Supporting Information to

Fast conversion of terminal thiocarbonylthio group of RAFT polymer to "clickable" thiol group *via* the versatile sodium azide

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Experimental part:

Materials

Monomers, methyl methacrylate (MMA), styrene (St), vinyl acetate (VAc) and butylacrylate were obtained from Shanghai Chemical Reagents Co. (Shanghai, China) and were filtered through basic aluminum oxide to remove the inhibitor. Tetrahydrofuran (THF) and toluene which were purchased from Chinasun Specialty Products Co. (Jiangsu, China). were distilled from sodium/benzophenone under argon before use. The initiator 2, 2'-azobis(isobutyronitrile) (AIBN) (Shanghai, China, 99%) was recrystallized three times from ethanol before use. The chain transfer agents (CTAs) such as 2-cyanopropan-2-yl dithiobenzoate (CPDB),[1] 2-cyanoprop-2-yl dithionaphthalenoate (CPDN),[2] (S)-2-(ethyl propionate)-(O-ethyl xanthate)[3] were synthesized according to the literatures. Sodium azide (NaN_3) (≥ 99.5%; Sigma-Aldrich) were used as received. Dithiothreitol (DTT) (99%, Sinopharm Chemical Reagent, China). Potassium tert-butanolate(Energy Chemical Reagent, China) were used as received. N-Propylmaleimide were purchased from Alfa and used without further purification. 1,8-Diazabicyclo[5.4.0]undec-7-ene(DBU) were purchased from TCI and used as received. N, N-dimethylformamide (DMF, 99.9%), hexane and methol were purchased from Shanghai Chemical Reagents Co. and used directly.

Characterization

The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were determined by an Agilent PL-50 size exclusion chromatography (SEC) equipped with refractive-index detector using PL Mixed gel D (5 μm beads size) columns with molecular weights ranging from 200 ~ 4×10^5 g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min and 40 °C. SEC samples were injected using a PL-AS RT autosampler and calibrated with PMMA and PS standards. Proton nuclear magnetic resonance (^{1}H NMR) spectra of the precipitated polymers were recorded on a Varian Inova 400 MHz NMR instrumentspectra using $CDCl_3$ as the solvent. Ultraviolet visible (UV-vis) absorption spectra of the samples were recorded on a Hitachi U-3900 spectrophotometer at room temperature. MALDI-TOF mass spectra were recorded using a autoflex III (Bruker) mass spectrometer equipped with a Nd:YAG laser at 355 nm.

Typical procedures for synthesis of RAFT-made polymers

Monomer, CTA, AIBN and solvent (if needed) were added to a 25 mL Schlenk flask equipped with a magnetic stirrer in proportion. The reaction mixture was deoxygenated with three standard freeze-pump-thaw cycles. Then, the Schlenk flask was closed and placed into an oil bath maintained at 60 °C for predetermined time. The Schlenk flask was taken out from the oil bath and put into iced water. After it was cooled, the polymerization mixture was diluted with THF and precipitated into 500 mL of cold methanol with stirring. The polymer was isolated by filtration and dried in a vacuum oven overnight at 25°C.

Typical procedures to remove the thiocarbonylthio end groups of RAFT-made polymers

The RAFT polymers (0.2 g) was dissolved in 1.0 mL DMF in a 5 mL-ampoule with a magnetic stirrer. A prescribed amount of NaN_3 was added. The ampoule was placed in a stirred water bath equipped with a thermostat at 25 °C. After predetermined time, the resulting solution was passed through a column of little neutral alumina to remove NaN_3. The polymer was isolated by precipitating into cold methanol and dried in a vacuum oven overnight at 25°C.

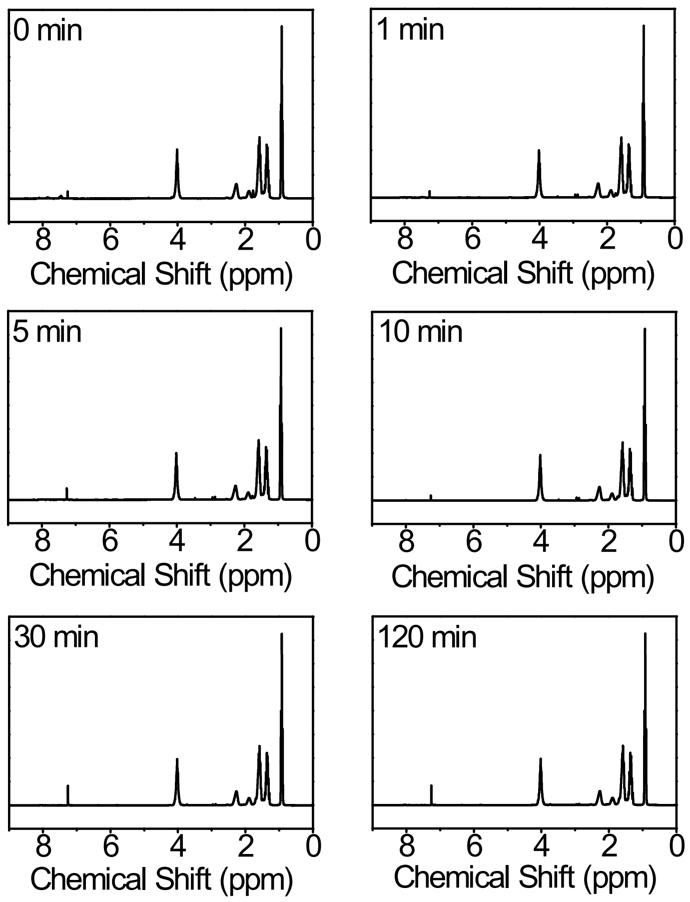
Typical procedures for the DTT reduction

The polymer with disulfide groups (0.2 g) was dissolved in 1.0 mL THF in a 5 mL-ampoule with a magnetic stirrer. A prescribed amount of DTT and little potassium t-butoxide was added. The reaction mixture was deoxygenated with three standard freeze-pump-thaw cycles. The ampoule was placed in a stirred water bath equipped with a thermostat at 25 °C. After predetermined time, the polymer was isolated by precipitating into cold methanol and dried in a vacuum oven overnight at 25°C.

