Polymer Chemistry

ARTICLE

Photo-induced Nitroxide Trapping Method to Prepare α,ω-Heterotelechelic Polymers

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Abstract text goes here. The abstract should be a single paragraph that summarises the content of the article

Supporting Information

Experimental Section

Materials:

4-Hydroxy-2,2,6,6-teramethylpiperidinyl-1-oxyl (TEMPO-OH, 98%, Aladdin Industrial Corporation [AIC], USA) was purified by recrystallization from cyclohexane before used. Sodium hydride (NaH, 60% in mineral oil, Tianjin Damao Chemical Reagent Factory, China), propargyl bromide (98%, AIC), epichlorohydrin (ECH, A.R., AIC), tetrabutylammonium hydrogen sulfate (TBASH, 98%, AIC), succinic anhydride (99%, AIC), methoxypolyethylene glycol (*m*PEG, M_n = 750 g/mol, AIC), *N,N*'-dicyclohexylcarbodiimide (DCC, 99%, AIC), 4-dimethylamiopyridine (DMAP, 99%, AIC) were used as received. All other reagents were analytically pure grade and purchased commercially and used as received without further purification.

Instrumentation:

FT-IR spectra were measured between 4000 and 500 cm^{-1} for 32 scans at 4 cm^{-1} resolution in KBr pellets using a Nicolet Magna 360 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker spectrometer (500 MHz) with $CDCl_3$ as a solvent at 25 °C with tetramethylsilane (TMS) as the internal reference. EI-MS experiments were performed with an EI-mass spectrometer (DSQ, Thermo, America). Elemental analysis were performed under a N_2 atmosphere using Elementar Vario EL CHNS equipment, and the content of C, H and N element in the product was determined respectively. Electron Spin Resonance (ESR) measurement was carried out with Bruker BioSpin A300-10-12 for testing unpaired electron in the product, and the sample was dissolved in CH_2Cl_2 as an inert solvent and performed in a quartz cylindrical tube. MALDI-TOF-MS was measured by an Applied Biosystems Voyager DE-STR spectrometer using trans-2-[3-(4-tert-butylphenyl)-2-methylpropenylidene] malononitrile (DCTB). Absorption spectra of the samples were obtained using a Shimadzu UV-450 spectrophotometer. The thermogravimetric analysis were performed with a Mettler TGA/SDTA 851 instrument between 25 and 600 ^{o}C at a heating rate of 10 ^{o}C/min under inert atmosphere.

Synthesis of 4-(propargyloxy)-2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO-≡)

The typical procedure of propargylation of TEMPO-OH was described in a protocol developed by Oliver Reisera et al[1] (Scheme S1). TEMPO-OH (3.000 g, 17.442 mmol) in dry DMF (10.00 mL) was added dropwise at 0 ^{o}C to a stirring suspension of NaH (60% in mineral oil, 0.880 g, 22.000 mmol) in DMF (100.00 mL) and reacted for further 30 mins after returning to room temperature. Then the above mixture was cooled to 0 ^{o}C again, propargyl bromide (1.90 mL, 22.0 mmol) in DMF (10 mL) was added dropwise and stirred for 3 hrs after return to room temperature. After that, water (100 mL) was added and the solution was extracted at least three times with ethyl acetate (50 mL). The combined organic phases were washed with water three times. After drying with magnesium sulphate and evaporation of ethyl acetate, the crude product was purified by a silica gel column chromatography (ethyl acetate/ether = 1:10) to obtained an orange solid. Analytical data should be reported as follows. Yield: 2.639 g, 72.05%. Melting point: 58-59 ^{o}C. Found: C 68.37%, H 9.63%, N 6.59%. Calc. for $C_{12}H_{20}NO_2$: C 68.54%, H 9.59%, N 6.66%. IR (KBr, v_{max}/cm^{-1}): 3208 (≡C-H), 2126 (C≡C), 1364 (N-O), 1091 (C-O-C). EI-MS (*m*/*z* (%)): 210 (M^+, 20). ESR (CH_2Cl_2): g = 2.0077, a_N

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= 15.74 mT.

Synthesis of 4-(Glycidyloxy)-2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO -Gly)

The synthesis procedure of TEMPO-Gly was described in a protocol developed by Huang et al[2] (Scheme S2). Typically, 50% *w*/*w* aqueous NaOH (10 mL), ECH (6.25 mL, 79.793 mmol) and TBASH (0.210 g, 0.619 mmol) were charged in a flask and stirred vigorously. TEMPO-OH (2.575 g, 14.884 mmol) was then slowly added during 1 h at room temperature. After stirring overnight, the mixture was poured in cool water and extracted at least three times with diethyl ether (50.00 mL), the organic phase was collected and washed with saturated NaCl solution to neutrality. After drying with magnesium sulphate and evaporation of diethyl ether, and then distilled under high vacuum. The fraction with b.p. as 130 °C/80 Pa was collected and then recrystallized in hexane at 2 °C. Yield: 2.119 g, 62.43%. Melting point: 38-39 °C. Found: C 62.82%, H 9.75%, N 5.94%. Calc. for $C_{12}H_{22}NO_3$: C, 63.13%; H, 9.71%; N, 6.13%. IR (KBr, ν_{max}/cm^{-1}): 1364 (N-O), 1094 (C-O-C), 914 (epoxy group). EI-MS (*m*/*z* (%)): 228 (M^+, 60). ESR (CH_2Cl_2): g = 2.0067, a_N = 15.54 mT.

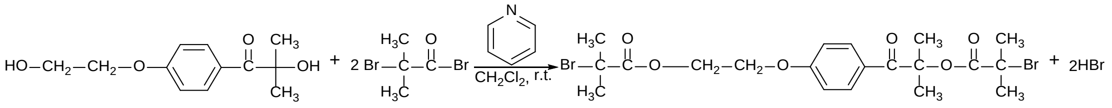
Synthesis of TEMPO-*m*PEG

The TEMPO-*m*PEG was prepared by a two-step sequence based on a protocol developed by Huang et al[3] (Scheme S3).

