

Electronic Supporting Information

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Initiator-Chain Transfer Agent Combo in the RAFT Polymerization of Styrene

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Experimental Part:

Chemicals. N-dodecyl mercaptan, aliquat 336, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) and 4-dimethylamioopyridine (DMAP) were purchased from Shanghai Chemical Reagents Co. Ltd. (Shanghai, China), and were used as received. 4, 4'-Azobis (4-cyano-1-pentanol) (ABCP) from Langfang Co. Ltd. (Hebei, China), was used as received. Other chemicals were purchased from Sigma-Aldrich. Solvents were carefully dried and distilled prior to use. Monomers (styrene (St), methyl methacrylate (MMA) (>99%) and methyl acrylate (MA)) were washed with 5 wt % aqueous sodium hydroxide solution, and were distilled over CaH₂ before use. N-Isopropyl acrylamide (NIPAM) was recrystallized from *n*-hexane three times.

Synthesis of diazene-1, 2-diyl bis (4-cyanopentane-4, 1-diyl) bis (2-(((dodecylthio)carbonothioyl) thio-2-methylpropanoate) (X6). The synthetic route was shown in Scheme 1. Firstly, X5 was synthesized according following procedure¹: N-dodecyl mercaptan (37.3 g, 0.184 mol), acetone (107 g, 1.84 mol), and aliquat 336 (2.99 g, 7.37 mol) were mixed at room temperature. For this mixture, an aqueous solution of sodium hydroxide (15.5 g, 0.193 mol, 50 wt %) was added by dropwise. The reaction mixture was stirred for 30 min at room temperature. Then carbon disulfide (14.0 g, 0.18 mol) in acetone (14.0 g, 0.18 mol) was added. The mixture was stirred for 10 min before chloroform (32.8 g, 0.28 mol) was added. Finally, the aqueous of 50% sodium hydroxide (73.7 g, 0.922 mol) was added dropwise with the temperature keeping below 25 °C. The reaction mixture was stirred overnight at room temperature. Water (300 mL) was added under vigorous stir. The aqueous layer was

acidified with concentrated HCl until pH \approx 2. The mixture was stirred for 30 min at room temperature before filtration. The collected solid product was dissolved in isopropanol (300mL). After removing the insoluble impurities by filtration, the solvent was distilled under reduced pressure to get the yellow solid. The product (s)-1-doceyl-(s)-(α,α' -dime thyl- α'' -acidic acid) trithiocarbonate (X5) was obtained after further purifying by recrystallization from acetone/water (16.5 g, yield: 48 %). ^1H NMR (CDCl_3): 3.28 (2H, t, $\text{CH}_2\text{-CH}_2\text{S(C=S)S}$), 1.73 (8H, m, $\text{CH}_2\text{-CH}_2\text{SC(S)SC(CH}_3)_2$), 1.26 (18H, m, $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{SC(S)S}$), 0.96 (3H, t, $(\text{CH}_2)_9\text{CH}_3$). Elementary analysis: calcd for $\text{C}_{17}\text{H}_{33}\text{O}_2\text{S}_3$ (%): C 55.85, H 9.10. Found (%): C 55.78, H 9.08.

To a solution of X5 (3 g, 8.2 mmol), ABCP (1.03 g, 4.1 mmol) and DMAP (0.092 g, 0.82 mmol) in CH_2Cl_2 (25 mL) were added EDC·HCl (1.44 g, 7.5 mmol) which was dissolved in 3 mL CH_2Cl_2 at 0 °C. The reaction mixture was stirred overnight at room temperature. After that, the solvent was removed under reduced pressure. The residue was purified by column chromatography (EtOAc : petroleum = 1 : 2) to get the final product X6 (2.1 g, yield:51 %) as yellow solid. ^1H NMR (CDCl_3): 4.16 (4H, t, $\text{C(O)OCH}_2\text{-CH}_2$), 3.29 (4H, t, $\text{CH}_2\text{-CH}_2\text{S(C=S)S}$), 2.15 (4H, m, $\text{CH}_2\text{-CH}_2\text{S(C=S)S}$), 1.76 (6H, s, $\text{CH}_3\text{-C(CN)}$), 1.71 (20H, m, $\text{SC(S)SC(CH}_3)_2$ and $\text{C(O)OCH}_2\text{-CH}_2\text{CH}_2$), 1.26(36H, m, $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{SC(S)S}$), 0.88 (6H, t, $(\text{CH}_2)_9\text{CH}_3$). Elementary analysis: calcd for $\text{C}_{46}\text{H}_{80}\text{N}_4\text{O}_4\text{S}_6$ (%): C 58.43, H 8.53, N 5.93. Found (%): C 58.78, H 8.45, N 5.89.

