaction mixture was then stirred under reflux for 12 h. After the reaction was complete, the resin was filtered off and washed with THF. The combined filtrates were concentrated by evaporation of solvent, and the concentrated solution was then poured into methanol. The precipitated product was dried in a vacuum oven at 40 °C for 24 h to afford 1.08 g PSt with two hydroxyl groups in each chain end, (HO)₂PSt(OH)₂ (yield: 90%).

2.5. CROP of DOP in the presence of (HO)₂PSt(OH)₂

A 10 ml two-necked flask with a magnetic stirring bar and a constant-pressure dropping funnel was evacuated and purged with pure nitrogen three times alternatively. Then,

(HO)₂PSt(OH)₂ was dissolved in CH₂Cl₂, and BF₃·OEt₂ was added. The flask was thermostated at 0 °C while stirring, and a solution of DOP in CH₂Cl₂ was dropped slowly. After a prescribed time, a small amount of the polymerization mixture was withdrawn with a syringe for the determination of conversion, and the polymerization was terminated by adding excess methanol. After evaporation of solvent, the mixture was poured into methanol. After the precipitate was collected by filtration and then dried in a vacuum oven at 40 °C for 24 h, the H-shaped copolymer, (PDOP)₂PSt(PDOP)₂, was obtained.

2.6. Hydrolysis of H-shaped copolymers (PDOP)₂PSt(PDOP)₂

The solution of (PDOP)₂PSt(PDOP)₂ (1.0 g) in THF (30 ml) and 10 ml of potassium hydroxide in methanol (1 M) were put together, and then reflux over 72 h. After the solvent was removed under reduced pressure, 20 ml of CH₂Cl₂ was added to dissolve the product. The polymer solution was washed with distilled water until neutralization and dried over anhydrous magnesium sulfate. PSt was precipitated by pouring the solution into methanol and then collected by filtration. The solution was then distilled under reduced pressure to afford PDOP. The obtained PSt was further dissolved in THF and treated with acetic acid and zinc powder under N₂ in 40 °C for 4 h. After the removal of the solid by filtration, PSt was obtained by pouring the concentrated solution into methanol. The hydrolysis products were dried at 40 °C overnight.

2.7. Characterization

The purity and conversion measurements of DOP were carried out on 102G gas chromatography (Shanghai Analysis Instrument, Co.). ¹H NMR spectra were recorded on a Bruker-300 MHz NMR instrument using CDCl₃ as solvent and tetramethylsilane as internal reference. FT-IR spectra were obtained on a Bruker VECTOR-22 infrared spectrometer. Molecular weight and molecular weight distribution (MWD, M_w/M_n) were determined on a Waters 150C gel permeation chromatography (GPC) equipped with ultra-styrigel columns (500, 10³ and 10⁴ Å) at 30 °C, using monodispersed polystyrene as calibration standard. THF was used as eluent at a flow rate of 1 ml/min.

Table 1
RAFT polymerizations of St in the presence of CTA-H at 100 °C in THF

No.	St (mol)	THF (g)	CTA-H (mmol)	AIBN (mmol)	Time (h)	Conv. ^a (%)	M_n (g/mol)			M_w/M_n^b
							th ^c	NMR ^d	GPC ^b	
PSt1	0.03	2.0	0.3	0.03	14	57	6500	6800	6700	1.16
PSt2	0.04	2.0	0.2	0.02	14	60	13,000	13,100	13,500	1.13
PSt3	0.04	2.0	0.1	0.01	18	64	27,000	27,200	28,000	1.06
PSt4	0.03	3.0	0.2	0.02	16	51	8600	8700	8900	1.21

^a Conversion was measured with gravimetric method.

^b Measured by GPC.

^c Theoretical number-average molecular weight M_n (th) was calculated according to Eq. (1).

^d Calculated by M_n (NMR) = $(I_{Ar}/5)/(I_a/2) \times 104 + 594$, where I_{Ar} and I_a were the integral values of the aromatic protons of PSt and the methine proton of St unit adjacent to the trithiocarbonate group, and 104, 594 were the molecular weights of St and CTA-H, respectively.

3. Results and discussion

3.1. RAFT polymerization of St with CTA-H as the RAFT agent

In the investigation on RAFT polymerization in the presence of trithiocarbonates, a series of linear polymers and block copolymers with controllable molecular weight and narrow molecular weight distribution were synthesized [29–33]. But no investigation on the preparation of H-shaped copolymers based on RAFT polymerization has been reported. In order to realize this aim, we synthesized a novel trithiocarbonate, CTA-H, having an acetonide protected dihydroxymethyl group in each end. The conditions and results of the RAFT polymerization of St with CTA-H as the RAFT agent are listed in Table 1. The theoretical number-average molecular weight, $M_{n, \text{PSt}}(\text{th})$ of the PSt obtained was calculated according to Eq. (1):

$$M_{n, \text{PSt}}(\text{th}) = \text{conversion} \times (N_{\text{St}} \times 104 / N_{\text{CTA-H}}) + 597 \quad (1)$$

where N_{St} and $N_{\text{CTA-H}}$ are the initial moles of St and CTA-H, 104 and 597 are the molecular weights of St and CTA-H, respectively.