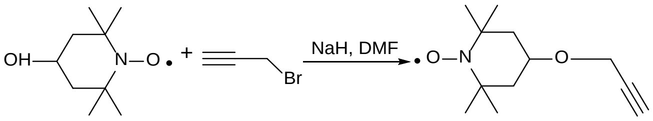
*Synthesis of m*PEG-COOH. In a typical procedure, *m*PEG (7.500 g, 10.000 mmol), succinic anhydride (2.500 g, 25.000 mmol), DMAP (0.122 g, 1.000 mmol), and dry chloroform (100 mL) were added to a flask and stirred at 80 °C for 20 hrs. After removing the solvent by reduced pressure, the crude product was dissolved in water and subsequently washed at least three times with a mixture of ethyl acetate and hexane (*v*/*v* = 1:1). The aqueous phase was extracted by CH_2Cl_2 and the organic phase was collected followed by drying with magnesium sulphate overnight. Then the filtrate was concentrated and dried in vacuum overnight to give a white solid. Yield: 9.670 g, 96.70%. IR (KBr, ν_{max}/cm^{-1}): 3501 (O-H), 2874 (C-H), 1733 (C=O, ester), 1643 (C=C), 1109 (C-O-C) ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 2.64 (t, 4H, -CH_2CH_2COOH), 3.37 (s, 3H, -OCH_3), 3.55 (t, 2H, O-CH_2-), 3.58-3.71 (m, 4H, OCH_2CH_2, repeating unit of PEG), 4.20-4.30 (s, 2H, -COO-CH_2-). MALDI-TOF-MS (*m*/*z*): found M^+ = 948.

Synthesis of TEMPO-mPEG. *m*PEO-COOH (9.480 g, 10.000 mmol), TEMPO-OH (5.160 g, 30.000 mmol), DMPA (0.122 g, 1.000 mmol) in CH_2Cl_2 were charged to a flask and stirred under an inert atmosphere. Then, the solution of DCC (2.060 g, 10.000 mmol) in CH_2Cl_2 was slowly dropped in the mixture over 1 h at -10 °C and reacted for further 24 hrs after returning to room temperature. After that, the reaction mixture was filtered and the solution was removed by rotary evaporation. The crude product was dissolved in water and washed at least three times with a mixture of ethyl acetate and hexane (*v*/*v* = 1:1). Then the aqueous phase was extracted by CH_2Cl_2 and the organic phase was collected followed by drying with magnesium sulphate overnight. Then filtrate was concentrated and dried in vacuum overnight to give a red solid. Yield: 9.142 g, 82.88%. IR (KBr, ν_{max}/cm^{-1}): 2875 (C-H), 1733 (C=O, ester), 1645 (C=C), 1323 (N-O), 1104 (C-O-C). MALDI-TOF-MS (*m*/*z*): found M^+ = 1103. ESR (CH_2Cl_2): g = 2.0068, a_N = 15.64 mT.

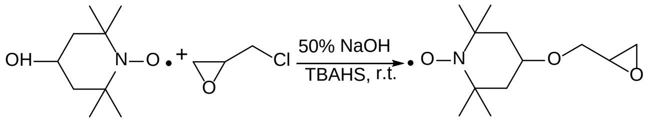
1. A. Gheorghe, A. Matsuno and O. Reiser, Advanced Synthesis & Catalysis, 2006, 348, 1016-1020.
2. Z. Jia, Q. Fu and J. Huang, Macromolecules, 2006, 39, 5190-5193.
3. Y. Li, Y. Zhang, S. Zhai, Y. Deng, H. Xiong, G. Lu and X. Huang, Journal of Polymer Science Part A: Polymer Chemistry, 2011, 49, 23-34.



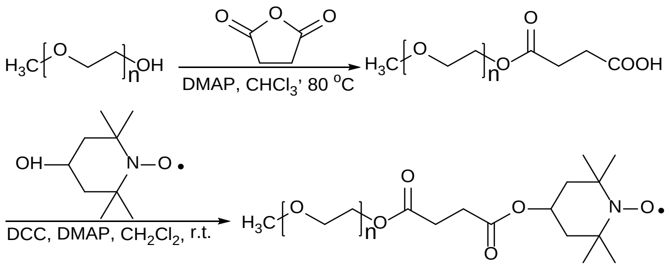
Scheme S1 Synthesis of photolysis-ATRP initiator 2-{4-[2-[(2-bromo-2-methylpropanoyl)oxy]-2-methylpropanoyl]phenoxy}ethyl 2-bromo-2-methylpropanoate



Scheme S2 Synthesis of TEMPO-≡



Scheme S3 Synthesis of TEMPO-Gly



Scheme S4 Synthesis of TEMPO-*m*PEG

Table S1 Values of cohesive Pressure (*c*), normalized reichardt solvent polarity constant (E_T^N) and viscosity (η) for Various Solvents

Parameter [a]	Benzene	THF	CH_2Cl_2	DMSO
c(MPa)	353.0	347.0	414.0	708.0
E_T^N	0.111	0.207	0.309	0.444
η(cP)	0.675	0.499	0.444	1.996

