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Synthesis of Diverse $\alpha,\omega$-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 $\alpha,\omega$-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 dithioester/thiocarbonylthio end group of PS-CTA and subsequently reacted with $n$-butyl acrylate and vinyl ferrocene, respectively, through thiol-ene “click” chemistry, to achieve $\alpha,\omega$-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 $\alpha,\omega$-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 $\alpha,\omega$-telechelic polystyrenes.

Introduction

In the last 16 years, the reversible addition-fragmentation chain transfer (RAFT) polymerization was increasingly used to synthesize a wide range of well-defined polymers such as monofunctional polymers, $\alpha,\omega$-telechelic functional polymers and block copolymers. Polymers containing dithioester/thiocarbonylthio end groups synthesized by RAFT polymerization can be converted to thiol-terminated polymers by aminolysis with primary or secondary amine. Such thiol-terminated polymers can be further employed in the synthesis of functional materials such as polymers with a variety of terminal groups, surface modified transition metal nanoparticles or films, functional hairy hollow microspheres, temperature-responsive DNA-carrying polymer micelles, functionalized carbon nanotube and well-defined polymers with diverse topological architectures.

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. 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 lead to bimodal polymer populations composed 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 after aminolysis and the addition of antioxidant sodium bisulfite in the system of aminolysis was employed and found to be the efficient methodologies. In addition, the combination of amine and phosphine compounds 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. Alternatively, a facile one-pot simultaneous aminolysis and thiol-ene “click” reaction using RAFT polymers and various thiol-reactive ene-bearing compounds as reactants showed high efficiency in synthesizing diverse $\alpha,\omega$-telechelic polymers without the formation of...
disulfide and the isolation of intermediate polymers.

Very recently, a variety of α-mono and α,ω-telechelic functional polystyrenes were synthesized via atom transfer radical polymerization based methodology and employed for fabricating highly ordered honeycomb films.

In this work, new α,ω-telechelic polystyrenes with di- and trifunctionality 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-(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate (DDMAT) as chain transfer agent (CTA) and then transformed to α-thiol-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 isocyanides-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 trifunctionality 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, n-Hexylamine (n-HA, Aladdin, 99%), acetic acid, tri-n-butylphosphine (BuPH, Adamas, 98%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aladdin), NaBH₃CN (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. Vinyllferrocene (VCp₂Fe) (>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. Tetrhydrofuran (THF) was refluxed over sodium/benzophenone and distilled under N₂ 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 N₂-filled dry box or using Schlenk techniques.

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

The synthetic procedure of α-thiol,ω-carboxylic telechelic PS (HS-PS-COOH) was depicted in Scheme 1. Firstly, in a similar procedure reported previously, 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: Mₙ = 3200 g mol⁻¹, Mₛ/ₚ = 1.08. ᵃ¹H NMR (CDCl₃): δ(ppm) = 7.30-6.30 (m, H₁), 5.03-4.60 (b, H₂), 3.34-3.19 (m, H₃), 2.50-1.13 (m, H₁⁻¹⁶⁻¹⁷⁻¹₈). FT-IR (KBr), max 3024, 3008, 2929 (vs, C-H on phenyl); 2922 (s, -CH₂); 2849 (m, -CH₂); 1743 (vs, -C=O); 1601, 1583, 1493, 1452 (s, -C-C on phenyl); 1069 (s, C=S); 841 (s, -C-S), 756, 697 (as, -CH₁ on phenyl) cm⁻¹.

Subsequently, PS-CTA (1.01 g, 0.32 mmol) was dissolved in THF (7 mL) and diethylamine (2.2 mL, 2.32 mmol) as chain transfer agent (CTA) and then transformed to thiol-ene “click” reaction of HS-PS-COOH with n-butyl acrylate (TFEA) (J&K, 99%), 1,3,5-triallyl isocyanurate (TAIC, Aldrich, 98%) was used as received without further purification. Vinyllferrocene (VCp₂Fe) (>98%) was kindly provided by Prof. Jun Yang and Master candidate Mu-Shuang Qian in SIOC(CAS).

In a similar procedure reported by Uygur and coworkers, a solution of HS-PS-COOH (1 equiv.), n-BuA or VCP₃Fe (10 equiv.), photoinitiator (DMPA, 5 equiv.) in 10 mL of THF were refluxed over sodium/benzophenone and distilled under vacuum and stored under dry nitrogen. Tetrhydrofuran (THF) was refluxed over sodium/benzophenone and distilled under N₂ 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 N₂-filled dry box or using Schlenk techniques.