The living nature for the RAFT polymerization of St with CTA-H and AIBN as the RAFT agent and the initiator could be confirmed by the following evidences. The MWDs of the PSt obtained are relatively narrow (MDW = 1.06–1.21 in Table 1 and Fig. 1); As listed in Table 1, the molecular weights of PSt determined by NMR and by GPC agree well with $M_{n, \text{PSt}}(\text{th})$; The plot of $\ln([M]_0/[M]_t)$ against polymerization time affords a straight line (Fig. 2), indicating the constant concentration of propagating chain radicals during the polymerization; The linear growth of the molecular weight with the increase of monomer conversion shown in Fig. 3 demonstrate that the molecular weight of PSt can be controlled by the initial molar ratio of the monomer to the RAFT agent and the conversion. All these results demonstrate that the RAFT polymerization of St in the presence of CAT-H is of living character.

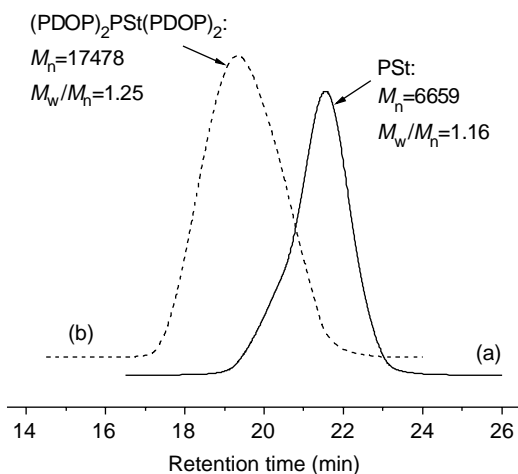


Fig. 1. GPC Curves of (a) PSt (PSt1 in Table 1) and (b) $(\text{PDOP})_2\text{PSt}(\text{PDOP})_2$ ($\text{PSt1}(\text{PD})_4\text{3}$ in Table 2) prepared by CROP of DOP using $(\text{HO})_2\text{PSt}(\text{OH})_2$ (PSt1 in Table 2) as the macro initiator.

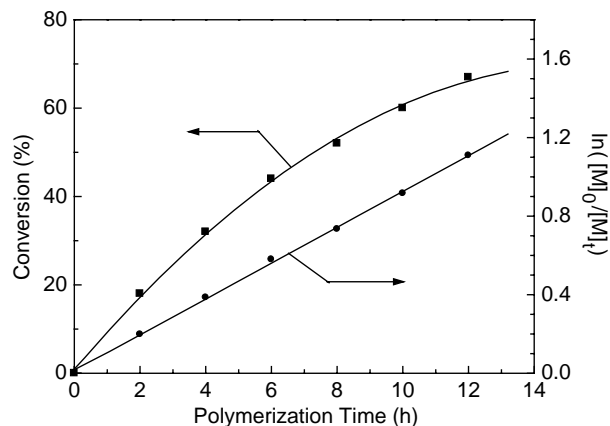


Fig. 2. Kinetic curves for the polymerization of St (3.0 g) in THF (1 g) at 100 °C in the presence of CTA-H (0.05 mmol).

3.2. Deprotection of the acetonide protected dihydroxyl groups in the PSt chain ends

The strategy for synthesis of the H-shaped copolymers of $(\text{PDOP})_2\text{PSt}(\text{PDOP})_2$ are described in Scheme 2. To ensure uniform structure of the H-shaped copolymers obtained, all the PSt with two hydroxyl groups in each end is necessary, which requires high deprotection reaction efficiency.