[a] The parameter are given by references 53

Table S2 ESR parameters of nitroxides with functional groups

	TEMPO-OH	TEMPO-≡	TEMPO-Gly	TEMPO-*m*PEG
g	2.0077	2.0075	2.0067	2.0068
a_N(Gs)	15.73	15.74	15.54	15.64

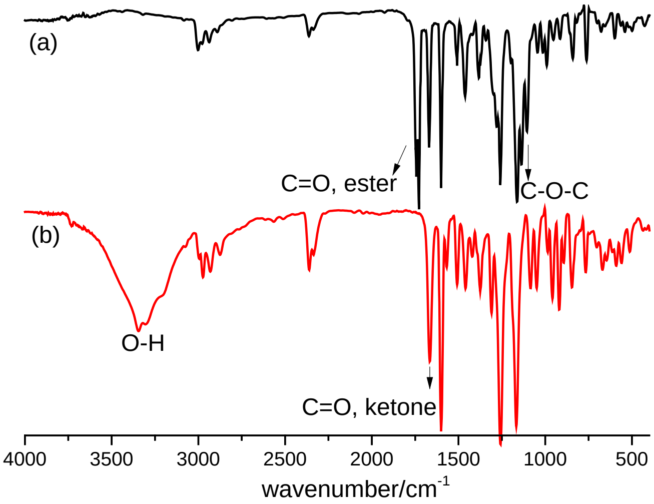


Fig. S1 FT-IR of (a) photolysis-ATRP initiator and (b) HHEMP

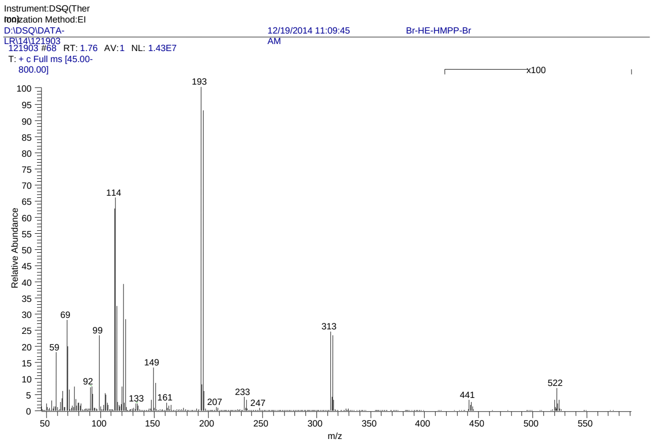


Fig. S2 EI-MS spectrum of photolysis-ATRP initiator

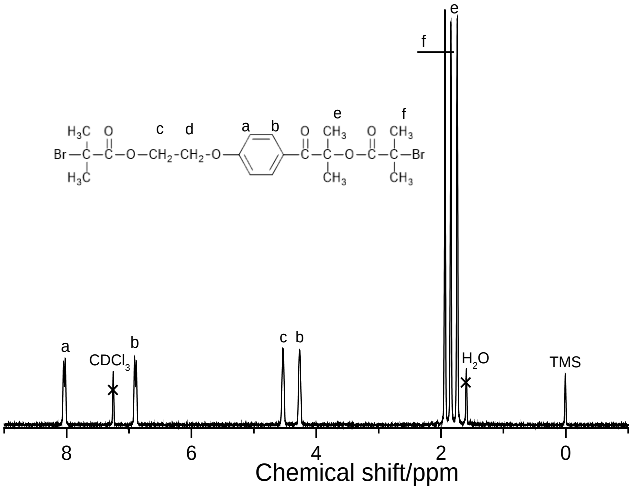


Fig. S3 ^{1}H NMR spectrum of photolysis-ATRP initiator

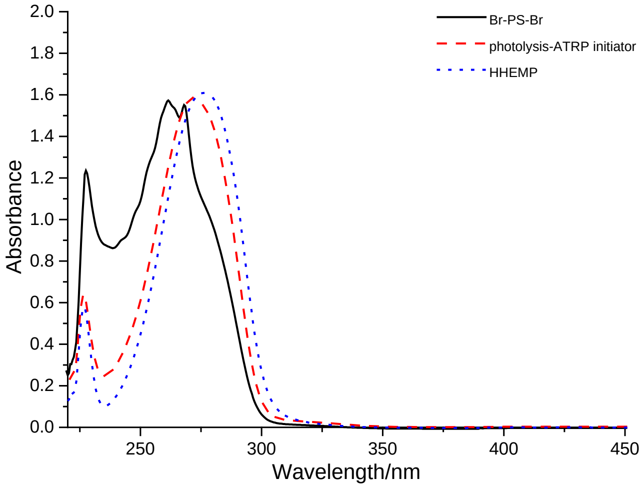


Fig. S4 Absorption spectra of (· · ·) HHEMP, (– – –) photolysis-ATRP initiator (10^{-4} mol/L) and (——) Br-PS-Br (0.6 g/L) in CH_2Cl_2