Typical procedures for polymerization in the presence of X6. The monomer (St, 0.5 mL, 4.34 mmol), X6 (0.021 g, 21.7 μmol) were added to a 2.0 mL ampule. The

solution was deoxygenated by freeze-pump-thaw three times. The ampule was then flame-sealed under argon atmosphere and placed in a stirred oil bath held by a thermostat at 60 °C to polymerize for 24 h. Then the ampule was cooled by immersion in ice water. Afterward, the ampule was opened, and the contents were dissolved in 2.0 mL THF and precipitated into 200 mL of cool methanol with stirring. The polymer was obtained by filtration and dried under vacuum until a constant weight at room temperature. The monomer conversion was determined by gravimetric method.

Aminolysis of polymer. To a THF solution of isopropyl amine (39.6 mg in 1 mL THF) was added the THF solution of PS (0.5 g in 1 mL THF). The mixture was stirred over night at room temperature. Polymer was collected by filtration after precipitation in methanol. The polymer was purified by redissolving in THF and precipitation in methanol for two times.

Hydrolysis of polymer. To a THF solution of PS (0.5 g in 1 mL THF) was added the aqueous sodium hydroxide (2 g in 2 mL water). The mixture was stirred over night at 70 °C. The polymer was collected by filtration after precipitation in methanol. It was purified by redissolving in THF and precipitation in methanol for two times.

Multiblock copolymer. To a solution of St (0.5 mL, 4.35 mmol) and 1 mL dry toluene in 10 mL reaction tube was added with X6 (0.21g, 0.22 mmol). The solution was deoxygenated by freeze-pump-thaw three times. The tube was then sealed under argon atmosphere and placed in a stirred oil bath held by a thermostat at 60 °C to polymerize for 24 h. A little portion of reaction mixture (~0.05 mL) was collected through syringe for GPC characterization. The degassed solution of MA (0.59 mL,

6.51 mmol) in 1.6 mL dry toluene was added into the tube through syringe. After polymerized for 6 h, sample was collected for analysis. Second portion of St was added, and allowed for another 24 h polymerization. After sample collection, second portion of MA was add, and allowed for another 6 h polymerization. After that, the final polymer was collected by filtration after precipitation in methanol.

Characterization. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were determined by using a Waters 1515 gel permeation chromatograph(GPC) equipped with a refractive-index detector(Waters 2414), using HR 1 (pore size: 100Å, 100-5000 Da), HR 2(pore size: 500Å, 500-20 000 Da) and HR 4 (pore size 10 000Å, 50-100 000 Da) columns (7.8×300 mm, 5 μm beads size) with molecular weights ranging from $10^2 \sim 5 \times 10^5$ g/mol. Tetrahydrofuran (THF)was used as the eluent at a flow rate of 1.0 mL/min and 30 °C. GPC samples were injected using a Waters 717 plus autosampler. The molecular weight was calculated under the calibration of PS standard. The ^1H NMR spectrum of the polymer was recorded on an NOVA 400 MHz nuclear magnetic resonance instrument using CDCl_3 as the solvent and tetramethylsilane (TMS) as an internal standard. Elemental analysis of C, H and N were conducted with an EA1110 CHNO-S instrument. Total sulfur and nitrogen content in polymer was analysis by Elab9100SN (Suzhou Elab Analytical Instrument Co. Ltd., China). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Daltonics, Inc.,

Billerica, MA) equipped with a Nd : YAG laser (355 nm). All spectra were measured in positive reflection mode.