According to the previous result of RAFT polymerization [15], the ends of the polymer chains obtained were terminated almost with residues from the chain transfer agent when a relatively small amount of AIBN was used. The cationic exchange resin with H^+ form is an effective catalyst in the deprotection of acetonide [34]. Both the resin and the byproduct 2,2-dimethyloxyl propane are easy to remove by filtration and the precipitation of PSt in methanol. Therefore, the deprotection reaction was carried out in the presence of the cationic exchange resin with H^+ form to afford PSt with two hydroxymethyl groups at both ends of the polymer chains. The ^1H NMR spectra of the obtained PSt are shown in Fig. 4. Except the characteristic signals of PSt, we can observe in Fig. 4(a) that the signal at 4.43–4.82 ppm (a) corresponds to methine proton of St unit next to

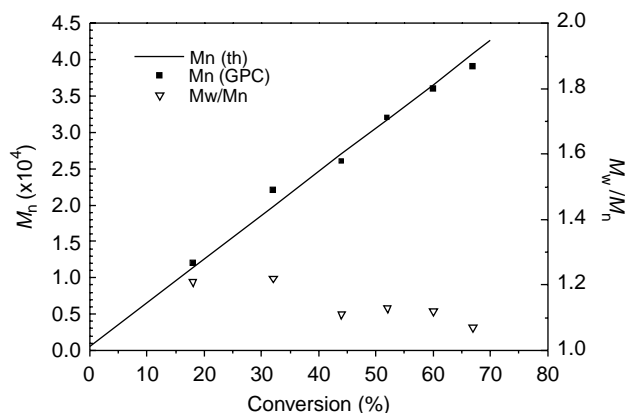


Fig. 3. Relationship of M_n and M_w/M_n with conversion for the polymerization of St (3.0 g) in THF (1 g) at 100 °C in the presence of CTA-H (0.05 mmol).

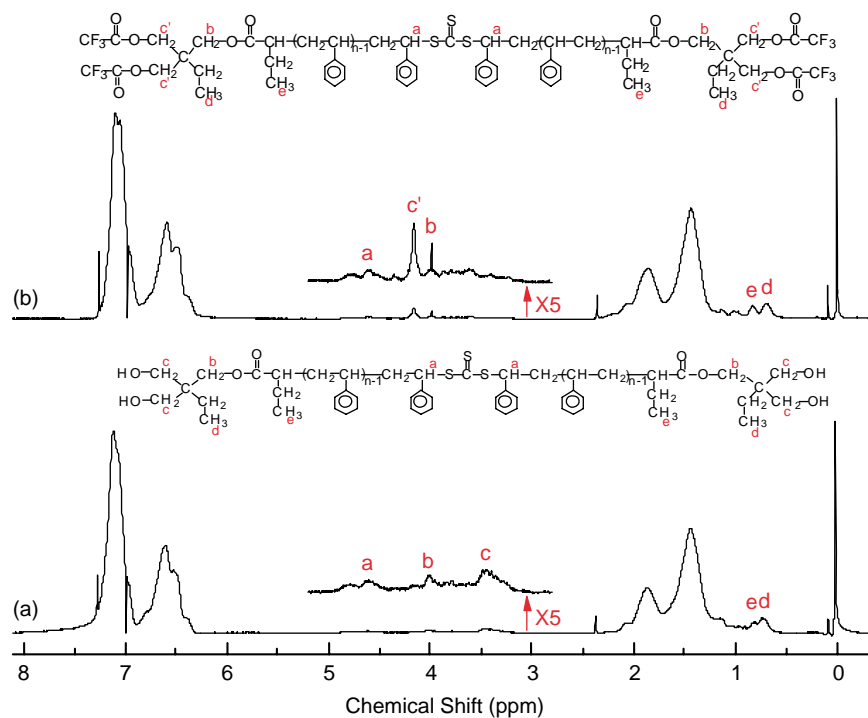
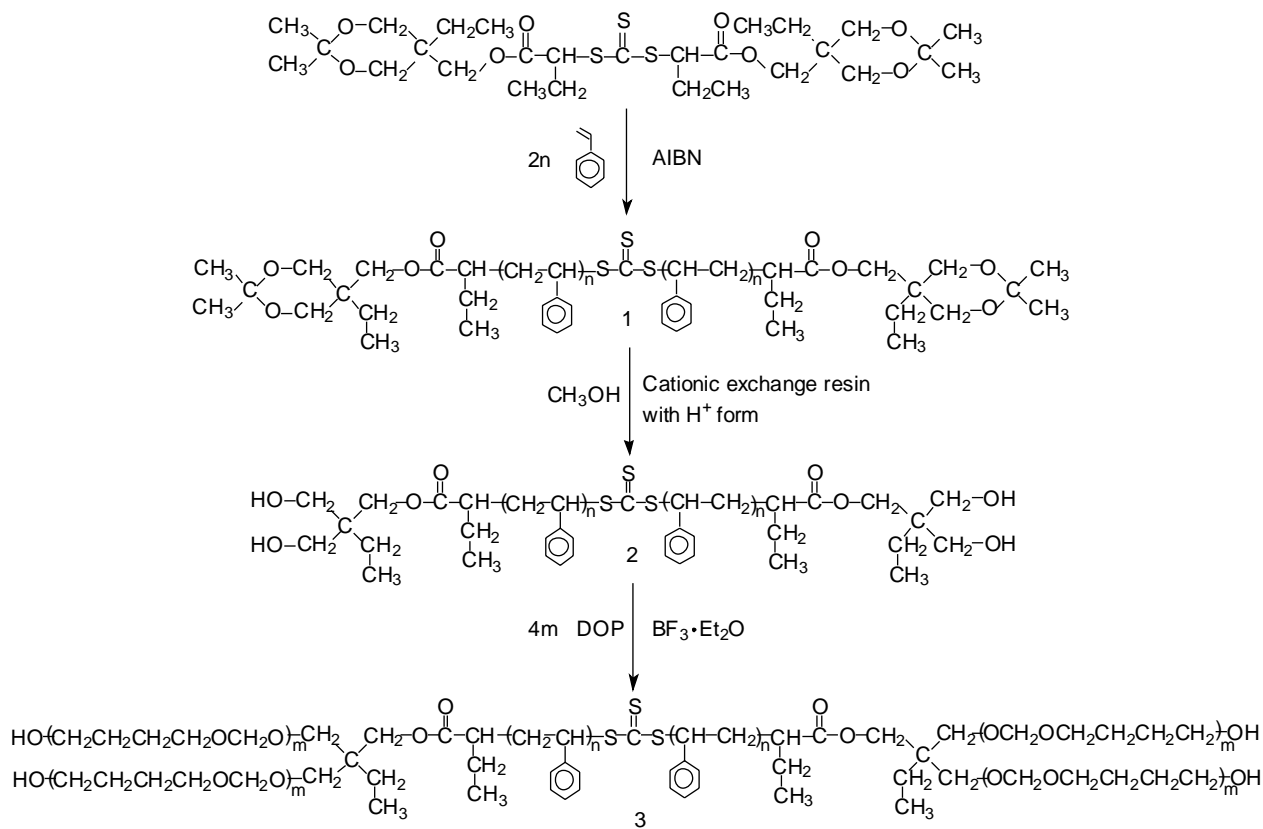