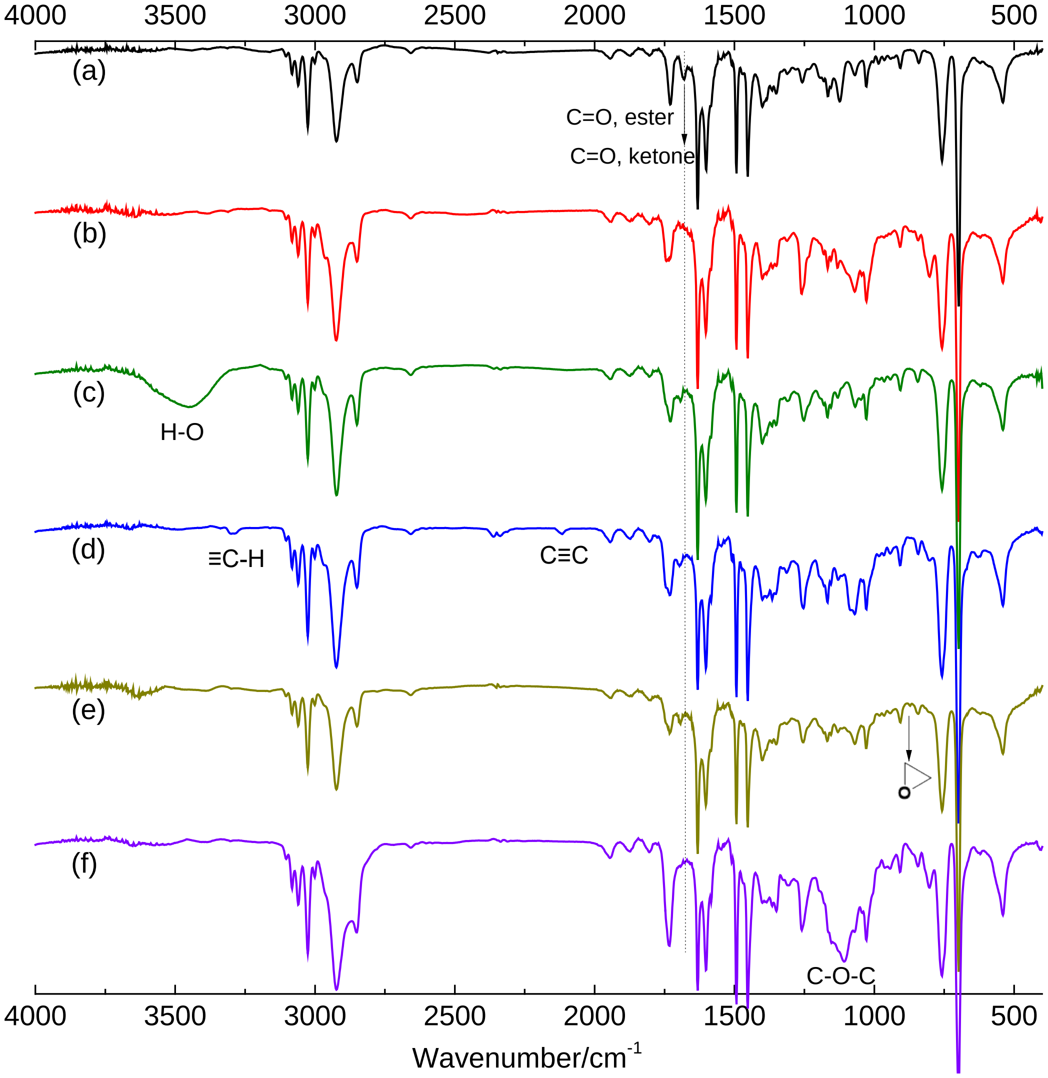


Fig. S5 FT-IR spectra of (a) Br-PS-Br, (b) Br-PS-TEMPO, (c) Br-PS-TEMPO-OH, (d) Br-PS-TEMPO-≡, (e) Br-PS-TEMPO-Gly, and (f) Br-PS-TEMPO-*m*PEG

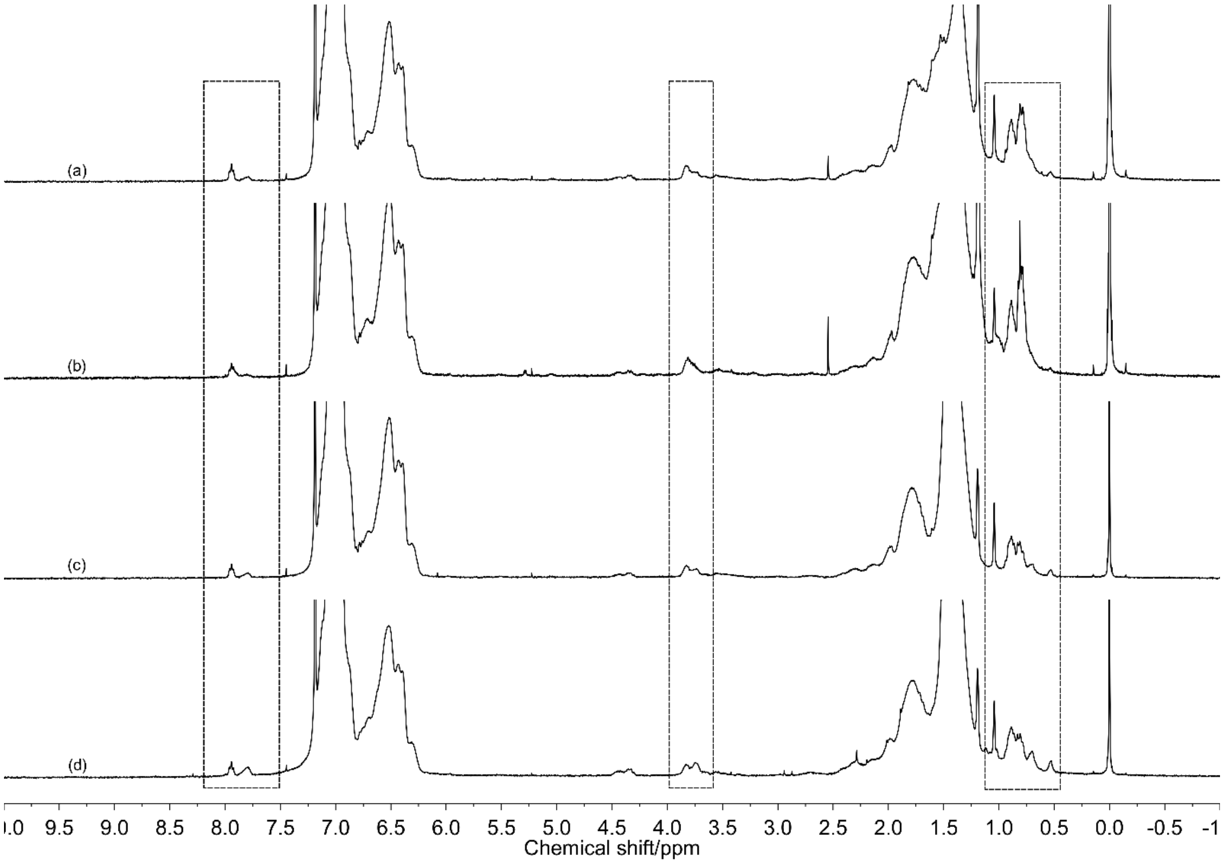


Fig. S6 ^{1}H NMR spectra of Br-PS-TEMPO under 3 hrs irradiation with different solvents (a. Benzene, b. THF, c. CH_2Cl_2, d. DMSO)