Typical procedures for the polymer with thiol groups reacting with N-Propylmaleimide

The polymer after DTT reduction(0.2 g) was dissolved in 1.0 mL THF in a 5 mL-ampoule with a magnetic stirrer. A prescribed amount of N-Propylmaleimide and a drop 1,8-Diazabicyclo[5.4.0]undec-7-ene(DBU) was added. The reaction mixture was deoxygenated with three standard freeze-pump-thaw cycles. The ampoule was placed in a stirred water bath equipped with a thermostat at 25 °C. After predetermined time, the polymer was isolated by precipitating into cold methanol and dried in a vacuum oven overnight at 25°C.

(a)



(b)

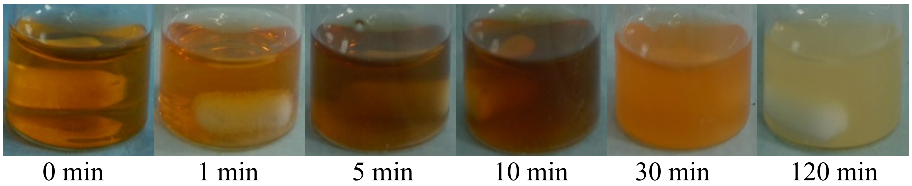
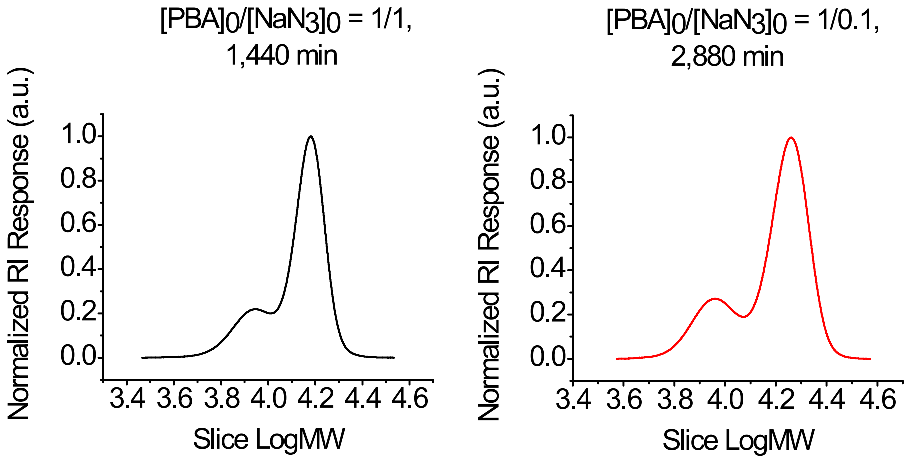


Fig. S1 ^{1}H NMR spectra of PBA (a) and Photographs of the reaction mixture (b) before and after the treatment by NaN_3. Original PBA: $[BA]_0/[CPDN]_0/[AIBN]_0 = 500/5/1$, time = 4.5 h, conversion = 45.9 %, 60 °C, BA = 10.0 mL, toluene = 4.0 mL; Treated conditions: $[PBA]_0/[NaN_3]_0 = 1/10$, PBA = 0.2000 g, DMF = 1.0 mL, 25 °C, 1 min, 5 min, 10 min, 30 min, 120 min.

(a)



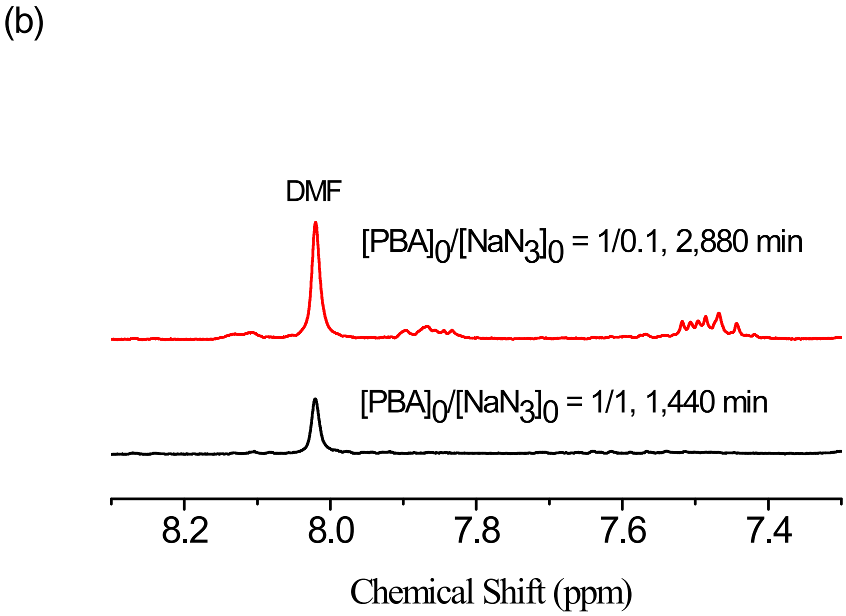


Fig. S2 SEC traces (a) and enlarged ^{1}H NMR signals of thiocarbonylthio groups (b) before and after the treatment of PBA by NaN_3. Original PBA: $[BA]_0/[CPDN]_0/[AIBN]_0$ = 500/5/1, time = 4.5 h, conversion = 45.9 %, 60 °C, BA= 10.0 mL, toluene = 4.0 mL; Treated conditions: $[PBA]_0/[NaN_3]_0$ = 1/1, PBA = 0.2000 g, DMF = 1.0 mL, 25 °C, 1,440 min and $[PBA]_0/[NaN_3]_0$ = 1/0.1, PBA = 0.2000 g, DMF = 1.0 mL, 25 °C, 2,880 min.