Synthesis of α,ω-telechelic PS via thiol-ene “click” reaction

In a similar procedure reported by Uygur and coworkers, a solution of HS-PS-COOH (1 equiv.), n-BuA or VCP₃Fe (10 equiv.), photoinitiator (DMPA, 5 equiv.) in 10 mL of THF were refluxed over sodium/benzophenone and distilled under vacuum and stored under dry nitrogen. Tetrhydrofuran (THF) was refluxed over sodium/benzophenone and distilled under N₂ 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 N₂-filled dry box or using Schlenk techniques.

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

The synthetic procedure of α-thiol,ω-carboxylic telechelic PS (HS-PS-COOH) was depicted in Scheme 1. Firstly, in a similar procedure reported previously, 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: Mₙ = 3200 g mol⁻¹, Mₛ/ₚ = 1.08. ᵃ¹H NMR (CDCl₃): δ(ppm) = 7.30-6.30 (m, H₁), 5.03-4.60 (b, H₂), 3.34-3.19 (m, H₃), 2.50-1.13 (m, H₁⁻¹⁶⁻¹⁷⁻¹₈). FT-IR (KBr), max 3024, 3008, 2929 (vs, C-H on phenyl); 2922 (s, -CH₂); 2849 (m, -CH₂); 1743 (vs, -C=O); 1601, 1583, 1493, 1452 (s, -C-C on phenyl); 1069 (s, C=S); 841 (s, -C-S), 756, 697 (as, -CH₁ 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 (BuPH) (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. Mₙ(GPC)= 3076 g mol⁻¹, Mₛ/ₚ = 1.08. ᵃ¹H NMR (CDCl₃): δ(ppm) = 7.30-6.30 (m, H₁), 3.60-3.40 (s, H₂), 2.50-1.32 (m, H₁⁻¹⁶⁻¹⁷⁻¹₈), 1.32-1.10 (s, H₃), 1.02-0.81 (m, H₂)
Polystyrene standards. FTIR spectra were recorded on a Nicolet AVATAR3360 FTIR spectrophotometer with a resolution of 4 cm⁻¹. UV-vis spectra were recorded on a Shimadzu UV3600 spectrophotometer with a resolution of 4 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) trifluoracetate 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,α-carboxyl telechelic PS (HS-PS-COOH)**

The synthetic procedure of α-thiol,α-carboxyl telechelic PS (HS-PS-COOH) was illustrated in Scheme 1. Firstly, a well-defined thiocarbonylthio terminated poly styrene (PS-CTA) was obtained by bulk RAFT polymerization of styrene using DDMAT as chain transfer agent. Subsequently, PS-CTA was aminolysed using n-hexylamine and then treated by Zn/HAc or tri-n-butylphosphine (Bu3P).

![Scheme 1. Synthesis of α-thiol, α-carboxyl telechelic PS (HS-PS-COOH) in bulk RAFT polymerization](image)

PS-CTA with molecular weight of Mₚ=3200 g·mol⁻¹ (the molecular weight at peak Mₚ=3509 g·mol⁻¹) was obtained and showed a single narrow peak (Mₚ/Mₙ=1.08) in its GPC curve (Fig. 1(a)). ¹H NMR spectrum of PS-CTA (Fig. 2(b)) confirmed its chain structure as reported previously. 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. 6-10 Herein, PS-CTA was transformed into α-thiol,α-carboxyl 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 M₉=6357 g·mol⁻¹ was approximately twice as the smaller M₉=3435 g·mol⁻¹ which was a little lower than Mₚ=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-PS-COOH) by the oxidative coupling of HS-PS-COOH.
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 \( M_p = 3396 \text{ g} \cdot \text{mol}^{-1} \) was a little lower than \( M_p = 3509 \text{ g} \cdot \text{mol}^{-1} \) of PS-CTA (Fig. 1(a)) because of the removal of thiocarbonylthio moiety from PS-CTA. As shown in \(^1\text{H} \) 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 aminolysis 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-CH(Ph)-) of PS-CTA (Fig. 2(a)) shifted to 3.65-3.40 ppm, indicating the presence of methine proton (e') (HS-CH(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, \( \text{Na}_2\text{S}_2\text{O}_4 \) and \( \text{Bu}_3\text{P} \) were employed as reducing agent to treat the reaction mixture of aminolysis, respectively. Neither of them showed advantage over Zn/HAc in our case.