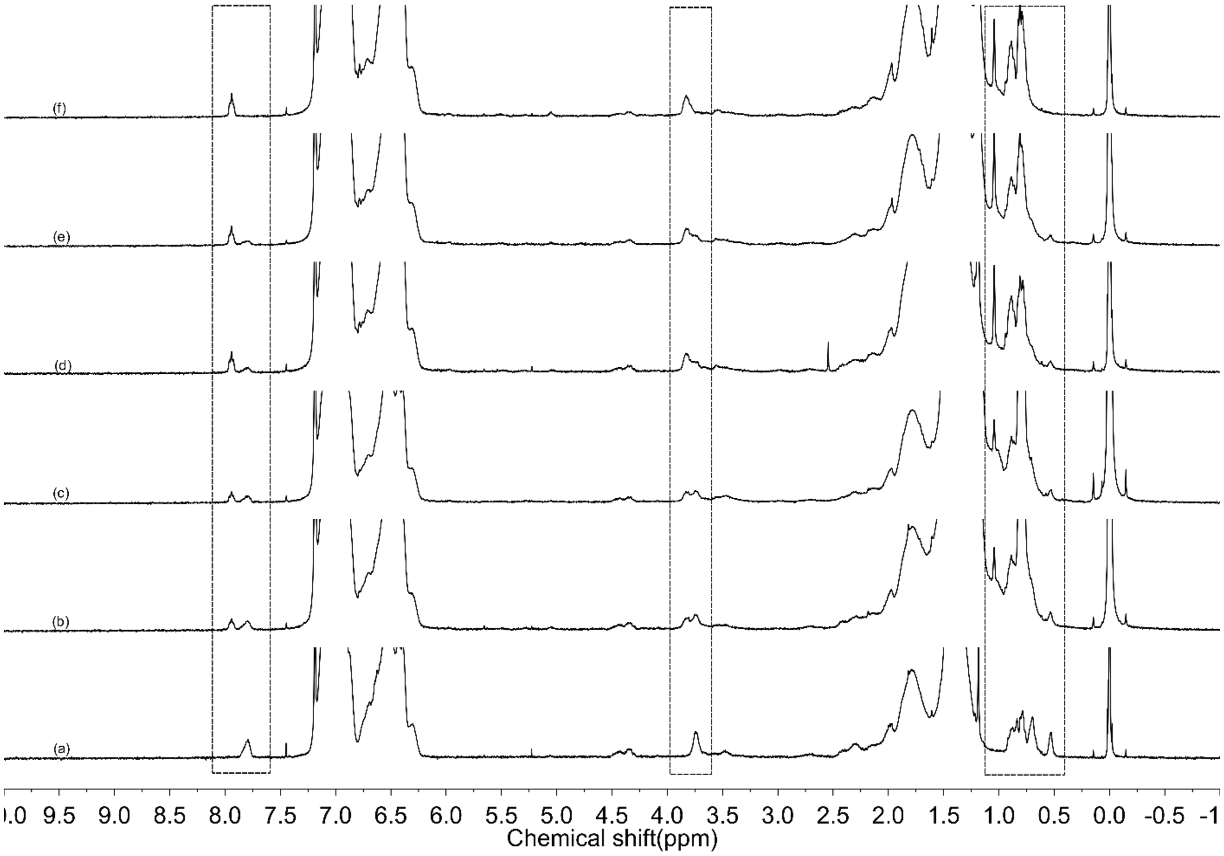


Fig. S7 ^{1}H NMR spectra of Br-PS-TEMPO under different irradiation time (a-f: 0-5 h)

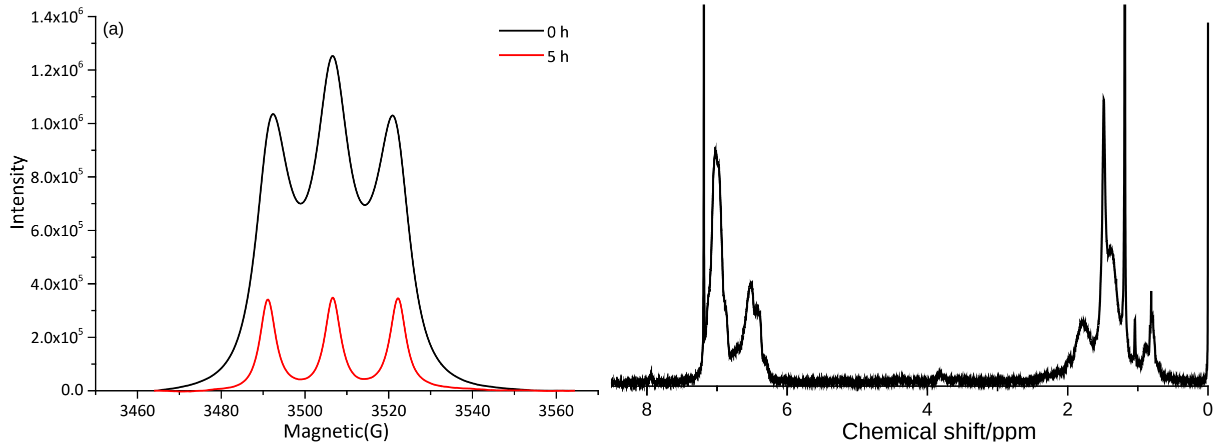


Fig. S8 (a) ESR signals of photo-induced nitroxide radical trapping reaction at 0 h and 5 h, (b) ^{1}H NMR result at 5 h, [PS-Br-PS]:[TEMPO] = 1:4 mol/mol