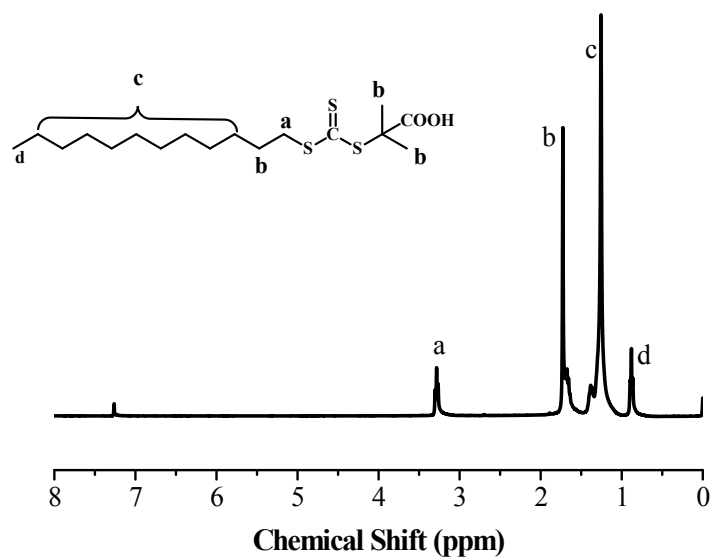


Figure S1. ¹H NMR of X5 in CDCl₃.

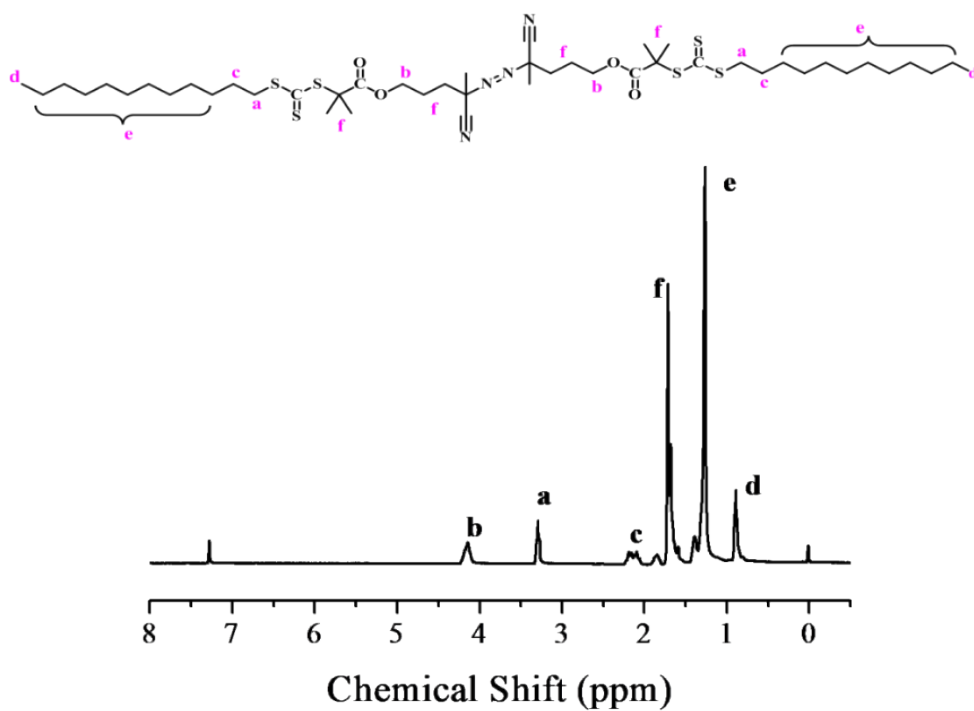


Figure S2. ¹H NMR of X6 in CDCl₃.