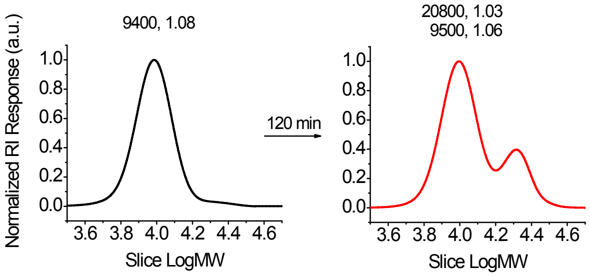


Fig. S3 SEC traces of PBA before and after the treatment by NaN_3 under nitrogen atmosphere. Original PBA: $[BA]_0/[CPDN]_0/[AIBN]_0$ = 500/5/1, time = 4.5 h, conversion = 56 %, 60 °C, BA = 10.0 mL, toluene = 4.0 mL; Treated conditions: $[PBA]_0/[NaN_3]_0$ = 1/10, PBA = 0.2000 g, DMF = 1.0 mL, 25 °C, 120 min, under nitrogen atmosphere.

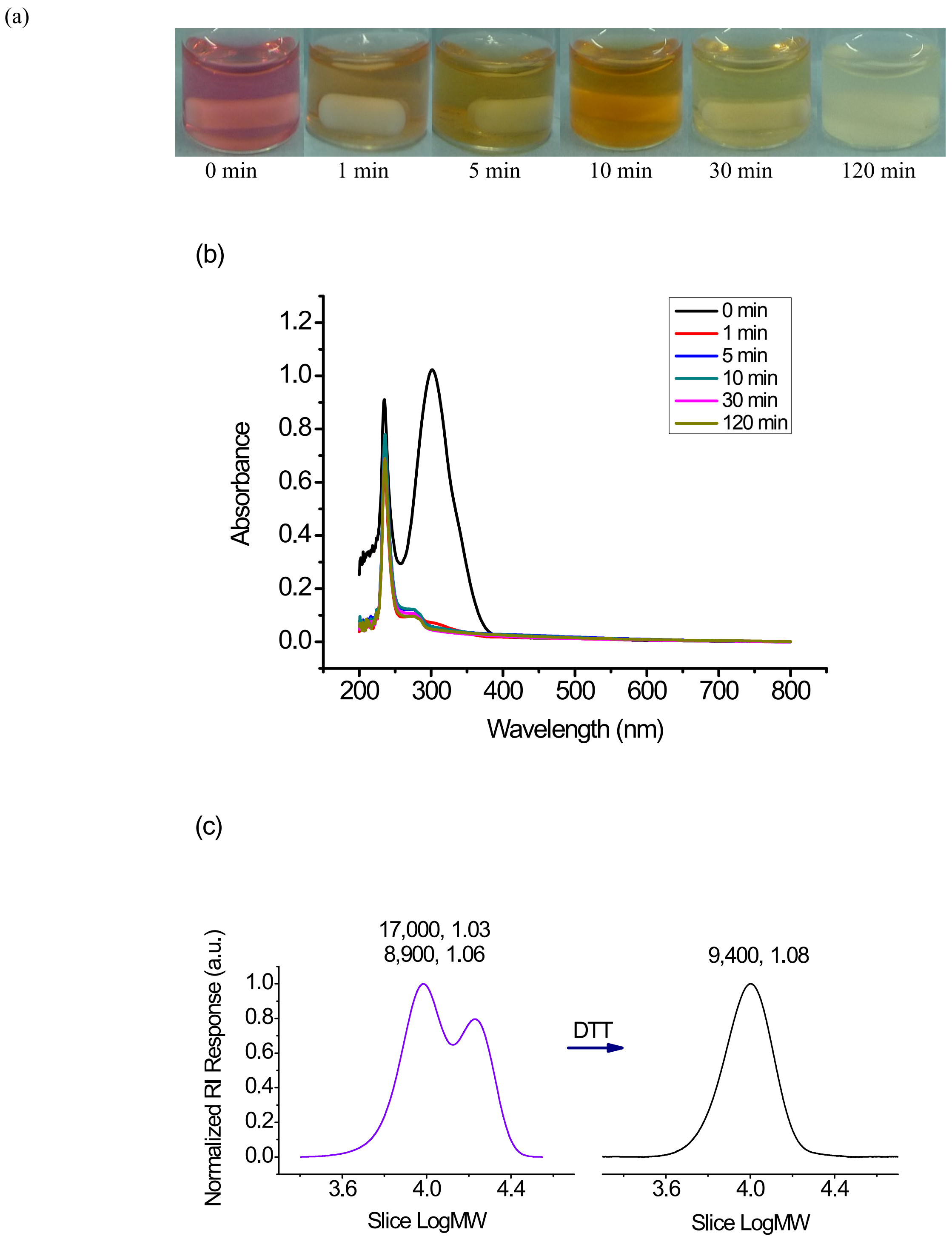


Fig. S4 The photographs of the reaction mixture (a) and the UV-vis absorption spectrum (b) before and after the treatment of PMMA by NaN_3. Original PMMA: $[MMA]_0/[CPDB]_0/[AIBN]_0 = 500/5/1$, time = 10 h, conversion = 51.2 %, 60 °C, MMA = 10.0 mL, toluene = 4.0 mL; Treated conditions: $[PS]_0$/[

$NaN_3]_0$ = 1/10, PS = 0.2000 g, DMF = 1.0 mL, 25 ^{o}C, 1 min, 5 min, 10 min, 30 min, 120 min. SEC traces (b) DTT reduction of the bimodal MWD PMMA ($[PMMA]_0/[NaN_3]_0$ = 1/10, 25 ^{o}C, 120 min).