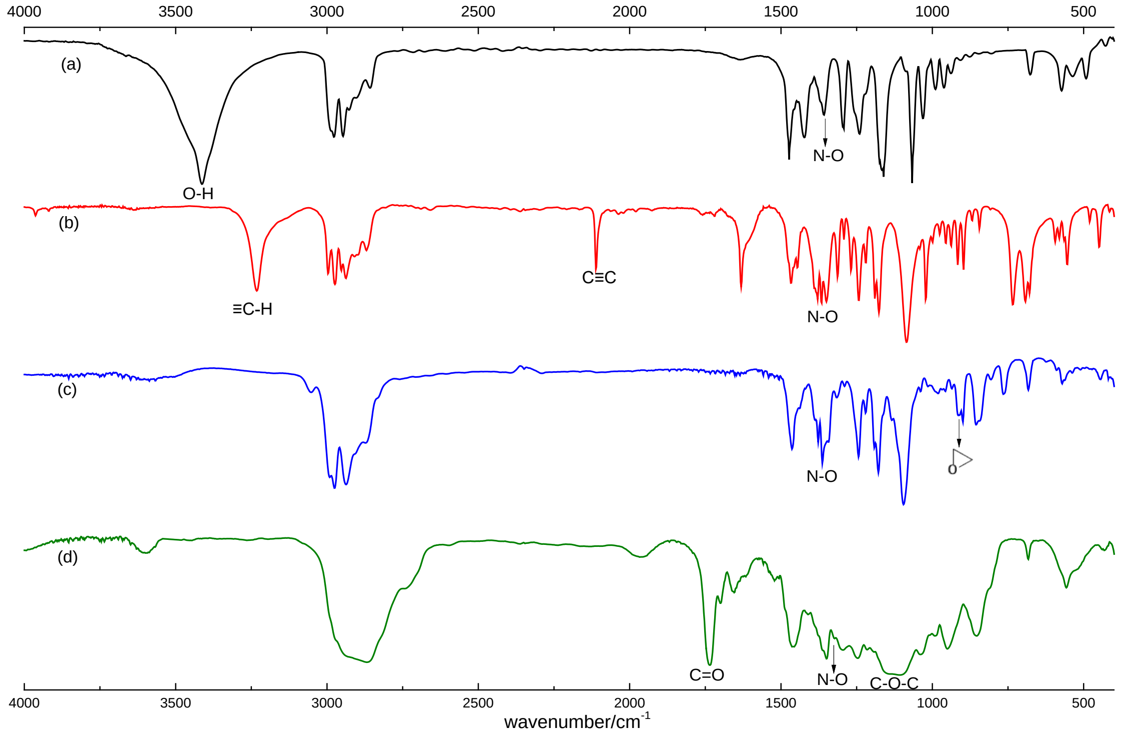


Fig. S9 FT-IR spectra of nitroxides with functional groups (a. TEMPO-OH, b. TEMPO-≡, c. TEMPO-Gly, d. TEMPO-mPEG)

