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Synthesis of Diverse α,ω-Telechelic Polystyrenes with Di- and Tri-functionality via Tandem or One-Pot Strategies Combining Aminolysis of RAFT-Polystyrene and Thiol-Ene "Click" Reaction

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Thiol-ene "click" reaction proceeds with facile reaction conditions for complete conversion, and displays a higher tolerance to various backbones and functional groups comparing with traditional coupling and functionalization strategies. Herein, well-defined α,ω-telechelic polystyrenes with trithiocarbonate and carboxyl terminal groups (PS-CTA) were firstly synthesized via reversible addition-fragmentation chain transfer (RAFT) radical polymerization. Then, the terminal thiol group was converted from thiocarbonylthio end group of PS-CTA and subsequently reacted with n-butyl acrylate and vinyl ferrocene, respectively, through thiol-ene "click" chemistry, to achieve α,ω-telechelic polystyrenes with difunctionality. Alternatively, a facile one-pot simultaneous aminolysis and thiol-ene "click" reaction using PS-CTA and various ene-bearing compounds as reactants was found to have high efficiency in synthesizing diverse α,ω-telechelic polystyrenes with di- and tri-functionality. Various functional groups such as hydroxyl, acrylate, fluorinated acrylate, ferrocene and allyl, etc. can be successfully incorporated as terminal groups of α,ω-telechelic polystyrenes

Introduction

In the last 16 years, the reversible addition-fragmentation chain transfer (RAFT) polymerization[1] was increasingly used to synthesize a wide range of well-defined polymers such as α-monofunctional polymers,[2] α,ω-telechelic functional polymers[3-12] and block copolymers.[13-16] Polymers containing dithioester/thiocarbonylthio end groups synthesized by RAFT polymerization can be converted to thiol-terminated polymers by aminolysis with primary or secondary amine.[8,17-21] Such thiol-terminated polymers can be further employed in the synthesis of functional materials such as polymers with a variety of terminal groups,[21-25] surface modified transition metal nanoparticles or films,[26-29] functional hairy hollow microspheres,[30] temperature-responsive DNA-carrying polymer micelles,[31] functionalized carbon nanotube[32] and well-defined polymers with diverse topological architectures,[33-36] etc.

More recently, thiol-ene chemistry has been introduced as a new "click" reaction and applied in many fields such as synthetic methodologies, biofunctionalization, surface modification, polymer and materials synthesis etc.[37-43] The compounds or polymers bearing thiol group play an important role in thiol-ene "click" reaction and need to be synthesized with high thiol-functionality. However, the oxidative coupling of the thiol end groups observed during the aminolysis of dithioester/thiocarbonylthio end groups of polymers[22,33,35,36,44-46] lead to bimodal polymer populations compose of thiol and disulfide polymers. In general, in order to avoid the oxidative coupling of thiols, the treatment of reaction mixture using Zn/acetic acid (Zn/HAc) after aminolysis[47] and the addition of antioxidant sodium bisulfite in the system of animolysis[4,5,48] was employed and found to be the efficient methodlogies. In addition, $NaBH_4$,[26-31] the combination of amine and phosphine compounds,[22,35,36,49] the combination of $NaBH_4$ and phosphine compounds[22] show their high capability for the reduction of dithioester/thiocarbonylthio end groups into thiols without the formation of disulfide byproduct. Phosphine compound was also utilized to cleave disulfide bond to generate thiol group at the chain end of block copolymer.[50] Alternatively, a facile one-pot simultaneous aminolysis and thiol-ene "click" reaction[7,11,35,36,51] using RAFT polymers and various thiol-reactive ene-bearing compounds as reactants showed high efficiency in synthesizing diverse α,ω-telechelic polymers without the formation of

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disulfide and the isolation of intermediate polymers.

Very recently, a variety of α-mono and α,ω-telechelic functional polystyrenes[52-54] were synthesized *via* atomic transfer radical polymerization based methodlogy and employed for fabricating highly ordered honeycomb films.

In this work, new α,ω-telechelic polystyrenes with di- and tri-functionality bearing carboxyl, (fluorinated) alkyl ester, ferrocene and single/di-allyl ester were synthesized for the first time *via* tandem or one-pot strategies. In a tandem procedure, polystyrene with terminal thiocarbonylthio group (PS-CTA) by RAFT polymerization was firstly synthesized using S-1-dodecyl-S'-bis(α, α'-dimethyl-α''-acetic acid)-trithiocarbonate (DDMAT)[55] as chain transfer agent (CTA) and then transformed to α-thiol,ω-carboxyl telechelic polystyrene (HS-PS-COOH) *via* aminolysis with different reduction reagents. Subsequently, thiol-ene "click" reaction of HS-PS-COOH with *n*-butyl acrylate and vinylferrocene in the presence of photoinitiator was incandescent-lamp irradiated at room temperature to achieve α,ω-telechelic PS. Moreover, a facile one-pot strategy combining aminolysis of RAFT-polystyrene and thiol-ene "click" reaction simultaneously targeting diverse new α,ω-telechelic polystyrenes with di- and tri-functionality bearing carboxyl, (fluorinated) alkyl ester and single/di-allyl ester was reported.