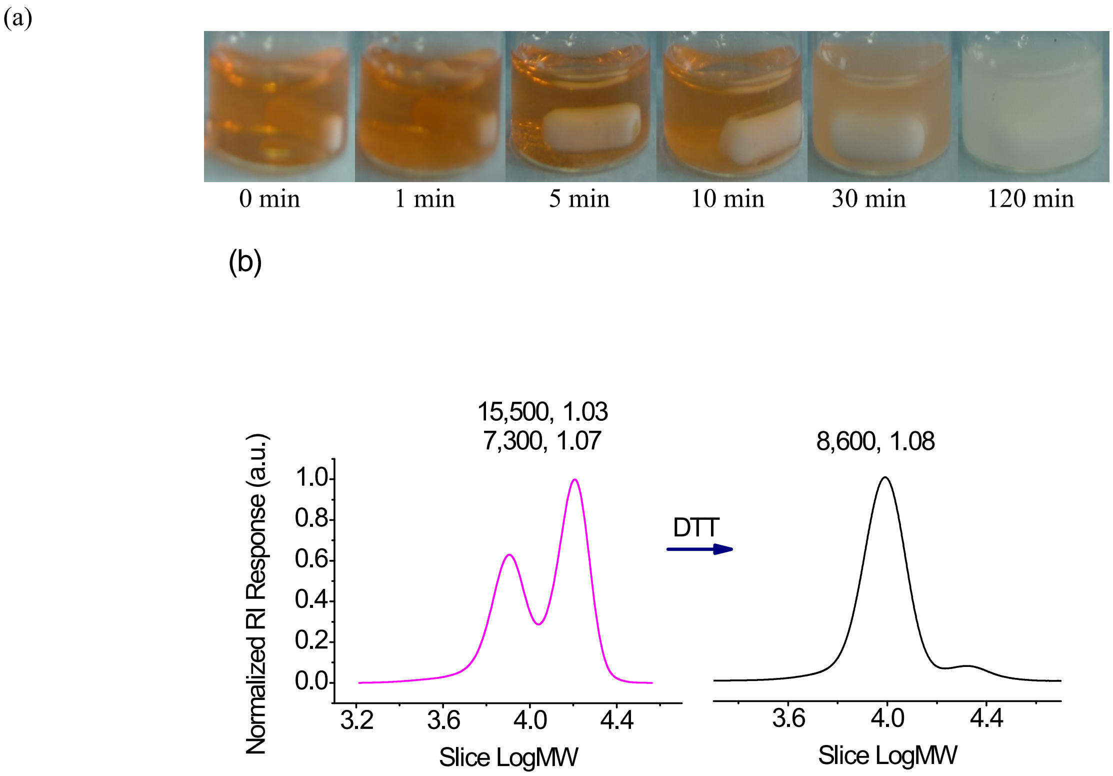
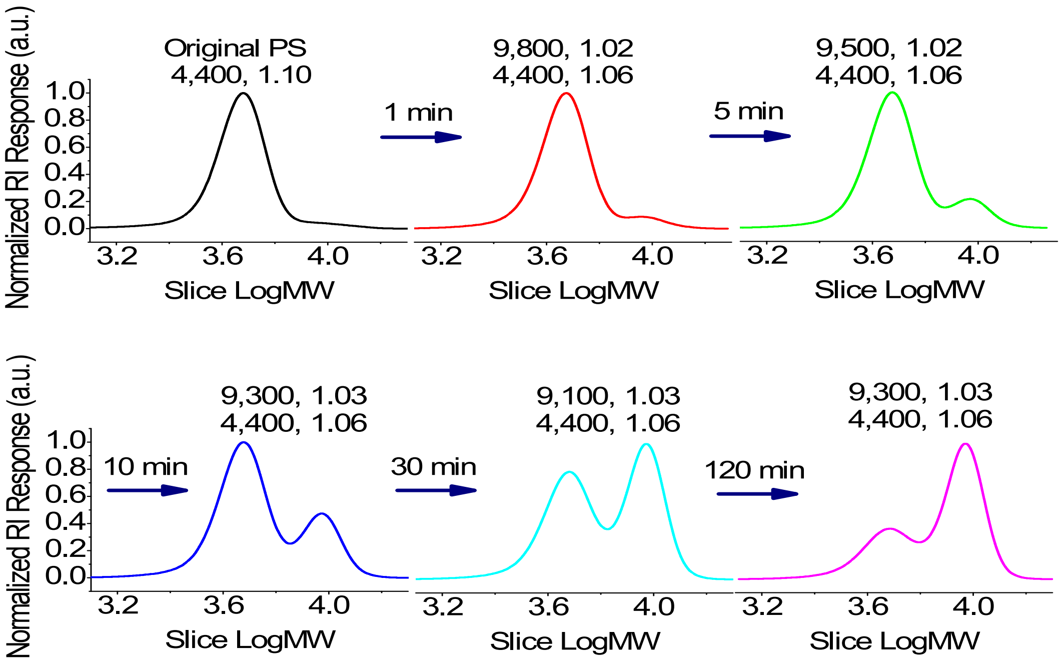
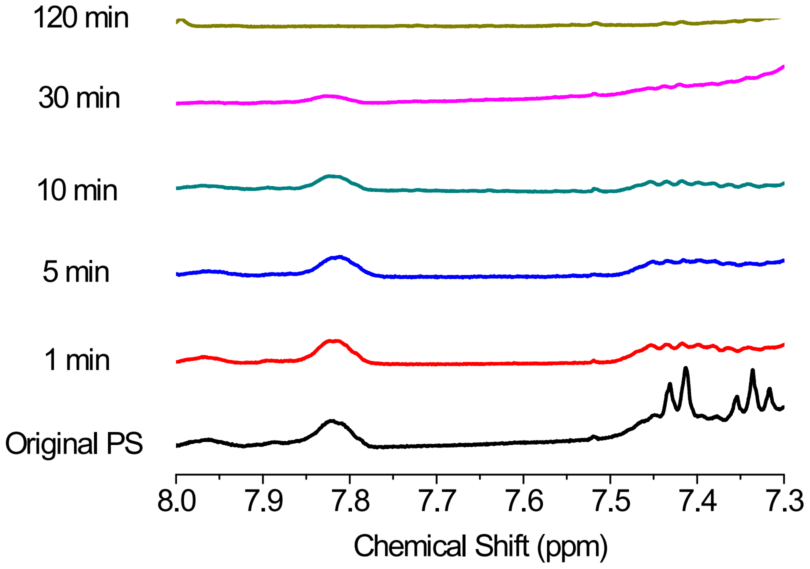