**Synthesis of \( \alpha,\omega \)-telechelic PS via thiol-ene “click” reaction**

The thiol-ene “click” reactions between HS-PS-COOH and enes (\( \text{n-butyl acrylate (} \text{n-BuA)} \) and vinylferrocene (\( \text{VCp}_2\text{Fe)} \), 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 \( \text{R}_1\text{-S-PS-COOH} \) showed similar molecular weights (\( M_n(\text{GPC}) = 3347 \text{ g} \cdot \text{mol}^{-1} \) vs \( M_n(\text{MALDI-TOF}) = 3335 \text{ g} \cdot \text{mol}^{-1} \)) 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 \(^1\text{H} \) 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 (\( \delta = 4.13-3.90 \text{ ppm} \)), k (\( \delta = 2.50-2.32 \text{ ppm} \)) and j (\( \delta = 2.31-2.16 \text{ ppm} \)) were observed and assigned to protons of -CH=O-CO-, -CO-CH= and -CH=CH-S, respectively. According to the analysis described above, the connection of thiol moiety with \( \text{n-BuA} \) via thiol-ene “click” reaction was confirmed and the targeting polymer \( \text{R}_1\text{-S-PS-COOH} \) was achieved.

**Scheme 2.** Synthesis of \( \alpha,\omega \)-telechelic polystyrenes via thiol-ene “click” reaction of between HS-PS-COOH and ene-bearing compound.
Unexpectedly, in the same reaction condition, HS-PS-COOH didn’t react with VCP$_2$Fe. It was worth noting that the addition of NaBH$_4$CN, 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$_2$Fe. 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 ($\delta = 4.50-3.60$ ppm), k ($\delta = 3.59-3.40$ ppm) and j ($\delta = 2.34-2.16$ ppm), were present and assigned to protons of dicyclopentadienyl ring, Cp-$\text{H}_2$- and -CH$_2$-$\text{S}$-, respectively. In addition, the characteristic infrared absorbances of C=O of dicyclopentadienyl ring at 1261.0, 1105.1, and 807.0 cm$^{-1}$ were appear. The molecular weight of R$_2$-S-PS-COOH determined by GPC is 3602 g mol$^{-1}$ ($M_n/M_w=1.02$) and close to 3480 g mol$^{-1}$ ($M_n/M_w=1.02$) determined by MALDI-TOF.

All the analysis described above indicated the formation of disulfide-containing polymer byproduct and the isolation of intermediate polymers. Herein, we used such strategy to prepare four new $\alpha_\omega$-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.

Firstly, for the comparison between one-pot and tandem strategies, $\eta$-BuA was employed as ene-bearing compound in the simultaneous aminolysis and thiol-ene “click” reaction irradiated 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$_2$-S-PS-COOH via one-pot strategy with high efficiency. Subsequently, VCP$_2$Fe 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 $\alpha$-fluorinated alkyl ester, $\alpha$-carboxyl-telechelic PS (R$_2$-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$_2$-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 thiocarboxylthio 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-CH(Ph)-) and methylene protons (c) next to thiocarboxylthio 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$_3$ moiety and methine proton (e") (-CH$_2$-S-CH(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.

Synthesis of $\alpha_\omega$-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 $\alpha_\omega$-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 $\alpha_\omega$-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 showed its high efficiency and versatility in the synthesis of diverse $\alpha_\omega$-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 $\alpha_\omega$-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.
spectrum. GPC and MALDI-TOF measurements showed similar molecular weight of R$_2$-S-PS-COOH ($M_n$(GPC) = 3432 g mol$^{-1}$ vs $M_n$(MALDI-TOF) = 3407 g mol$^{-1}$) with narrow molecular weight distribution ($M_n/M_w$=1.10).

Figure 6. $^1$H NMR spectrum of R$_2$-S-PS-COOH synthesized via one-pot strategy Combining aminolysis of PS-CTA and thiol-ene “click” reaction simultaneously.

An α,ω-carboxyl-telechelic PS (R$_2$-S-PS-COOH) was prepared efficiently via one-pot strategy using AMA as end-capping 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$^{-1}$, $M_n/M_w$=1.03) of R$_2$-S-PS-COOH is close to that determined by MALDI-TOF($M_n$(MALDI-TOF)= 3352 g mol$^{-1}$, $M_n/M_w$=1.02). Both the allyl and carboxyl moieties can be further employed to constructing new polymer architecture with various components and functions.

Moreover, α,ω-telechelic PS with tri-functionality (R$_3$-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$_3$-S-PS-COOH. The molecular weight ($M_n$(GPC)= 3308 g mol$^{-1}$, $M_n/M_w$=1.13) of R$_3$-S-PS-COOH measured by GPC is almost the same as that determined by MALDI-TOF ($M_n$(MALDI-TOF)= 3314 g mol$^{-1}$, $M_n/M_w$=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” ($\delta$=3.36 ppm), j ($\delta$=3.10 ppm), l ($\delta$=3.70 ppm), m ($\delta$=5.85 ppm), p ($\delta$=5.25 ppm) and n ($\delta$=4.45 ppm) indicating the formation of R$_2$-S-PS-COOH. The further study on the role of AIBN in such one-pot procedure and the application of R$_2$-S-PS-COOH with di-allyl moieties is under investigation.

Figure 7. $^1$H NMR spectrum of R$_2$-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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Notes and references