Experimental

Materials

Styrene were dried over calcium hydride, distilled under reduced pressure, passed through a neutral alumina column to remove stabilizer, and degassed with nitrogen prior to use. The chain transfer agent of S-1-dodecyl-S'-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (DDMAT) was synthesized as previously reported[55]. *n*-Hexylamine (*n*-HA, Aladdin, 99%), acetic acid, tri-*n*-butylphosphine (Bu_3P, Adamas, 98%+), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aladdin), $NaBH_3CN$ (J&K Scientific Ltd., 95%), *n*-butyl acrylate (*n*-BuA, Aladdin, 99%), allyl methacrylate (AMA) (Aldrich, 98%), 2,2,2-trifluoroethyl acrylate (TFEA) (J&K, 99%), 1,3,5-triallyl isocyanurate (TAIC, Aldrich, 98%) were used as received without further purification. Vinylferrocene (VCp_2Fe) (>98%) was kindly provided by Prof. Jun Yang and Master candidate Mu-Shuang Qian in SIOC(CAS). Zinc powder (Aladdin) was purified by stirring in 3 wt-% hydrochloric acid for 3 h, filtered and washed three times with deionized water and acetone. The purified zinc powder was then dried in vacuo and stored under dry nitrogen. Tetrahydrofuran (THF) were refluxed over sodium/benzophenone and distilled under N_2 before use. 2,2-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol at 40 °C and dried under vacuum. Other reagents were purchased from Sinopharm Chemical Reagent, unless specified, and purified by standard procedures. All manipulations involving air- and/or moisture-sensitive compounds were carried out in a N_2-filled dry box or using Schlenk techniques.

Synthesis of α-thiol,ω-carboxyl telechelic PS (HS-PS-COOH)

The synthetic procedure of α-thiol,ω-carboxyl telechelic PS (HS-PS-COOH) was depicted in Scheme 1. Firstly, in a similar procedure reported previously,[56] styrene (16.2 mL, 141.5 mmol) and *S*-1-dodecyl-*S*'-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (DDMAT) (1.45 g, 3.97 mmol) were added to a 50 mL Schlenk flask equipped with a stirring bar. The mixture was degassed with three freeze-evacuate-thaw cycles, followed by heating to 140 °C for 6 h in a thermostated oil bath. The flask was quenched to 0 °C, then the PS was isolated by precipitation of the reaction mixture into methanol, filtered and washed three times with methanol, and dried in a vacuum oven at room temperature for 24 h. PS-CTA: M_n= 3200 g·mol^{-1}, M_w/M_n=1.08. ^{1}H NMR ($CDCl_3$): δ(ppm)= 7.30-6.30 (*m*, H^d), 5.03-4.60 (*b*, H^e), 3.34-3.19 (*m*, H^c), 2.50-1.13 (*m*, $H^{b+f+g+h+i_2}$), 1.02-0.82 (*m*, H^{a+i_1}). FT-IR (KBr), max 3082, 3059, 3025 (*vs*, C-H on phenyl); 2922 (*s*, -CH_3); 2849 (m, -CH_2-); 1743 (*vs*, C=O); 1601,1583,1493,1452 (*s*, C-C on phenyl); 1069 (*s*, C=S); 841 (*s*, -C-S); 756, 697 (*as*, -CH- on phenyl) cm^{-1}.

Subsequently, PS-CTA (1.01 g, 0.32 mmol) was dissolved in 20 mL of anhydrous THF. The solution was purged with dry nitrogen for 15 min and a 10-fold molar excess *n*-hexylamine was added and then stirred for 1 h at room temperature. After that, the treatment of such reaction mixture was performed by adding Zn/HAc (molar ratio=1:1) or tri-*n*-butylphosphine (Bu_3P) (5 equiv. relative to thiol moiety) shown in Scheme 1. HS-PS-COOH was isolated by precipitation of the reaction mixture into methanol, filtered and washed three times with methanol, and dried in a vacuum oven at room temperature for 24 h. $M_{n(GPC)}$= 3076 g·mol^{-1}, M_w/M_n=1.08. ^{1}H NMR ($CDCl_3$): δ(ppm)= 7.30-6.30 (*m*, H^d), 3.60-3.40 (*s*, $H^{e'}$), 2.50-1.32 (*m*, H^{f+g+h}), 1.32-1.10 (*s*, H^{i2}), 1.02-0.81 (*m*, H^{i1}).