Fig. S5 The photographs of the reaction mixture (a) before and after the treatment of PS by NaN_3. Original PS: $[St]_0/[CPDN]_0/[AIBN]_0$ = 1000/5/1, time = 94 h, conversion = 29.8 %, 60 ^{o}C, St = 10.0 mL, toluene = 4.0 mL; Treated conditions: $[PS]_0/[NaN_3]_0$ = 1/10, PS = 0.2000 g, DMF = 1.0 mL, 25 ^{o}C, 1 min, 5 min, 10 min, 30 min, 120 min. SEC traces (b) DTT reduction of the bimodal MWD PS ($[PS]_0/[\ NaN_3]_0$ = 1/10, 25 ^{o}C, 120 min).

(a)


Normalized RI Response (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
Original PS
4,400, 1.10
1 min
9,800, 1.02
4,400, 1.06
5 min
9,500, 1.02
4,400, 1.06
3.2
3.6
4.0
Slice LogMW
10 min
9,300, 1.03
4,400, 1.06
30 min
9,100, 1.03
4,400, 1.06
120 min
9,300, 1.03
4,400, 1.06

(b)


120 min
30 min
10 min
5 min
1 min
Original PS
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
Chemical Shift (ppm)

(c)

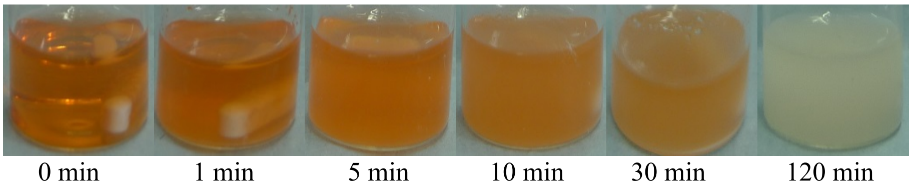
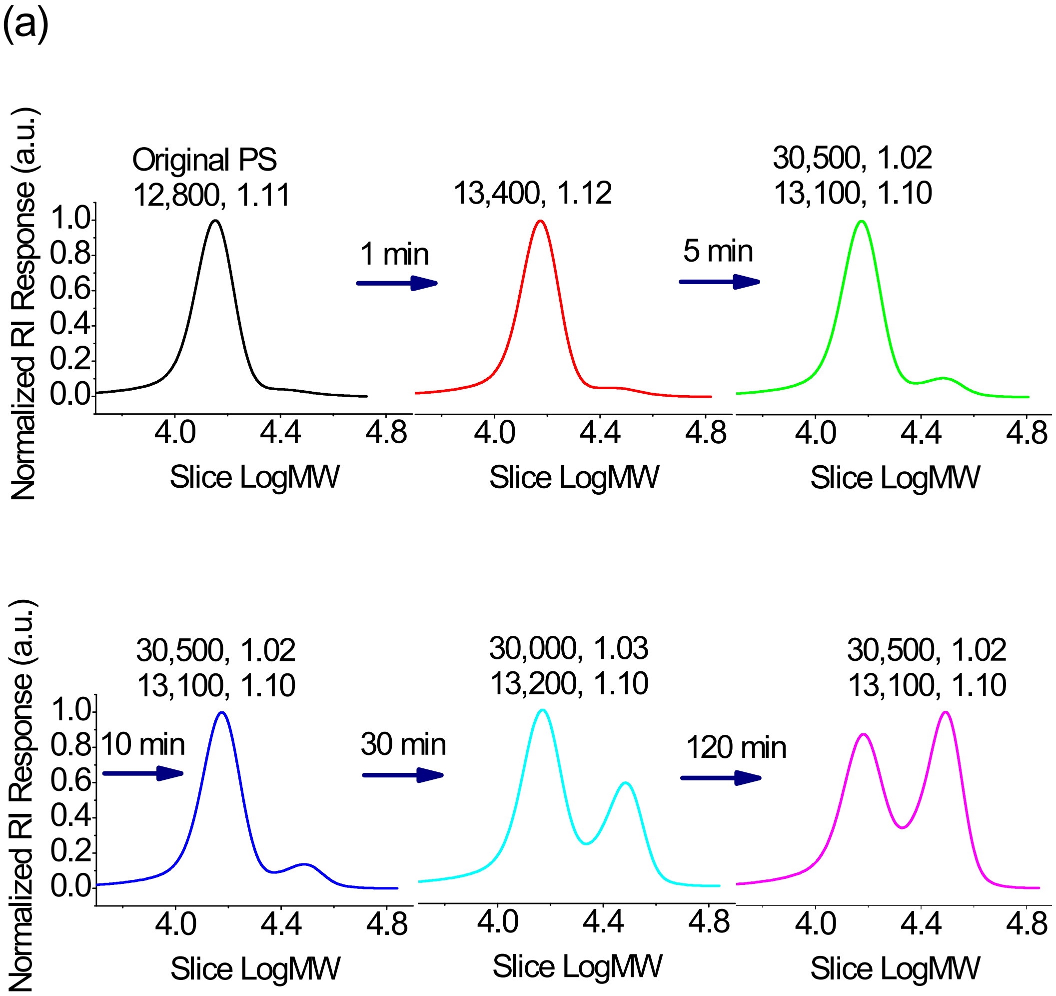
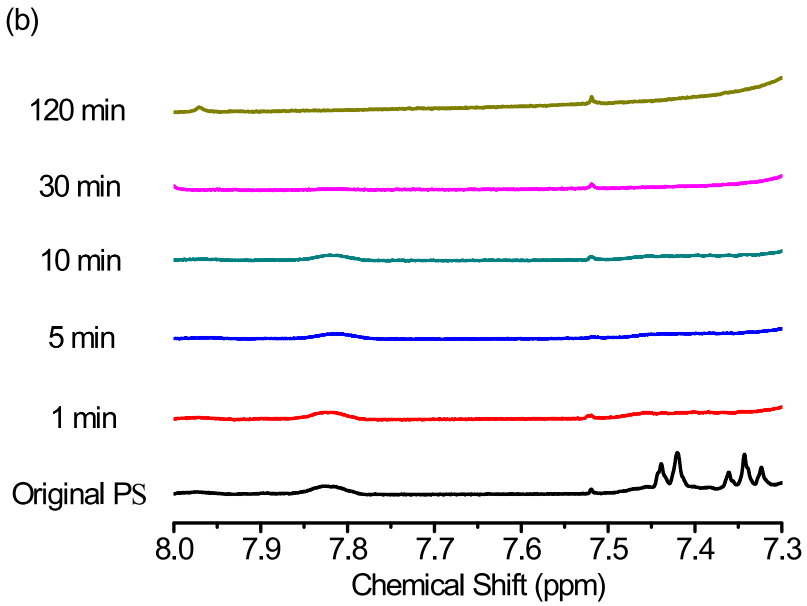
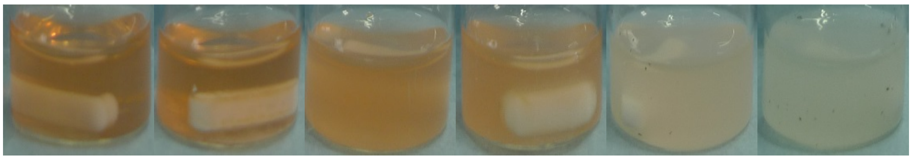

0 min
1 min
5 min
10 min
30 min
120 min

Fig. S6 SEC traces (a), enlarged ^{1}H NMR signals of thiocarbonylthio groups (b) and the photographs of the reaction mixture (c) before and after the treatment of PS by NaN_3. Original PS: $[St]_0/[CPDN]_0/[AIBN]_0$ = 300/5/1, time = 75 h, conversion = 52.8 %, 60 °C, St = 10.0 mL, toluene = 4.0 mL; Treated conditions: $[PS]_0/[NaN_3]_0$ = 1/10, PS = 0.2000 g, DMF = 1.0 mL, 25 °C, 1 min, 5 min, 10 min, 30 min, 120 min.



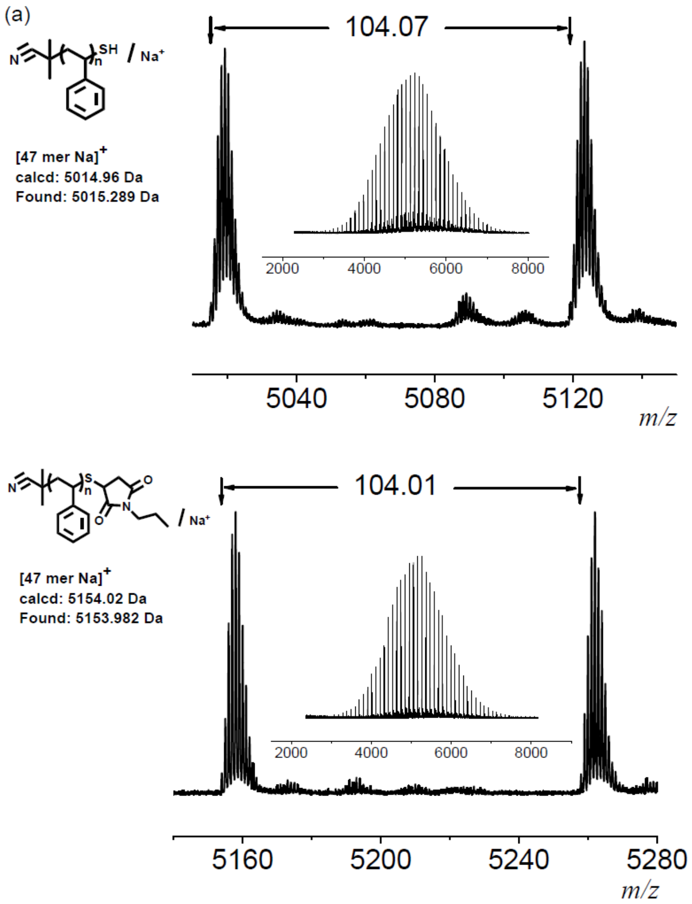


(c)