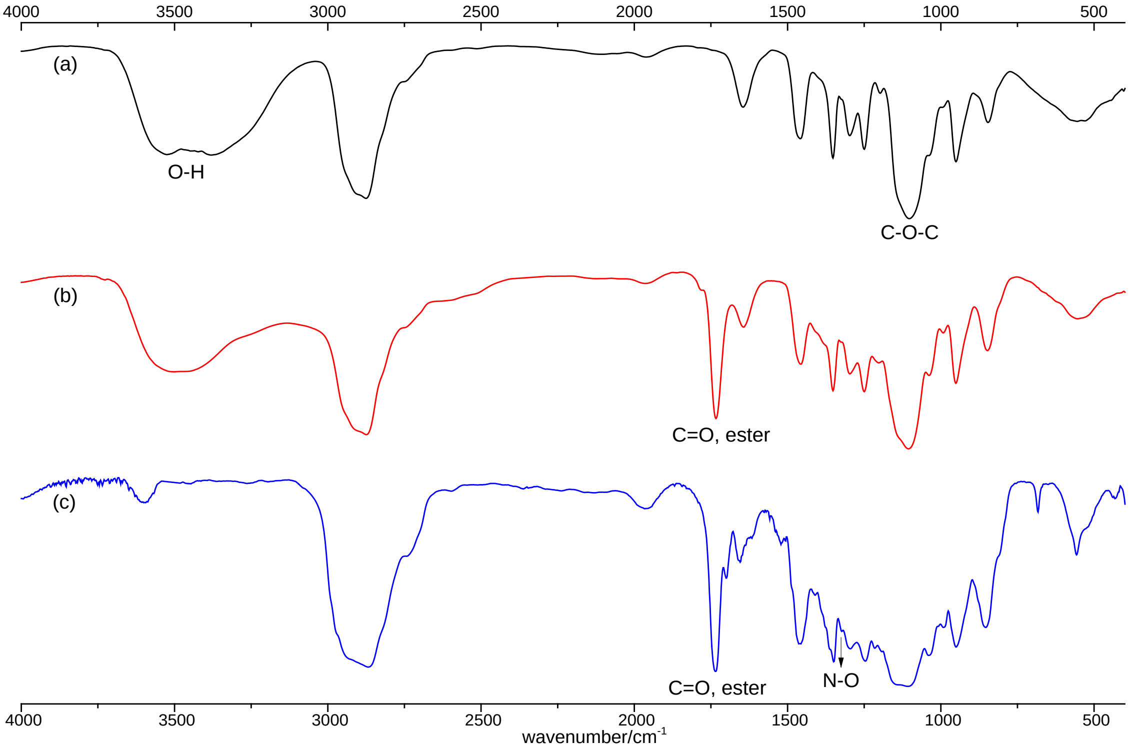


Fig. S10 FT-IR spectra of (a) *m*PEG, (b) *m*PEG-COOH and (c) TEMPO-*m*PEG

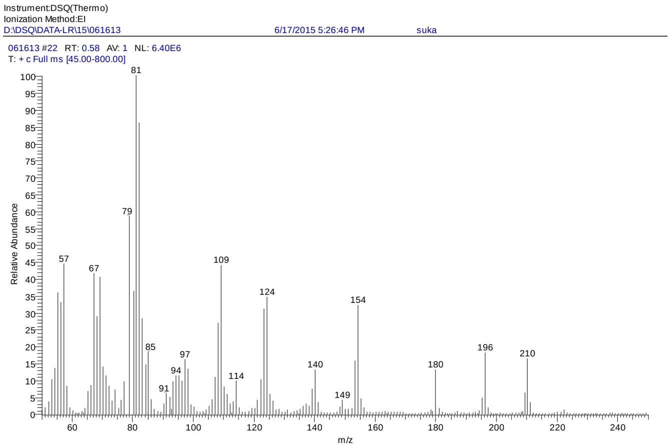


Fig. S11 EI-MS spectrum of TEMPO-≡

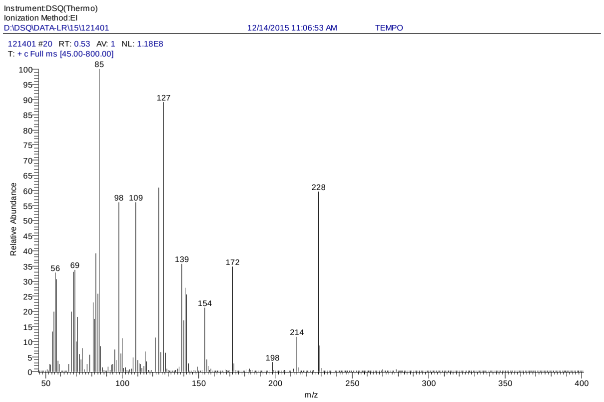


Fig. S12 EI-MS spectrum of TEMPO-Gly

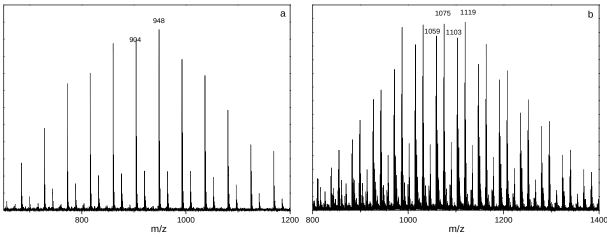


Fig. S13 Maldi-Tof-MS spectra of (a) *m*PEG-COOH and (b) TEMPO-*m*PEG*M*peg

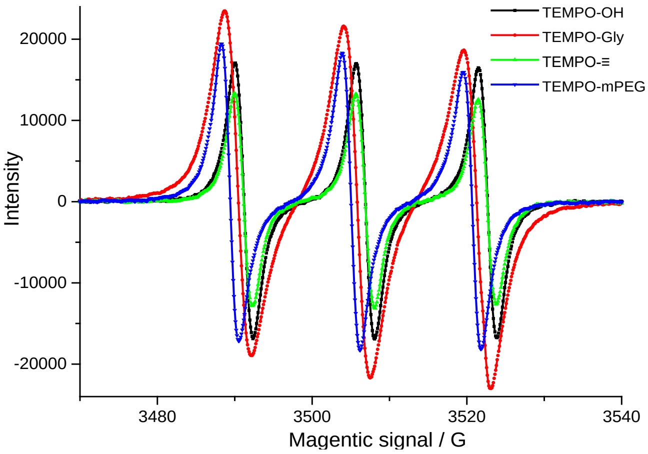


Fig. S14 ESR signals of nitroxides with functional groups (a. TEMPO-OH b. TEMPO-≡ c. TEMPO-Gly d. TEMPO-*m*PEG)

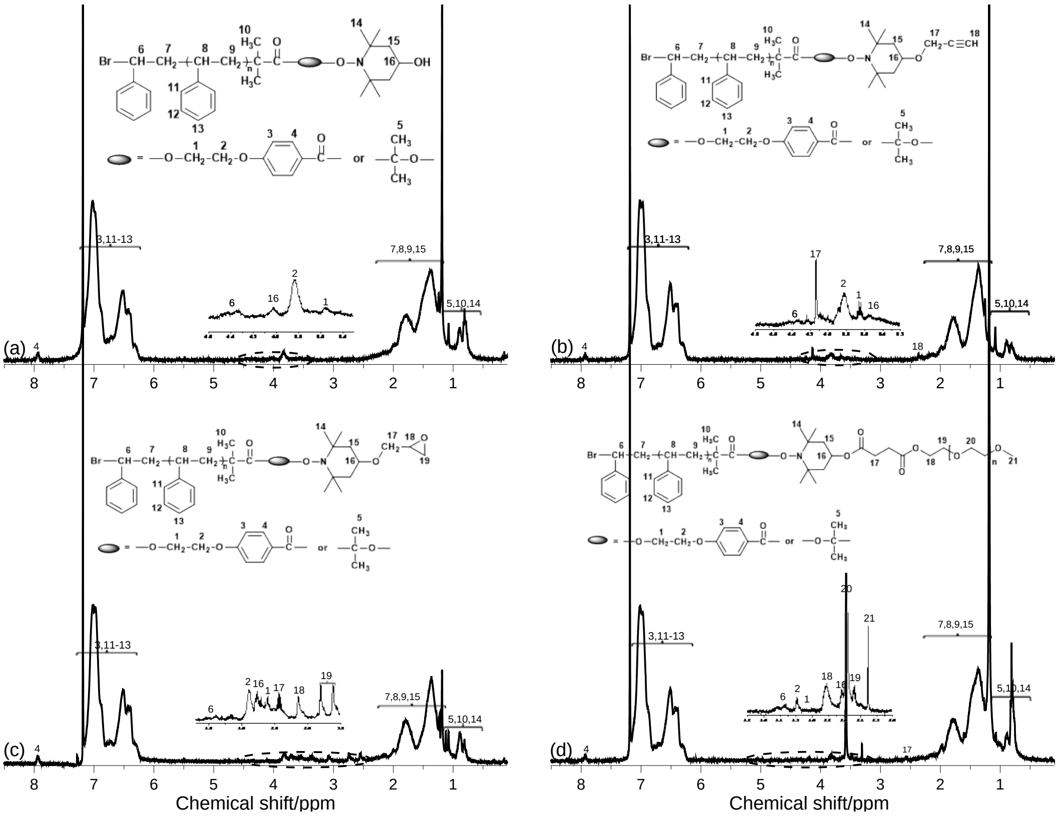


Fig. S15 ^{1}H NMR spectra of *α,ω*-heterotelechelic polystyrene with various functional groups (a) Br-PS-TEMPO-OH, (b) Br-PS-TEMPO-≡, (c) Br-PS-TEMPO-Gly, and (d) Br-PS-TEMPO-*m*PEG