Fig. 4. ¹H NMR spectra of (a) (HO)₂PS(OH)₂ (PS1 in Table 2) and (b) the PS treated with trifluoroacetic anhydride.

Table 2
CROP of DOP in the presence of (HO)₂PSt(OH)₂ at 0 °C in DCM

No.	DOP (mol)	DCM (mL)	TFBE (mmol)	Time (h)	Conv. ^a (%)	M_n (g/mol)			M_w/M_n^b
						th ^c	NMR ^d	GPC ^b	
PSt1 ^c						6500	6700	7000	1.16
PSt1(PD) ₄ 1	0.02	2.0	0.2	3	20	14,700	14,900	11,700	1.22
PSt1(PD) ₄ 2	0.02	2.0	0.2	5	43	24,300	25,100	13,500	1.42
PSt1(PD) ₄ 3	0.02	2.0	0.2	6	56	29,700	31,200	17,500	1.25
PSt ^f						3300 ^g		3200	1.08
PDOP ^f						11,600 ^g	12,500 ^h	12,300	1.24
PSt2 ^c						13,000	13,100	13,500	1.13
PSt2(PD) ₄ 1	0.02	4.0	0.1	4	30	25,300	25,300	17,100	1.30

^a Conversion of DOP was measured by GC.

^b Measured by GPC.

^c Theoretical number-average molecular weight M_n (th) was calculated according to M_n (th) = $N_{DOP} \times 102 / N_{PSt} + M_{n,PSt}$ (NMR), where N_{DOP} and 102, N_{PSt} and M_n , PSt(NMR) are the initial moles and the molecular weights of DOP and the macro initiator (HO)₂PSt(OH)₂, respectively.

^d Calculated according to Eq. (2).

^e PSt1 and PSt2 correspond to the deprotected product of PSt1 and PSt2 in Table 1, respectively. The moles used in polymerization are all 0.05 mmol.

^f PSt and PDOP were obtained from the hydrolysis of PSt1(PD)₄3.

^g The M_n (th) of PSt and PDOP were calculated according to: $M_{n,PSt}$ (th) = $M_{n,PSt1}$ (th)/2 and $M_{n,PDOP}$ (th) = ($M_{n,PSt1(PD)43}$ (th) - $M_{n,PSt1}$ (th))/2.

^h Calculated according to Eq. (3).

the trithiocarbonate group, and the signals at 4.0 (b), 3.4 (c), 0.81 (e) and 0.72 ppm (d), respectively belong to the ester methylene protons, the methylene protons adjacent to the terminal hydroxyl groups and the protons of two types of methyl groups in CTA-H. In comparison with the ¹H NMR data of CTA-H, the signal of the methyl protons close to the trithiocarbonate group shift completely from 1.03 to 0.81 ppm, indicating the high chain transfer efficiency of this trithiocarbonate compound during the RAFT polymerization. In order to estimate the relative amount of the terminal dihydroxymethyl groups in the each end, trifluoroacetic anhydride was added into the NMR tube. After mixing for about 5 min, the ¹H NMR spectrum was measured again.