Synthesis of α,ω-telechelic PS *via* thiol-ene "click" reaction

In a similar procedure reported by Uygun and coworkers[57], a solution of HS-PS-COOH (1 equiv.), ene (*n*-BuA or VCp_2Fe) (10 equiv.), photoinitiator (DMPA, 5 equiv.) in 10 mL of THF were introduced in a Schlenk flask and incandescent-lamp irradiated at room temperature (RT) for 2-7 h. The intensity of electric current was 25A as measured by Xenon lamp XQ500W adjustable radiometer. The reaction mixture was precipitated in methanol and the obtained polymers were reprecipitated in acetonitrile, filtered and washed three times with acetonitrile, and then dried in a vacuum oven at room temperature for 24 h. The synthetic procedure was shown in Scheme 2. R_1-S-PS-COOH (ene: *n*-BuA): $M_{n(GPC)}$= 3347 g·mol^{-1}, M_w/M_n=1.13. $M_{n(MALDI-TOF)}$= 3335 g·mol^{-1}, M_w/M_n=1.04. ^{1}H NMR ($CDCl_3$): δ(ppm)= 7.36-6.30 (*m*, H^d), 4.13-3.90 (*b*, H^l), 3.40-3.20 (*s*, $H^{e''}$), 2.50-2.32 (*s*, H^k), 2.31-2.16 (*s*, H^j), 2.15-1.30 (*m*, $H^{f+g+h+m+n}$), 1.29-1.10 (*s*, H^{i2}), 1.02-0.79 (*m*, H^{i1+p}). R_2-S-PS-COOH (ene: VCp_2Fe): $M_{n(GPC)}$= 3602 g·mol^{-1}, M_w/M_n=1.02. $M_{n(MALDI-TOF)}$= 3480 g·mol^{-1}, M_w/M_n=1.02. ^{1}H NMR ($CDCl_3$): δ(ppm)= 7.36-6.28 (*m*, H^d), 4.50-3.60 (*m*, H^l), 3.59-3.40 (*b*, H^k), 3.25-3.06 (*b*, $H^{e''}$), 2.34-2.16 (*s*, H^j), 1.23-1.16 (*s*, H^{i2}), 1.03-0.80 (*m*, H^{i1}). FT-IR (KBr): max 3082, 3059, 3025 (*vs*, C-H on phenyl); 2922 (*s*, -CH_3); 2849 (*m*, -CH_2-); 1743 (*vs*, C=O); 1601,1583,1493,1452 (*s*, C-C on phenyl); 1261.0, 1105.1, 807.0 (*m*, C-H on dicyclopentadienyl ring); 756, 697 (*as*, -CH- on phenyl) cm^{-1}; 625 (*w*, -C-S-) cm^{-1}. The content of Fe was 1.35 wt-% by elemental analysis.

Synthesis of α,ω-telechelic PS *via* one-pot strategy combining aminolysis of RAFT-Polystyrene and thiol-ene "click" reaction simultaneously

In a typical synthetic proceduce as shown in Scheme 3, PS-CTA (1 equiv., 0.01 mmol), ene (*n*-BuA, TFEA, AMA and TAIC, respectively) (10 equiv., 0.1 mmol) and DMPA (5equiv., 0.05 mmol, only in the case of TFEA) were dissolved in THF (10 mL). *n*-hexylamine (10 equiv., 0.1 m mol) was added dropwise under nitrogen. The solution was purged with nitrogen for 30 min. The solution was stirred in a Schlenk flask and irradiated at RT for 2-5 h. The intensity of electric current was 25A as measured by Xenon lamp XQ500W adjustable radiometer. During the reaction, the characteristic yellow color of the solution disappeared. The product was purified in methanol (3 times) and dried in a vacuum oven at room temperature for 24 h. R_3-S-PS-COOH (ene: TFEA**)**: $M_{n(GPC)}$= 3432 g·mol^{-1}, M_w/M_n=1.05. $M_{n(MALDI-TOF)}$= 3407 g·mol^{-1}, M_w/M_n=1.10 ^{1}H NMR ($CDCl_3$): δ(ppm) = 7.43-6.30 (*m*, H^d), 4.46-4.30 (*m*, H^l), 3.40-3.23 (*m*, $H^{e''}$), 2.50-1.35 (*m*, $H^{f+g+h+k+j}$), 1.33-1.20 (*s*, H^{i2}), 1.06-0.82 (*m*, H^{i1}). ^{19}F NMR ($CDCl_3$): δ(ppm) = -73.67, -73.70, -73.72 ppm. R_4-S-PS-COOH (ene: AMA**)**: $M_{n(GPC)}$= 3674 g·mol^{-1}, M_w/M_n=1.03. $M_{n(MALDI-TOF)}$= 3352 g·mol^{-1}, M_w/M_n=1.02. ^{1}H NMR ($CDCl_3$): δ(ppm)= 7.30-6.30 (*m*, H^d), 5.94-5.70 (*s*, H^m), 5.35-5.11 (*m*, H^n), 4.60-4.35 (*b*, H^l), 3.40-3.20 (*s*, $H^{e''}$), 2.50-1.29 (*m*, $H^{f+g+h+p+j}$), 1.29-1.15 (*s*, H^{i2}),1.12-0.81 (*m*, H^{k+i1}). R_5-S-PS-COOH (ene: TAIC)**:** $M_{n(GPC)}$= 3308 g·mol^{-1}, M_w/M_n=1.13. $M_{n(MALDI-TOF)}$= 3314 g·mol^{-1}, M_w/M_n=1.02. ^{1}H NMR ($CDCl_3$): δ(ppm)= 7.30-6.30 (*m*, H^d), 5.96-5.70 (*s*, H^m), 5.41-5.10 (*m*, H^p), 4,55-4.34 (*t*, H^n), 3.87-3.60 (*s*, H^l), 3.42-3.30 (*s*, $H^{e''}$), 3.22-2.97 (*m*, H^j), 2.54-1.20 (*m*, $H^{f+g+h+k}$), 1.18-1.07 (*s*, H^{i2}),1.05-0.74 (*m*, H^{i1}).