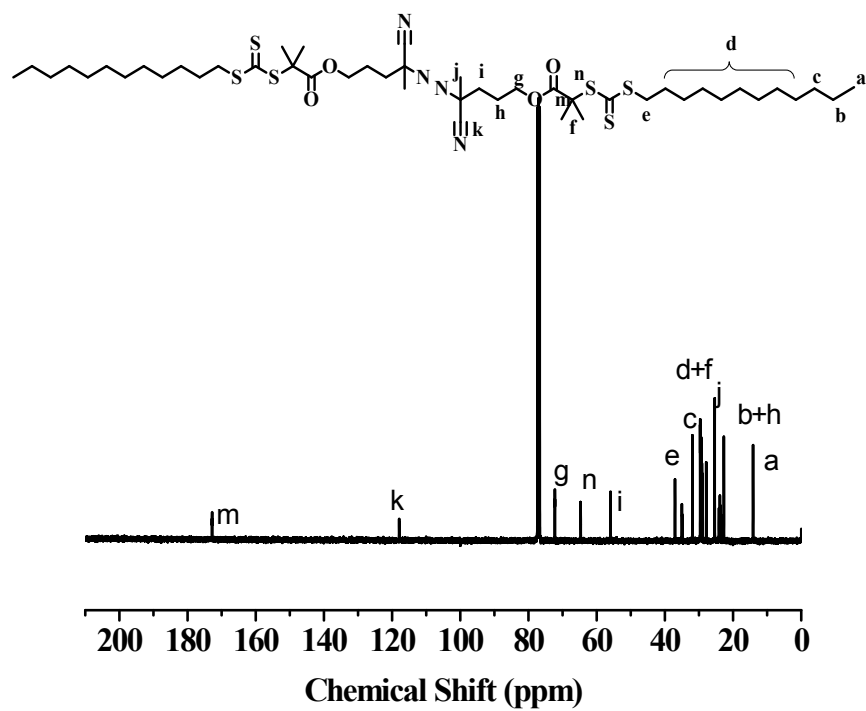


Figure S3. ¹³C NMR of X6 in CDCl₃.

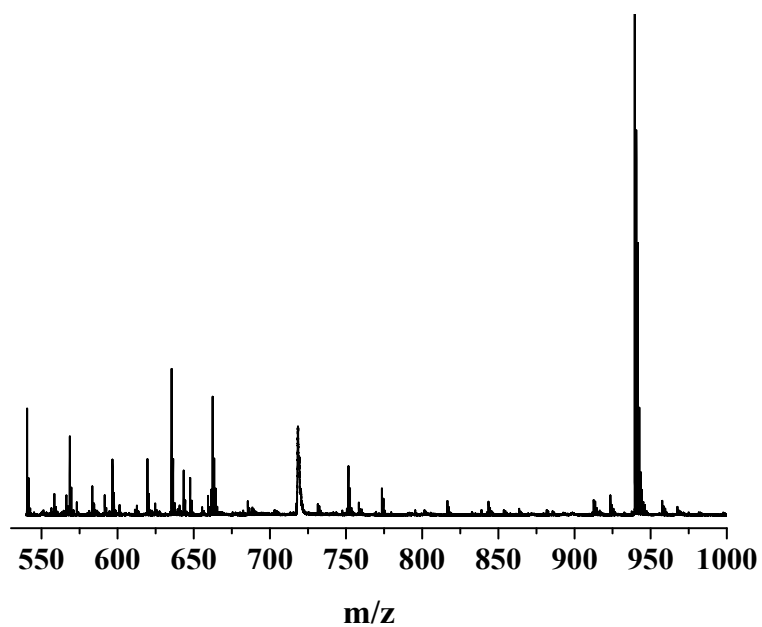
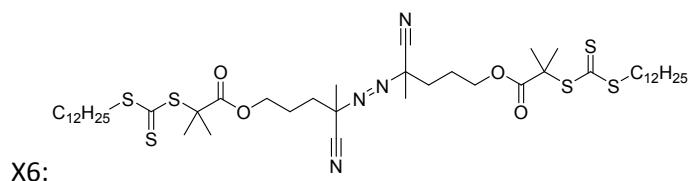


Figure S4. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry of X6 ($M_n=945.496$).

Thermogravimetric analysis of X6 : 10.14 mg X6 was tested for TGA analysis at 60 °C holding for 2 h. For X6, the half-life is the time when the azo moiety decomposed halfly. (The Thermo Gravimetric Analyzer is from Perkin Elmer Inc., USA)



$$M_{\text{azo}} / M_{\text{X6}} = 28 / 945.53 = 0.0296, 0.5(M_{\text{azo}} / M_{\text{X6}}) = 0.0148,$$

$$1 - 0.5(M_{\text{azo}} / M_{\text{X6}}) = 0.98519 \longrightarrow \text{time : 299.3 min} \sim 4.99 \text{ h}$$

So, $t_{1/2} = 4.99 \text{ h (60 } ^\circ\text{C)}$

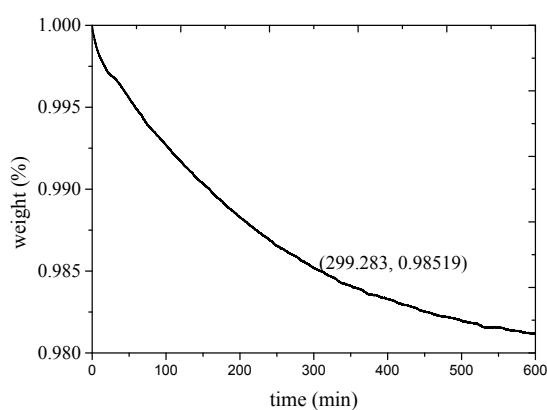


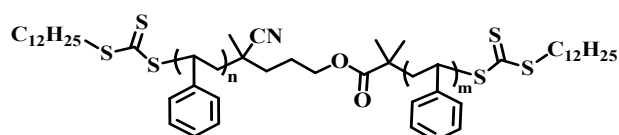
Figure S5. The curves of TGA of X6 at 60 °C