As shown in Fig. 4(b), the signal at 3.4 ppm (c) in Fig. 4(a) shifts completely to 4.3 ppm (c') because the hydroxyl groups in the chain ends are changed into trifluoroacetate groups. The integration ratio of $a/b/c/d/e \approx a'/b'/c'/d'/e' \approx 1:2:4:3:3$ equals almost to their corresponding hydrogen, which confirms further the high efficiency (~100%) of the deprotection reaction and all the PSt obtained having two hydroxymethyl groups in each chain end.

3.3. CROP of DOP in the presence of (HO)₂PSt(OH)₂

For the CROP of DOP with BF₃·OEt₂, there are two polymerization mechanisms: active chain end (ACE) and active monomer (AM) mechanisms. The propagation reaction via ACE mechanism is easier to yield oligomers. To reduce the homo PDOP via chain transfer reaction, the CROP of DOP was carried out with slow addition of DOP into the reaction mixture of DOP, macro initiator and BF₃·OEt₂. The condition and results are listed in Table 2.

The typical IR spectra are shown in Fig. 5. The absorption band at 1067 cm⁻¹ in Fig. 5(a) confirms the existence of trithiocarbonate groups in the macro initiator (HO)₂PSt(OH)₂. When comparing the spectrum of the obtained copolymer in Fig. 5(b) with that of the macro initiator in Fig. 5(a), besides

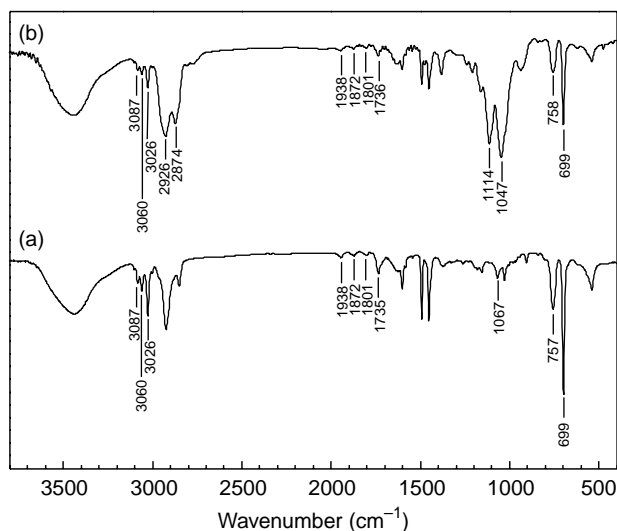
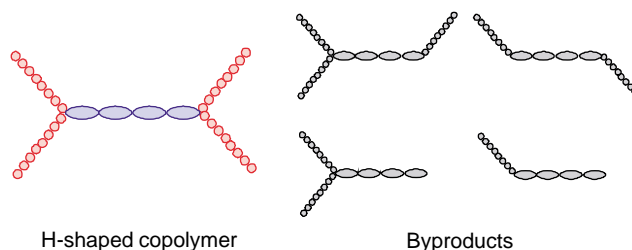


Fig. 5. FT-IR spectra of (a) (HO)₂PSt(OH)₂ (PSt1 in Table 2) and (b) (PDOP)₂PSt(PDOP)₂ (PSt1(PD)₄3 in Table 2) prepared by CROP of DOP using PSt1 as the macro initiator.



Scheme 3. Structures of the H-shaped copolymer and some byproducts in case of partial initiation.