Polymers characterization

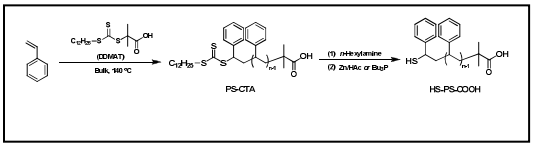
^{1}H NMR and ^{19}F NMR spectra of polymers were obtained on a Bruker AV 300 spectrometer (300 MHz) at room temperature with $CDCl_3$ as the solvent. The number molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymers were measured by a Waters gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (RI), a Waters 2487 dual k absorbance detector (UV) and a set of Waters Styragel columns (HR3, HR4 and HR5, 7.8×300 mm). GPC measurements were carried out at 35 °C using tetrahydrofuran (THF) as eluent with a flow rate of 4.0 μL min^{-1}. The system was calibrated with polystyrene standards. FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a resolution of 4 cm^{-1}. UV-vis spectra were recorded on U-3900 Spectrophotometer with scan speed of 2400 nm/min and sampling interval of 5.00 nm. Measurements were performed with a Shimadzu AXIMA Performance MALDI-TOF /TOFMS(matrix-assisted laser desorption and ionization time-of-flight) mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. 1,8,9-anthracenetriol (dithranol) was used as matrix. Samples were prepared by dissolving the polymer in dichloromethane at a concentration of 3 g/L. A 1 μL aliquot of this solution was added to 10 μL of a 20 g/L matrix solution and 1 μL of a silver(I) trifluoroacetate solution (cationization agent). A 1 μL aliquot of the resulting mixture was applied to a multistage target to evaporate the dichloromethane and create a thin matrix/analyte film. The ions were measured in the reflectron mode of the spectrometer. Only lithium-cationized ions (M + Li+) were detected. TOFmix was used for an external calibration immediately before the measurement.

Results and Discussion

Synthesis of α-thiol,ω-carboxyl telechelic PS (HS-PS-COOH)

The synthetic procedure of α-thiol,ω-carboxyl telechelic PS (HS-PS-COOH) was illustrated in Scheme 1. Firstly, a well-defined thiocarbonylthio terminated polystyrene (PS-CTA) was obtained by bulk RAFT polymerization of styrene using DDMAT as chain transfer agent. Subsequently, PS-CTA was aminolysized using *n*-hexylamine and then treated by Zn/HAc or tri-*n*-butylphosphine (Bu_3P).

Scheme 1. Synthesis of PS-CTA and HS-PS-COOH



PS-CTA with molecular weight of M_n=3200 g·mol^{-1} (the molecular weight at peak M_p=3509 g·mol^{-1}) was obtained and showed a single narrow peak (M_w/M_n=1.08) in its GPC curve (Fig. 1(a)). ^{1}H NMR spectrum of PS-CTA (Fig. 2(b)) confirmed its chain structure as reported previously.[56] Upon cleavage of the thiocarbonylthio group at the chain end of PS-CTA, primary or secondary amines was well-known to react with thiocarbonylthio group rapidly at ambient temperature leading irreversibly to thioamides and thiols.[4-8, 17-21] Herein, PS-CTA was transformed into α-thiol,ω-caboxyl telechelic PS by aminolysis using *n*-hexylamine alone. The aminolysis of the thiocarbonylthio end group was confirmed by a rapid color change from yellow to colourless. However, the oxidative coupling of the thiol end-groups to produce disulfide was also observed by the presence of bimodal molecular weight distribution in GPC curve of the resulted polymer as shown in Fig. 1(b). The higher molecular weight at peak (M_p=6537 g·mol^{-1}) was approximately twice as the smaller M_p (3435 g·mol^{-1}) which was a little lower than M_p=3509 g·mol^{-1} of PS-CTA (Fig. 1(a)) due to the transformation of thiocarbonylthio moiety into thiol moiety. It was attributed to the formation of disulfide (HOOC-PS-S-S-PS-COOH) by the oxidative coupling of HS-PS-COOH.