Table S1. Effect of the amount of X6 on bulk polymerization of St at 60 °C

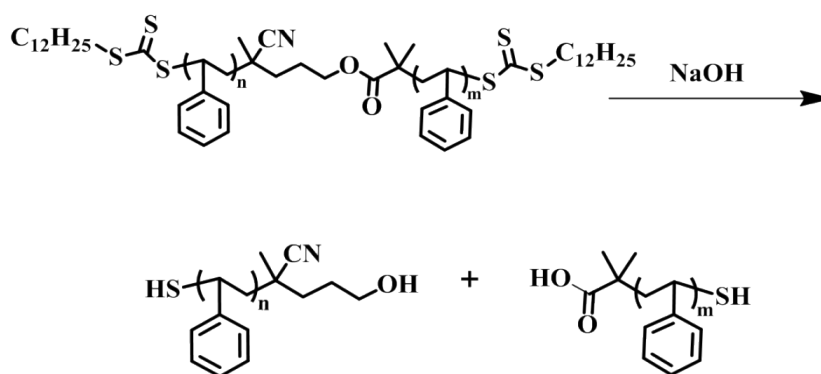
Entry	[St] ₀ : [X6] ₀	Time (h)	Conv. (%)	$M_{n,th}^a$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n

1	100:1	7	39.6	4100	4200	1.07
2	100:1	24	81.1	8400	8300	1.10
3	200:1	24	64.1	13400	12700	1.11
4	400:1	24	50.0	20800	19900	1.14
5	500:1	24	45.3	23500	22500	1.15
6	1000:1	24	32.4	33700	33100	1.17
7	2000:1	24	28.0	58300	56700	1.21

^a $M_{n,th} = ([St]_0/[X6]_0) \times M_{St} \times \text{conversion } \%$, $[St]_0 = 0.5 \text{ mL (4.35 mmol)}$.



Scheme S1. The probably structure of polymer.



Scheme S2. The reaction route for PS obtained in the presence of X6 by hydrolysis.

MALDI-TOF of PS

The typical MALDI-TOF spectrum in Figure S4 indicated that the obtained PS showed one series of mass peak with the interval of 104.06, which was equal to the

mass of repeat unit in PS, e.g. 104.06. No any side mass peak was found in the MALDI-TOF spectrum indicated that the obtained PS has same structure. By assuming the structure of obtained PS as showed in Scheme S2, the mass of each polymer can be calculated by following equation:

$$M_{\text{theo}} = 735.34 + (n+m) \times 104.06 + 106.90 - 556.22$$

Where, 735.34 was the mass of moiety derived from X6 (showed in the inset of Figure S5), $n+m$ and 104.06 was the repeat number and the mass of repeat unit in PS respectively, 106.90 was the mass of silver ion, and 556.22 was the mass of bi-trithiocarbonate moiety which was lost in MALDI condition (showed in the inset of Figure S5). The calculated molecular weight was 1430.676 with the DP of 11, which was close to the experimental value of 1431.067. The dithiocarbonyl group was unstable in the MALDI condition, and decomposed to the vinyl structure.²