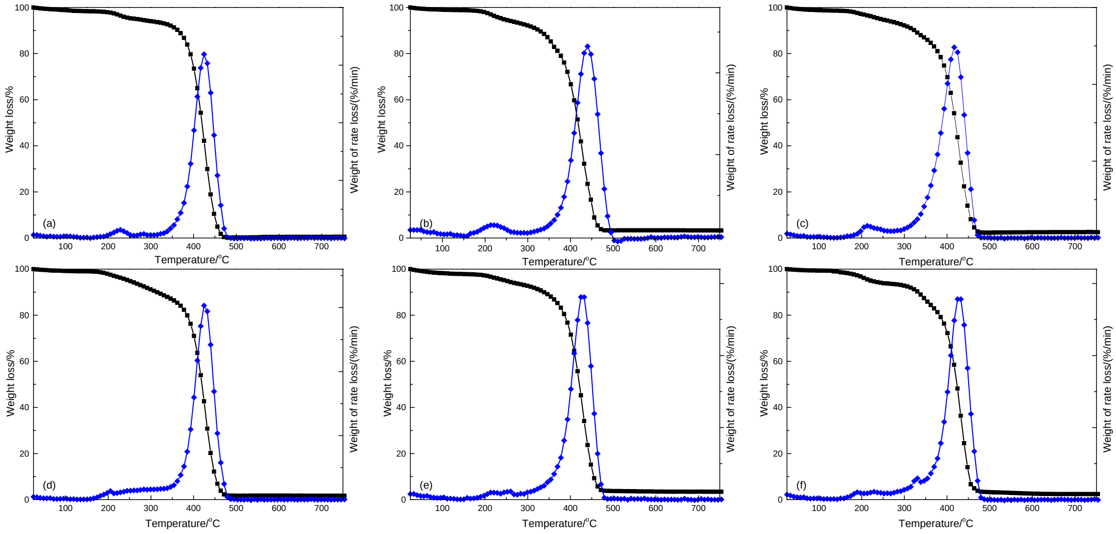


Fig. S16 Thermogravimetric analysis of (a) Br-PS-Br, (b) Br-PS-TEMPO, (c) Br-PS-TEMPO-OH, (d) Br-PS-TEMPO-≡, (e) Br-PS-TEMPO-Gly, and (f) Br-PS-TEMPO-*m*PEG

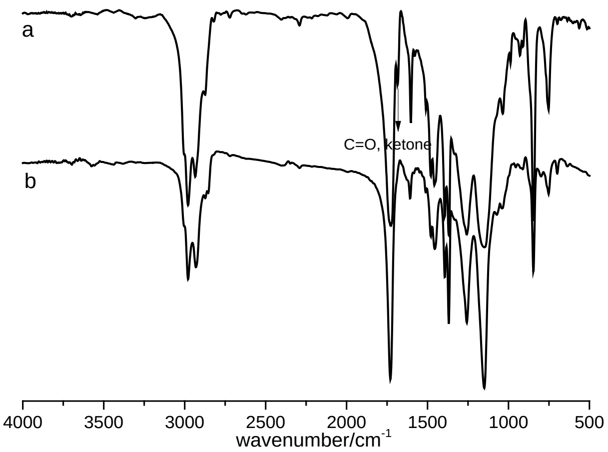


Fig. S17 FT-IR spectra of Br-P*t*BA-Br and Br-P*t*BA-TEMPO

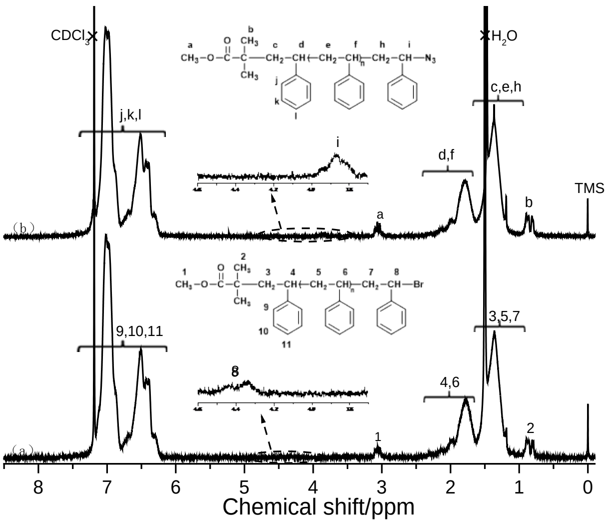


Fig. S18 ^{1}H NMR spectra of (a) PS-Br and (b) PS-N_3

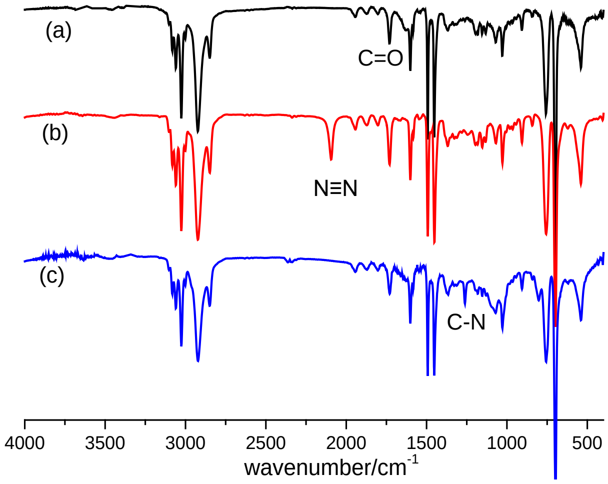


Fig. S19 FT-IR spectra of (a) PS-Br, (b) PS-N_3 and (c) polystyrene after CuAAC reaction