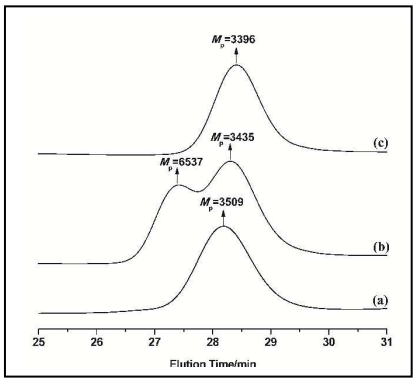


Fig. 1 GPC traces of (a) PS-CTA, (b) α,ω-telechelic polystyrene PS prepared only *via* the aminolysis of PS-CTA and (c) HS-PS-COOH obtained by the aminolysis of PS-CTA followed by the treatment of Zn/HAc.

Despite taking all precautions, such as degassing the reaction mixture, the oxidative coupling of the thiol moiety can still occur upon treatment with *n*-hexylamine. To avoid the oxidative coupling of the thiol moiety, such reaction mixture after aminolysis was treated by Zn/HAc. A unimodal molecular weight distribution was observed in GPC curve (Fig. 1(c)) and its M_p (3396 g·mol^{-1}) was a little lower than M_p=3509 g·mol^{-1} of PS-CTA (Fig. 1(a)) because of the removal of thiocarbonylthio moiety from PS-CTA. As shown in ^{1}H NMR spectra (Fig. 2), the singlet at 3.39-3.16 ppm assigned to the methylene proton (c) next to thiocarbonylthio (Fig. 2(a)) of PS-CTA could not be observed (Fig. 2(b)) after its animolysis by *n*-hexylamine and the treatment of Zn/HAc. Meanwhile, the singlet at 5.03-4.60 ppm assigned to the methine proton (e) (-SC(=S)S-C*H*(Ph)-) of PS-CTA (Fig. 2(a)) shifted to 3.65-3.40 ppm, indicating the presence of methine proton (e') (HS-C*H*(Ph)-). Moreover, the strong absorbance of thiocarbonylthio moiety of PS-CTA at 315 nm in UV-Vis spectra (Fig. 3) was almost completely disappeared also indicating the formation of HS-PS-COOH.

Alternatively, in order to avoid the oxidative coupling of thiol moiety, $Na_2S_2O_4$ and Bu_3P were employed as reducing agent to treat the reaction mixture of aminolysis, respectively. Neither of them showed advantage over Zn/HAc in our case.

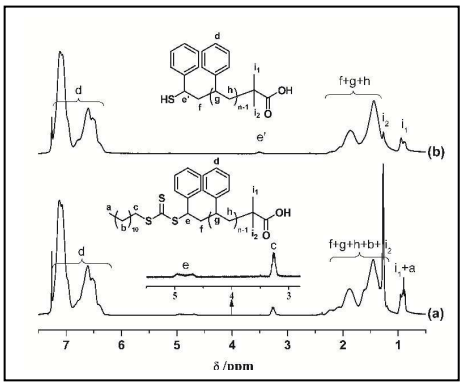


Fig. 2. ^{1}H NMR spectra of (a) **PS-CTA** and (b) **HS-PS-COOH**.

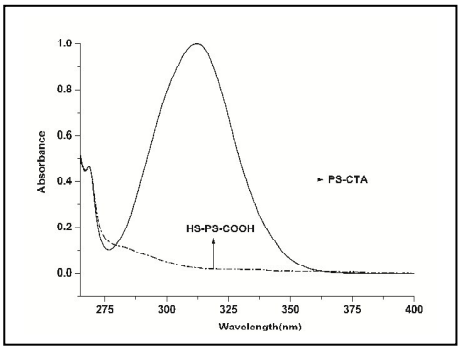
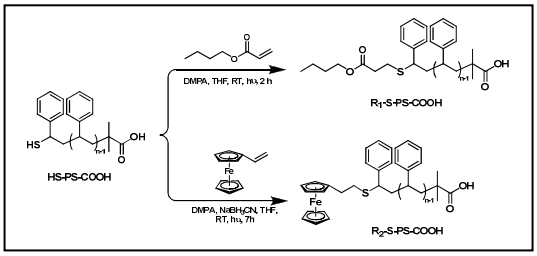


Fig. 3. UV-vis spectra of PS-CTA and HS-PS-COOH.