0 min 1 min 5 min 10 min 30 min 120 min

Fig. S7 SEC traces (a), enlarged ^{1}H NMR signals of thiocarbonylthio groups (b) and the photographs of the reaction mixture (c) before and after the treatment of PS by NaN_3. Original PS: $[St]_0/[CPDN]_0/[AIBN]_0 = 1500/5/1$, time = 79 h, conversion = 39.1 %, 60 ^oC, St = 10.0 mL, toluene = 4.0 mL; Treated conditions: $[PS]_0/[NaN_3]_0 = 1/10$, PS = 0.2000 g, DMF = 1.0 mL, 25 ^oC, 1 min, 5 min, 10 min, 30 min, 120 min.



(c)

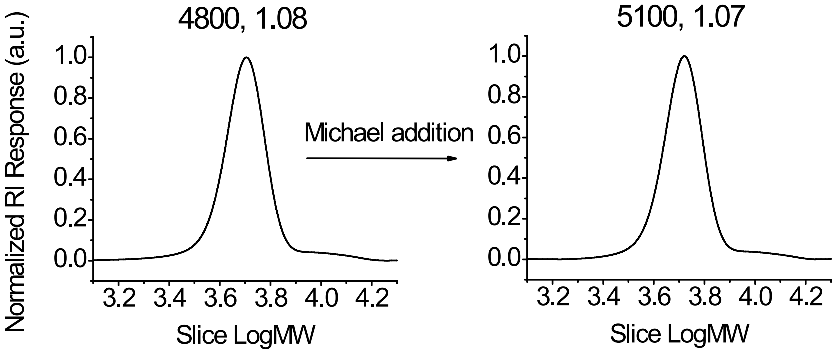
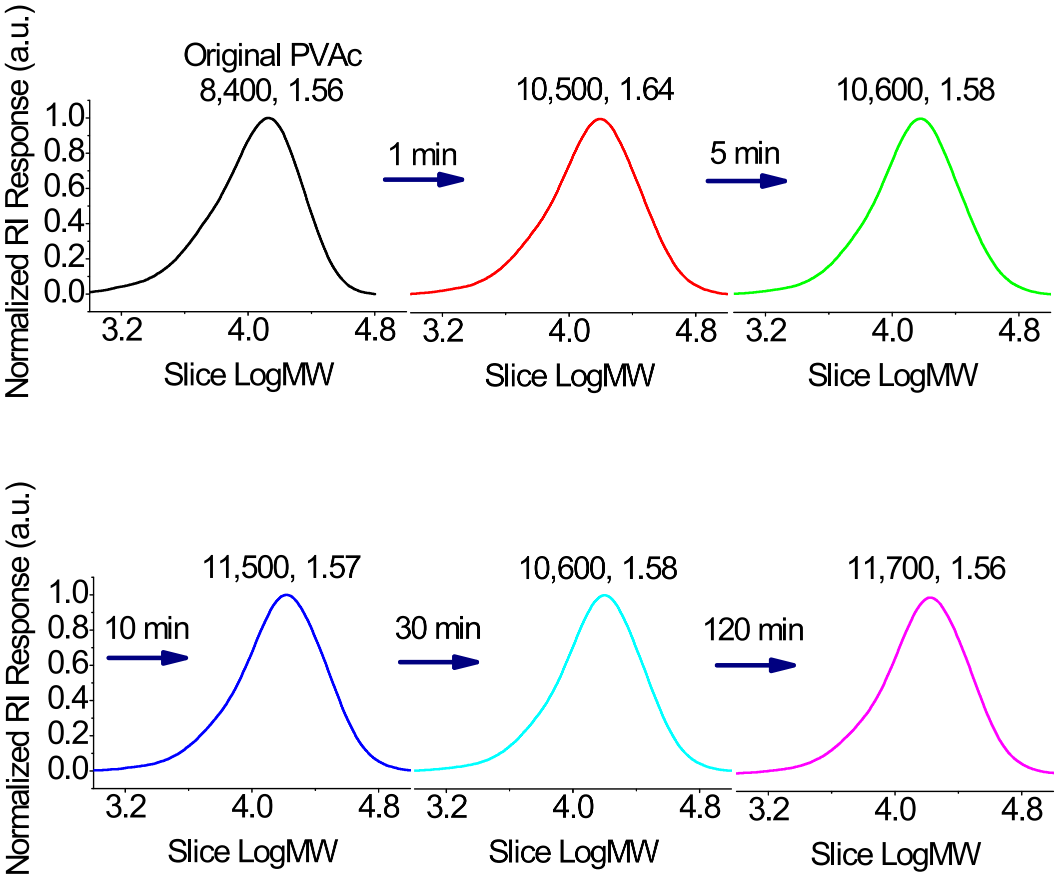
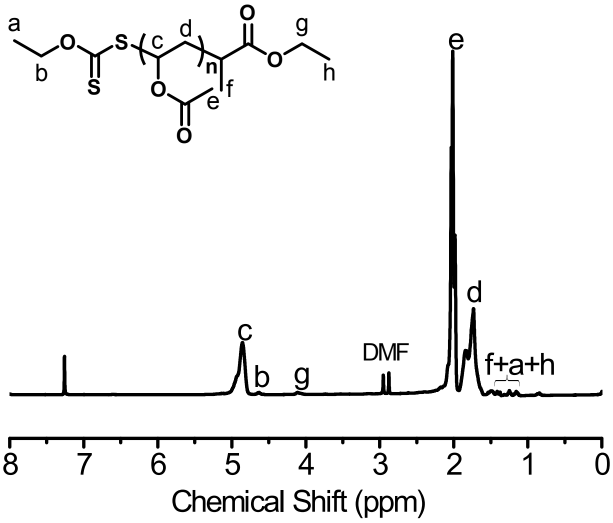


Fig. S8 Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry (a) and the SEC traces (b) of the PS before and after the Michael addition reaction with N-propylmaleimide.