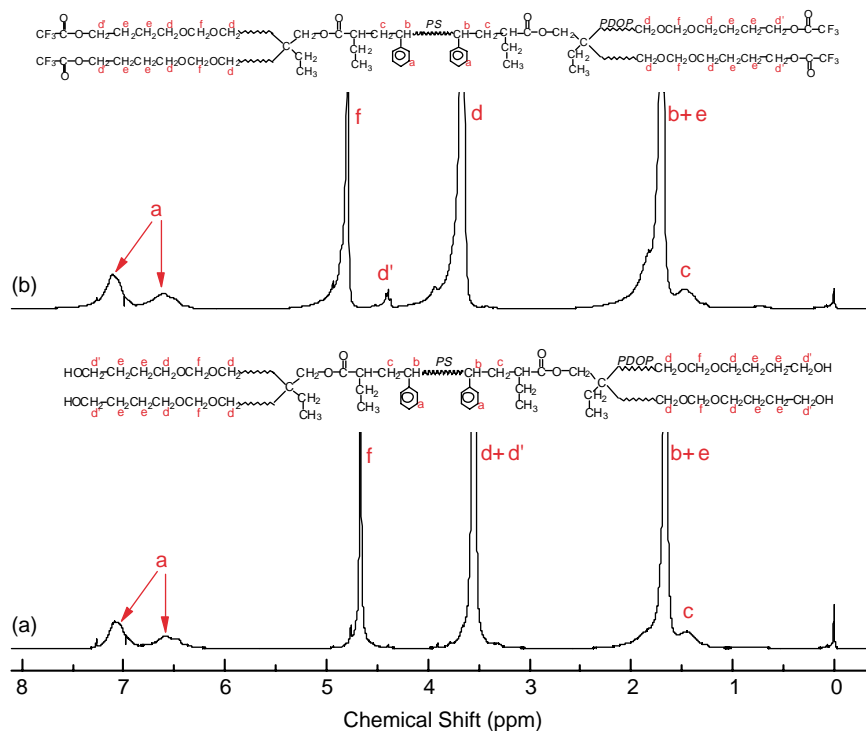


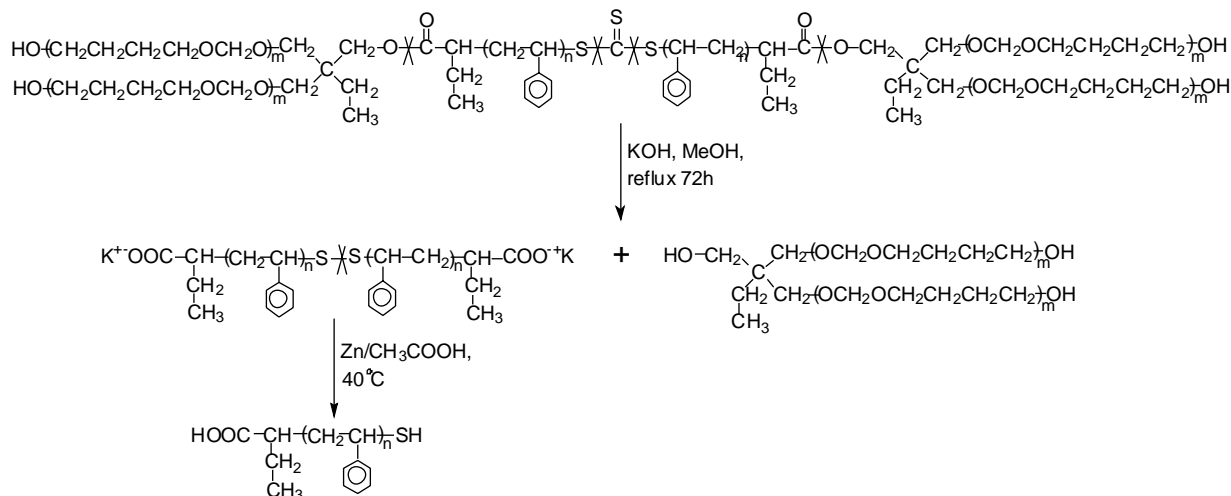
Fig. 6. ^1H NMR spectra of (a) $(\text{PDOP})_2\text{PSt}(\text{PDOP})_2$ and (b) the $(\text{PDOP})_2\text{PSt}(\text{PDOP})_2$ treated with trifluoroacetic anhydride.

the characteristic bands of PSt, we can also find the absorption bands at 1114 and 1047 cm^{-1} corresponding to the C–O of the PDOP segments, which clearly demonstrates the formation of the copolymers of PSt and PDOP.

Since the four terminal hydroxyl groups are all the primary alcohol, and they should have the approximate initiating reactivity. Thus, there is the biggest possibility to form the H-shaped $(\text{PDOP})_2\text{PSt}(\text{PDOP})_2$. If not all the four hydroxyl groups initiated the CROP of DOP, there would be the byproducts with several other structures shown in Scheme 3. As a consequence, the GPC curve should display more than one peak, or the curve would be unsymmetric. However, Fig. 1(b)

of the copolymer obtained from CROP of DOP is symmetric, and the curve is completely shifted to the high molecular weight position. The MWD ($M_w/M_n=1.25$) is narrow. All the facts demonstrate that the product is uniformly H-shaped copolymer.

For confirming the structure of H-shaped copolymer, their ^1H NMR spectra were measured. Fig. 6(a) is a typical ^1H NMR spectrum. The signals at 4.65 (f), 3.55 (d), and 1.66 ppm (e) in Fig. 6 are assigned to the acetal methylene protons, the methylene protons next to oxygen, and the protons of the two middle methylene groups of the tetramethylene unit, respectively, which indicates



Scheme 4. Hydrolysis of H-shaped copolymer, $(\text{PDOP})_2\text{PSt}(\text{PDOP})_2$.