Synthesis of α,ω-telechelic PS *via* thiol-ene "click" reaction

The thiol-ene "click" reactions between HS-PS-COOH and enes (*n*-butyl acrylate (*n*-BuA) and vinylferrocene (VCp_2Fe), respectively) were carried out at room temperature (RT) by irradiation with an incandescent-lamp using DMPA as photoinitiator (see Scheme 2). The GPC and MALDI-TOF analysis of R_1-S-PS-COOH showed similar molecular weights ($M_{n(GPC)}$= 3347 g·mol^{-1} *vs* $M_{n(MALDI-TOF)}$= 3335 g·mol^{-1}) and narrow molecular weight distributions (M_w/M_n=1.13 and 1.04, respectively). The structure of polymer was ascertained by analysis of its ^{1}H NMR spectrum. As shown in Fig. 4, the signal of the methine proton next to thiol moiety at 3.65-3.40 ppm (e' in Fig. 2(b)) shifted to 3.40-3.20 ppm (e" in Fig. 4). Simultaneously, new singlets l (δ = 4.13-3.90 ppm), k (δ = 2.50-2.32 ppm) and j (δ = 2.31-2.16 ppm) were observed and assigned to protons of -CH_2-O-CO-, -O-CO-CH_2- and -CH_2-S-, respectively. According to the analysis described above, the connection of thiol moiety with *n*-BuA *via* thiol-ene "click" reaction was confirmed and the targeting polymer R_1-S-PS-COOH was achieved.



Scheme 2. Synthesis of α,ω-telechelic polystyrenes *via* thiol-ene "click" reaction of between HS-PS-COOH and ene-bearing compound.

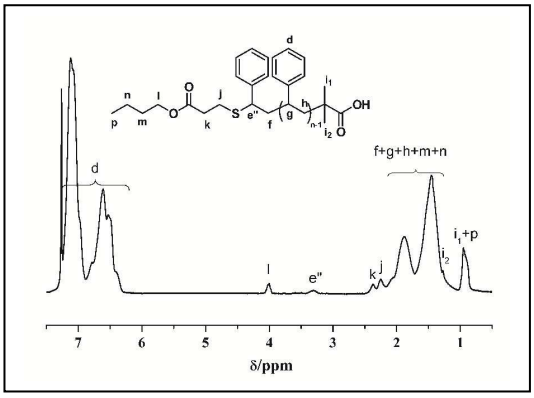


Fig. 4. ^{1}H NMR spectrum of R_1-S-PS-COOH synthesized *via* tandem strategy combining aminolysis of PS-CTA and thiol-ene "click" reaction.

Unexpectedly, in the same reaction condition, HS-PS-COOH didn't react with VCp_2Fe. It was worth noting that the addition of $NaBH_3CN$[58], a reducing agent with milder reactivity and easier manipulation than those of $NaBH_4$, accelerated the thiol-ene "click" reaction between HS-PS-COOH and VCp_2Fe. The possible explanation for such phenomenon is underwork.

As shown in Fig. 5, the signal of the methine proton next to thiol moiety at 3.65-3.40 ppm (e', in Fig. 2(b)) shifted to 3.26-3.00 ppm (e" in Fig. 5). Simultaneously, new singlets l (δ = 4.50-3.60 ppm), k (δ = 3.59-3.40 ppm) and j (δ = 2.34-2.16 ppm), were present and assigned to protons of dicyclopentadienyl ring, Cp-CH_2- and -CH_2-S-, respectively. In addition, the characteristic infrared absorbances of C-H of dicyclopentadienyl ring at 1261.0, 1105.1, 807.0 cm^{-1} were appear. The molecular weight of R_2-S-PS-COOH determined by GPC is 3602 $g{\cdot}mol^{-1}$(M_w/M_n=1.02) and close to 3480 $g{\cdot}mol^{-1}$ (M_w/M_n=1.02) determined by MALDI-TOF. All the analysis described above indicated the formation of the targeting polymer R_2-S-PS-COOH.

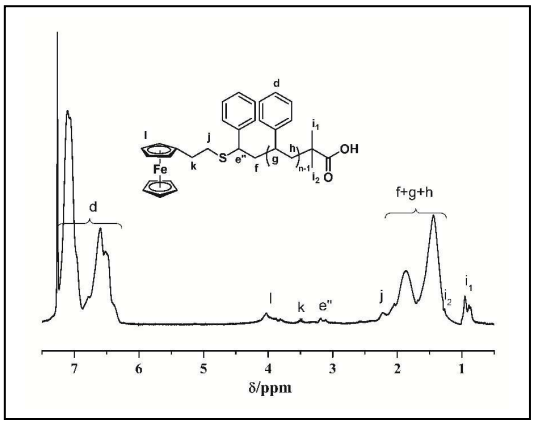
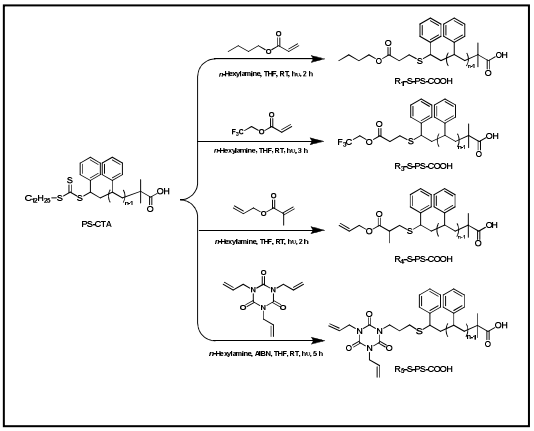


Figure 5. ^{1}H NMR spectrum of R_2-S-PS-COOH synthesized *via* tandem strategy combining aminolysis of PS-CTA and thiol-ene "click" reaction.