(a)


Normalized RI Response (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
Original PVAc
8,400, 1.56
1 min
10,500, 1.64
5 min
10,600, 1.58
3.2
4.0
4.8
Slice LogMW
Normalized RI Response (a.u.)
10 min
11,500, 1.57
30 min
10,600, 1.58
120 min
11,700, 1.56
Slice LogMW

(b)


a
b
O
S
S
c
d
n
f
O
e
O
O
g
h
e
d
c
b
g
DMF
f+a+h
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

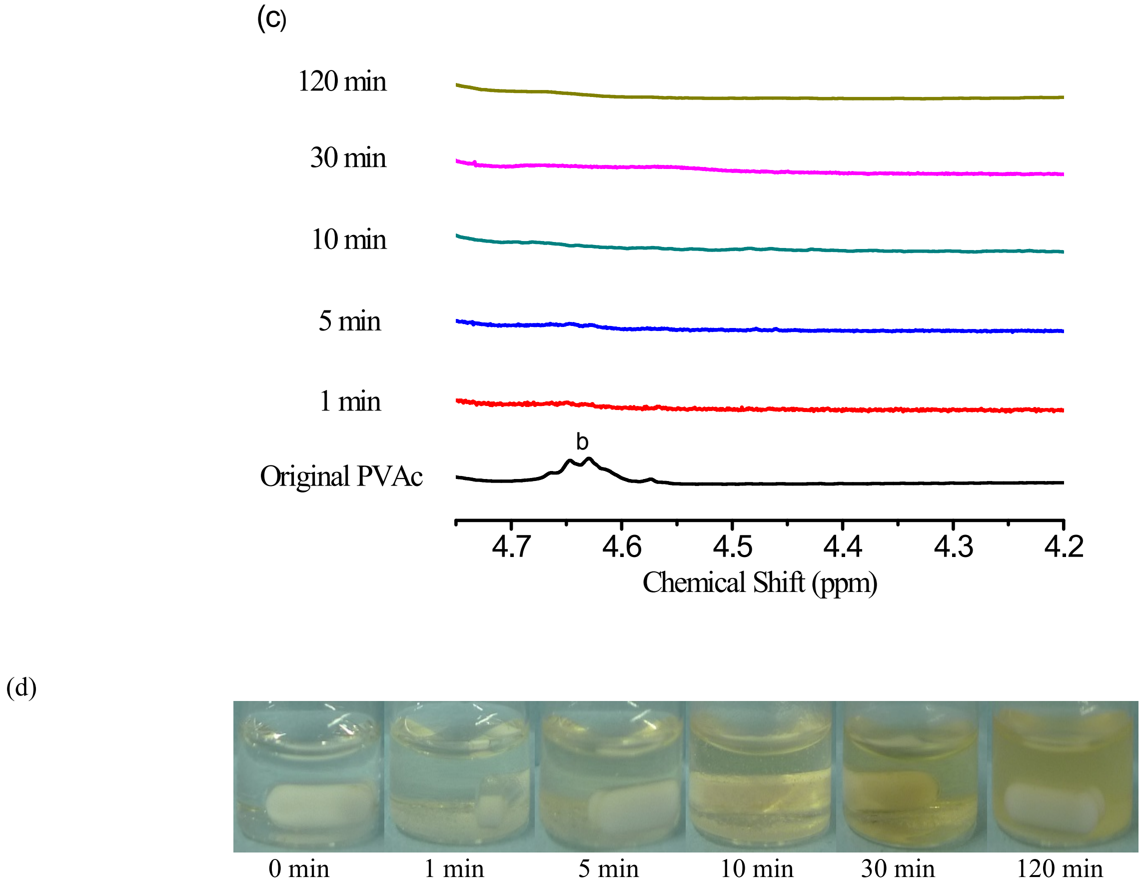


Fig. S9 SEC traces (a), full ^{1}H NMR spectrum (b), enlarged ^{1}H NMR signals of thiocarbonylthio groups (c) and the photographs of the reaction mixture (d) before and after the treatment of PVAc by NaN_3. Original PVAc: $[VAc]_0/[Xanthate]_0/[AIBN]_0 = 2000/10/3$, time = 14 h, conversion = 45 %, 60 ^{o}C, VAc = 10.0 mL; Treated conditions: $[VAc]_0/[NaN_3]_0 = 1/10$, PS = 0.2000 g, DMF = 1.0 mL, 25 ^{o}C, 1 min, 5 min, 10 min, 30 min, 120 min.

References

[1]. (a) R. Radičević, S. Kisin and I. Krakovsky, *Chromatographia*, 2004, 59, 621-624; (b) X. Sun, H. Shen, B. Xie, W. Yang and M. Yang, *Polymer*, 2011, 52, 564-570; (c) J. Qin, L. Zhang, H. Jiang, J. Zhu, Z. Zhang, W. Zhang, N. Zhou, Z. Cheng and X. Zhu, *Chemistry-A European Journal*, 2012, 18, 6015-6021.

[2]. A. Asandei and V. Percec, *Journal of Polymer Science Part A: Polymer Chemistry*, 2001, 39, 3392-3418.

[3]. V. K. Patel, N. K. Vishwakarma, A. K. Mishra, C. S. Biswas and B. Ray, *Journal of Applied Polymer Science*, 2012, 125, 2946-2955.