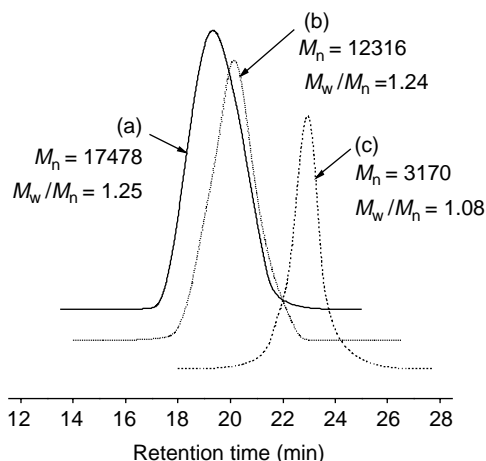


Fig. 7. GPC curves of (a) H-shaped copolymer $(\text{PDOP})_2\text{PSt}(\text{PDOP})_2$ ($\text{PSt}1(\text{PD})_{4,3}$ in Table 2), and its hydrolysis product: (b) PDOP (PDOP in Table 2) and (c) PSt (PSt in Table 2).

the existence of PDOP blocks in the copolymers. When trifluoroacetic anhydride was added into the NMR tube, a new signal at 4.3 ppm (d'), ascribed to the terminal ester methylene group, appeared in Fig. 6(b). Assume that each macromolecule has four terminal hydroxymethyl groups, the number-average molecular weight of the copolymer obtained, $M_{n,H}(\text{NMR})$ can be calculated according to Eq. (2):

$$M_{n,H}(\text{NMR}) = \left[\frac{I_{4.65}/2}{I_{4.30}/8} \right] \times 102 + M_{n,\text{PSt}}(\text{NMR}) \quad (2)$$

where $I_{4.65}$ and $I_{4.30}$ are the integral values of the signals at 4.65 (f) and 4.30 ppm (d') in Fig. 6(b), respectively, 102

and $M_{n,\text{PSt}}(\text{NMR})$ are the molecular weights of DOP and the macro initiator $(\text{HO})_2\text{PSt}(\text{OH})_2$. The agreement of $M_{n,H}(\text{NMR})$ with $M_n(\text{th})$ (Table 2) further verifies the formation of H-shaped copolymers, $(\text{PDOP})_2\text{PSt}(\text{PDOP})_2$. In general, the number-average molecular weights of the H-shaped polymers determined by GPC, $M_n(\text{GPC})$ are lower than $M_n(\text{NMR})$ and $M_n(\text{th})$ due to the lower hydrodynamic parameters. It is reasonable that all $M_n(\text{GPC})$ s are lower than $M_n(\text{NMR})$ s and $M_n(\text{th})$ s in Table 2.

For further confirmation of the H-shaped copolymers formed, the H-shaped copolymer was hydrolyzed. As shown in Scheme 4, the H-shaped copolymers can be considered as the connection of two PDOP blocks to the two ends of PSt block via ester linkage in the middle of each PDOP block, and we will find that there is a trithiocarbonate group in the center of PSt segment. Thus the copolymers were hydrolyzed in the basic solution. The data of hydrolyzed products are listed in Table 2.

After separation, PDOP and PSt were obtained. The GPC curve of PSt showed two peaks, which might be resulted from the oxidation of $-\text{SH}$ to form $-\text{S}-\text{S}-$. After the PSt was treated with acetic acid and zinc powder to decompose $-\text{S}-\text{S}-$, the GPC curve became a single, symmetrical. Fig. 7 shows typical GPC curves of the H-shaped copolymer (a), the hydrolyzed product PDOP (b) and PSt (c). The single and symmetrical curves in Fig. 7(b) and (c) may be ascribed to the almost same propagation possibilities of the hydroxyl groups in CROP of DOP. The molecular weight of PSt obtained is about half of the molecular weight of $(\text{HO})_2\text{PSt}(\text{OH})_2$ used as the macro initiator, which indicates that the trithiocarbonate group is stable during the CROP of DOP.