Synthesis of α,ω-telechelic PS *via* one-pot strategy combining aminolysis of RAFT-Polystyrene and thiol-ene "click" reaction simultaneously

As described above, the synthesis of thiol-terminated polymer (HS-PS-COOH) without any disulfide byproduct was the key to such tandem strategy targeting α,ω-telechelic PS. Thus, after the aminolysis of PS-CTA, an additional treatment of such reaction mixture by Zn/HAc had to be performed in order to avoid the formation of disulfide. Finally, the α,ω-telechelic PS was obtained by thiol-ene "click" reaction of HS-PS-COOH with ene-bearing compound. Alternatively, a facile one-pot strategy combining aminolysis with thiol-ene "click" reaction simultaneously[7,11,35,36,51] showed its high efficiency and versatility in the synthesis of diverse α,ω-telechelic polymers avoiding the formation of disulfide-containing polymer byproduct and the isolation of intermediate polymers. Herein, we used such strategy to prepare four new α,ω-telechelic polystyrenes with di- and tri-functionality bearing carboxyl, alkyl ester, fluorinated alkyl ester and single/bi-allyl ester under incandescent-lamp irradiation without photoinitiator as shown in Scheme 3.



Scheme 3. Synthesis of diverse α,ω-telechelic polystyrene via one-pot simultaneous aminolysis and thiol-ene "click" reaction of PS-CTA and ene-bearing compound.

Firstly, for the comparison between one-pot and tandem strategies, *n*-BuA was employed as ene-bearing compound in the simultaneous aminolysis and thiol-ene "click" reaction irridiated by an incandescent-lamp without any photoinitiator at RT for 2 h. The analysis of the resulted polymer by ^{1}H NMR (the same spectrum as that shown in Fig. 4) and UV-vis spectra (no absorbance of C=S band at ~315 nm) indicated the successful synthesis of R_1-S-PS-COOH *via* such one-pot strategy with high efficiency. Subsequently, VCp_2Fe was used to prepare R_2-S-PS-COOH under a similar reaction condition but didn't work. The further research on this reaction system is underway.

One α-fluorinated alkyl ester,ω-carboxyl-telechelic PS (R_3-S-PS-COOH) can be prepared in one-pot procedure using TFEA as ene-bearing compound under photoinitiation only in the presence of DMPA. The detail research was underway. The chain structure of the purified R_3-S-PS-COOH was confirmed by UV-vis, ^{1}H NMR and ^{19}F NMR spectra. The disappearance of C=S band at ~315 nm in UV-vis spectrum indicated the removal of thiocarbonylthio moiety. As shown in Fig. 6, both of the singlets at 5.03-4.60 and 3.25 ppm assigned to the methine proton (e) (-SC(=S)S-C*H*(Ph)-) and methylene protons (c) next to thiocarbonylthio of PS-CTA (Fig. 2(a)) were disappeared, while new singlets at 4.40 and 3.30 ppm assigned to methylene protons (l) next to CF_3 moitey and methine proton (e") (-CH_2-S-C*H*(Ph)-) present. The incorporation of CF_3 moiety was also confirmed by three singlets at -73.67, -73.70 and -73.72 ppm in ^{19}F NMR

spectrum. GPC and MALDI-TOF measurements showed similar molecular weight of R_3-S-PS-COOH ($M_{n(GPC)}$= 3432 g·mol^{-1} *vs* $M_{n(MALDI-TOF)}$= 3407 g·mol^{-1}) with narrow molecular weight distribution (M_w/M_n=1.10).

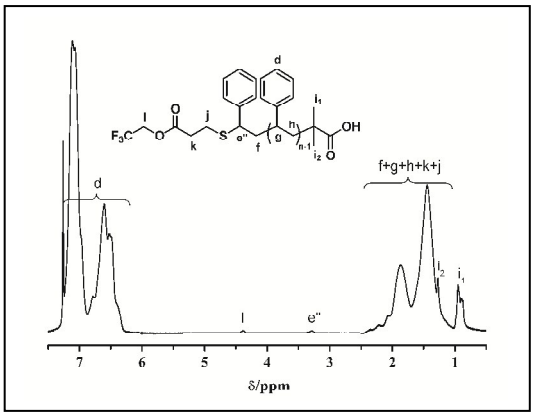


Figure 6. ^{1}H NMR spectrum of R_3-S-PS-COOH synthesized *via* one-pot strategy Combining aminolysis of PS-CTA and thiol-ene "click" reaction simultaneously.