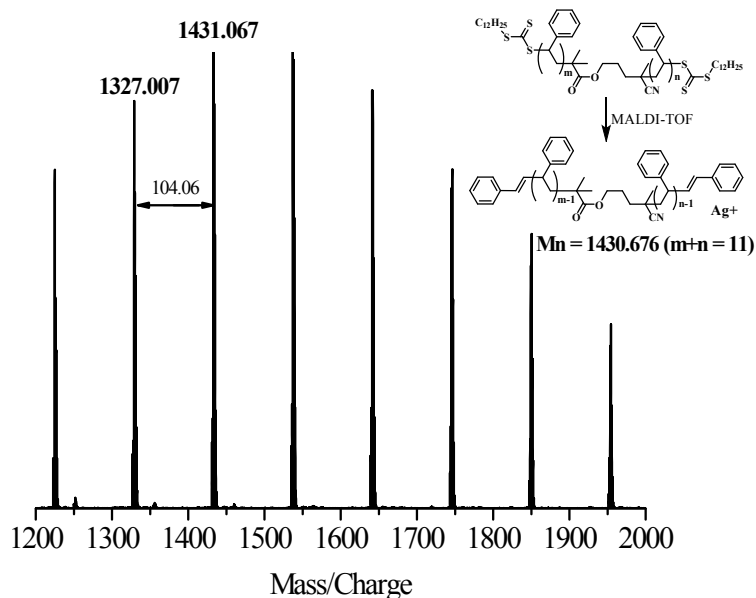
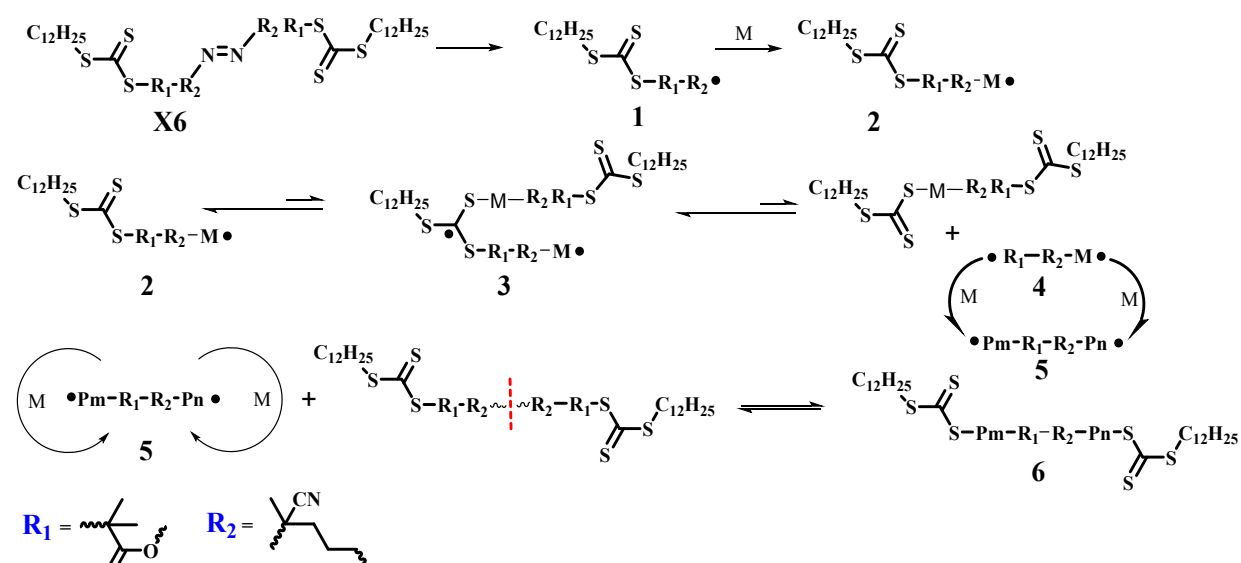


Figure S6. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry of polystyrene (PSt, $M_{n,\text{GPC}} = 3500$ g/mol, $M_w/M_n = 1.05$) obtained

from the X6 mediated RAFT, $M_{n, \text{GPC}}$ and M_w/M_n refer to the number average molecular weight and molecular weight distribution by GPC, respectively.

Polymerization mechanism. The polymerization mechanism was proposed from above results and showed in Scheme 4. The X6 decomposed under heat to produce radical species **1** for initiating. The initial radical species **1** reacted with monomer to generate initial radical **2**. Such radical **2** reacted with trithiocarbonate species by the addition reaction to produce the intermediate **3**. The intermediate **3** further fragmented to form the biradical species **4**. After that, species **4** polymerized with monomer to form the propagating species **5** followed with the reversible addition and fragmentation with trithiocarbonate species. The final polymer **6** with trithiocarbonates in both ends can be obtained. Due to the structure difference in R1 and R2, the fragmentation reaction of intermediate **3** preferred to form the biradical intermediate **4**,⁴ which possibly was the key step in the reaction for the formation of polymer with bi-trithiocarbonate functional groups.



Scheme S3. The proposed mechanism for polymerization in the presence of X6.

REFERENCES:

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