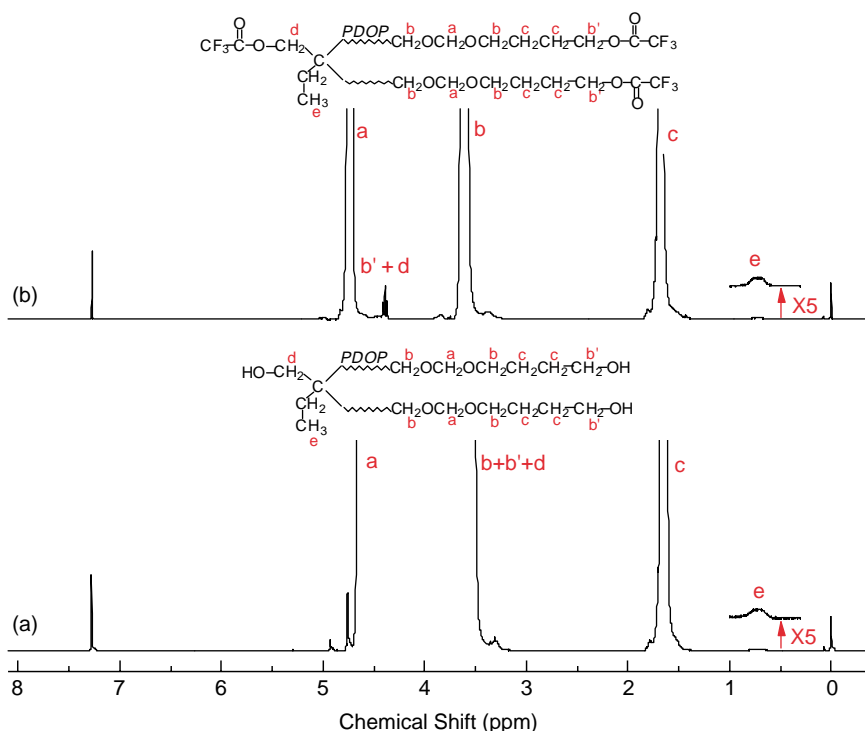


Fig. 8. ^1H NMR spectra of (a) PDOP PDOP (PDOP in Table 2) obtained from the hydrolysis of H-shaped copolymer $(\text{PDOP})_2\text{PSt}(\text{PDOP})_2$ ($\text{PSt}1(\text{PD})_{4,3}$ in Table 2) and (b) the corresponding PDOP treated with trifluoroacetic anhydride.

^1H NMR spectra of the hydrolyzed product PDOP before and after treated with TFA are shown in Fig. 8. The signals of PSt disappear completely and a typical spectrum for PDOP is observed (Fig. 8(a)). After treated with TFA, the signal at 4.39 ppm ($b' + d$) in Fig. 8(b) corresponds to the methylene protons next to the terminal hydroxyl groups and next to the hydroxyl group formed from the hydrolysis of ester group, and they are shifted from 3.55 ppm ($b + b' + d$) in Fig. 8(a). The integral ratio of signals at 4.39 ($b' + d$) and 0.68 ppm (e) is nearly 2:1, which demonstrates that the PDOP obtained from the hydrolysis of H-shaped copolymer does have a structure shown in Fig. 8. Its molecular weight can be calculated according to Eq. (3):

$$M_{n,\text{PDOP}}(\text{NMR}) = \left[\frac{I_{4.65}/2}{I_{4.39}/6} \right] \times 102 \quad (3)$$

where $I_{4.65}$ and $I_{4.39}$ are the integral value of the signals at 4.65 (a) and 4.39 ppm ($b' + d$), and 102 is the molecular weight of DOP.

The results listed in Table 2 show that the molecular weight, $M_n(\text{th})$ or $M_n(\text{NMR})$ of the H-shaped copolymers almost equals to the twice of the $M_n(\text{th})$ s or $M_n(\text{NMR})$ s of the hydrolyzed products PDOP and PSt. The GPC curves of H-shaped copolymer, PSt1(PD)₄3 shown in Fig. 7(a) and its hydrolyzed product PDOP in Fig. 7(b) are all single and symmetrical, and their MWDs are almost the same. Therefore, the two PDOP blocks in the both sides of the copolymer obtained have almost the same molecular weight, and almost all the terminal hydroxyl groups took part in the initiate reaction. As shown in Scheme 2, the H-shaped copolymers, (PDOP)₂PSt(PDOP)₂ with a uniform architecture have been successfully prepared.

4. Conclusion

A novel trithiocarbonate CTA-H, having acetonide protected dihydroxymethyl groups, has been successfully synthesized by the reaction of CS₂ and (5-ethyl-2,2-dimethyl-1,3-dioxane-5-yl)methyl 2'-bromobutyrate in the presence of anion-exchange resin with OH⁻ form. It is an efficient chain transfer agent in the RAFT polymerization of St. The PSt with two terminal hydroxyl groups in both chain ends, (HO)₂-PSt(OH)₂ can be efficiently obtained by the deprotection of the PSt having acetonide protected dihydroxymethyl groups in each end. It can be used as the macro initiator in the CROP of DOP to prepare the H-shaped copolymer (PDOP)₂PSt(PDOP)₂ with a uniform structure. This preparation method of H-shaped copolymer is easy, timesaving and effective.

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