An α-allyl,ω-carboxyl-telechelic PS (R_4-S-PS-COOH) was prepared efficiently *via* one-pot strategy using AMA as ene-bearing compound under photoinitiation without DMPA. Its chain structure was confirmed by the analysis of UV-vis and ^{1}H NMR spectra (Fig.7). The GPC data ($M_{n(GPC)}$=3674 g·mol^{-1}, M_w/M_n=1.03) of R_4-S-PS-COOH is close to that determined by MALDI-TOF($M_{n(MALDI-TOF)}$= 3352 g·mol^{-1}, M_w/M_n=1.02). Both the allyl and carboxyl moieties can be further employed to constructing new polymer architecture with various components and functions.

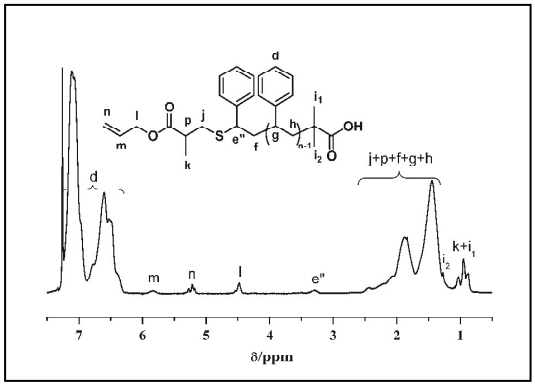


Figure 7. ^{1}H NMR spectrum of R_4-S-PS-COOH synthesized *via* one-pot strategy combining aminolysis of PS-CTA and thiol-ene "click" reaction simultaneously.

Moreover, α,ω-telechelic PS with tri-functionality (R_5-S-PS-COOH) was also synthesized using TAIC containing tri-allyl moieties to test the versatility of one-pot strategy. However, such reaction didn't go well without or with DMPA in an increasing reaction time of 5 h. After several trials, it was found that AIBN can accelerate the one-pot simultaneous aminolysis and thiol-ene "click" reaction between PS-CTA and TAIC forming R_5-S-PS-COOH. The molecular weight ($M_{n(GPC)}$= 3308 g·mol^{-1}, M_w/M_n=1.13) of R_5-S-PS-COOH measured by GPC is almost the same as that determined by MALDI-TOF ($M_{n(MALDI-TOF)}$= 3314 g·mol^{-1}, M_w/M_n=1.02). The characteristic C=S band of PS-CTA at ~315 nm disappeared completely. In the ^{1}H NMR spectrum (Fig. 8) of the purified polymer, the appearance of new singlets of e" (δ =3.36 ppm), j (δ =3.10 ppm), l (δ =3.70 ppm), m (δ =5.85 ppm), p (δ =5.25 ppm) and n (δ =4.45 ppm) indicating the formation of R_5-S-PS-COOH. The further study on the role of AIBN in such one-pot procedure and the application of R_5-S-PS-COOH with di-allyl moieties is under investigation.

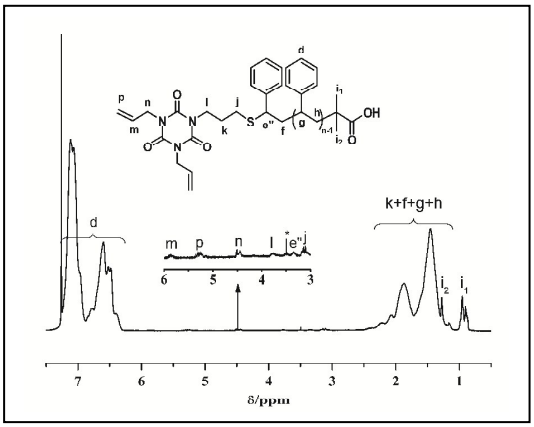


Figure 8. ^{1}H NMR spectrum of R_5-S-PS-COOH synthesized *via* one-pot strategy combining aminolysis of PS-CTA and thiol-ene "click" reaction simultaneously.

Conclusions

Diverse well-defined α,ω-functional telechelic polystyrenes with di- and tri-functionality were synthesized *via* tandem or one-pot strategies combining aminolysis of RAFT-polystyrene and thiol-ene "click" reaction under incandescent-lamp irradiation with even without photoinitiator. On the one hand, disulfide byproduct produced by the oxidative coupling of thiol moiety during the aminolysis of RAFT-polystyrene can be avoided efficiently by using such one-pot strategy. On the other hand, a variety of terminal functionalized polystyrenes bearing different moieties such as carboxyl, (fluorinated) alkyl ester, ferrocene and single/di-allyl ester were prepared for the first time and possibly find their applications in constructing polymers or their composites with new architecture and functionality.

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