

Supporting Information

Natural RAFT Polymerization: Recyclable-catalyst-aided, Opened to Air, and Sunlight-photolyzed RAFT Polymerizations

Jie Wang[†], Maria Rivero[§], Alexandra Muñoz Bonilla[§], Jorge Sanchez-Marcos[§], Wentao Xue[†], Gaojian Chen^{*†‡}, Weidong Zhang^{*†‡} and Xiulin Zhu[‡]

[†]Center for Soft Condensed Matter Physics and Interdisciplinary Research, Soochow University, Suzhou 215006, P. R. China

[‡]State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry Engineering and Materials Science of Soochow University, Soochow University, Suzhou 215123, China

[§]Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, C/Francisco Tomás y Valiente, 7, Cantoblanco, 28049 Madrid, Spain

Experimental Section

Materials

Methyl methacrylate (MMA) (Shanghai Chemical Reagent Co., Ltd., China >99%), methyl acrylate (MA) (Shanghai Chemical Reagent Co., Ltd., China >99%), Vinyl acetate (AR, Chinasun Specialty Products Co., Ltd., China) were purified by passing through neutral alumina column to remove the inhibitor before use. *N*-isopropylacrylamide (NIPAAm) was purchased from Shanghai Macklin Biochemical Co, Ltd (Shanghai, China). The RAFT agent 3-azidopropyl 3-((((2-methoxy-2-oxo-1-phenylethyl)thio)carbonothioyl)thio) propanoate (AMP)

was synthesized through the literature.^[S1,S2] Ethyl 2-((ethoxycarbonothioy)thio)propanoate (EXEP) was synthesized according to the literature.^[S3] 4-cyano-4-((phenylcarbonothioyl)thio)pentanoic acid (CPADB) was purchased from Aldrich and used as received. The zinc ferrite nanoparticle ($\text{Zn}_{0.64}\text{Fe}_{2.36}\text{O}_4$) was prepared via the literature with slight modifications.^[S4] In the current work the nanoparticles synthesis was carried out with 20 mA of current intensity in the Zn anode and at 40 °C of temperature to obtain the nanoparticles with a diameter of 16 nm. 2-cyanopropan-2-yl naphthalene-1-carbodithioate (CPDN) was prepared as reported previously.^[S5] Dimethyl sulphoxide (DMSO) (analytical reagent, Shanghai Chemical Reagent Co. Ltd) was dried by 4 Å molecular sieves before use. All other reagents and solvents were analytical grade and used as received.

Characterizations

The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the obtained polymers were determined by TOSOH HLC-8320 (GPC) equipped with TSK gel Multi pore HZ-N (3) 4.6*150 mm column at 40 °C. Tetrahydrofuran and dimethyl formamide were served as the eluent with a flow rate of 0.35 mL/min. GPC samples were injected using a TOSOH HLC-8320 GPC plus auto sampler. The molecular weights were calibrated with PS or PMMA standard. The ^1H NMR spectra of the polymers were recorded on an INOVA 300 MHz nuclear magnetic resonance instrument using CDCl_3 and DMSO-d_6 as the solvent and tetramethylsilane (TMS) as an internal standard. FT-IR spectrum was recorded on a Nicolette-6700 FT-IR spectrometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker UltraflexIII TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd : YAG laser (355 nm). The simulated “sunlight” was obtained through the xenon lamp (CEL-HXUV300) bought from CEAULIGHT. The wavelengths range from 300 nm to 1100 nm. The average intensity of the “sunlight” is 2.5 mW/cm². The UV region of the xenon lamp was filtered off using CEL-UVIRCUT400 filter to obtain the simulated sunlight.

Photopolymerization of MMA Opened to Air for Kinetic Studies

The process for the photopolymerization of MMA opened to air is as follows: MMA (0.472 g, 4.71 mmol), CPDN (3.2 mg, 0.0118 mmol), $\text{Zn}_{0.64}\text{Fe}_{2.36}\text{O}_4$ (1 mg, 0.0042 mmol), DMSO (0.5 mL) were added to a 5 mL dry ampoule bottle. The ampoule bottle was not sealed and allowed to be completely open to air. Then, the polymerization was conducted under the irradiation of simulated sunlight (2.5 mW/cm²). At the designed time, the mixture was diluted with 2 mL of THF and precipitated into 250 mL of cool methanol (0 °C). The product was obtained by filtration and dried to keep constant weight under vacuum. The conversion of MMA was calculated by gravimetric method. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by GPC. The polymerization procedures of MA, VAc, NIPAAm opened to air were similar to those described above.

General Procedures for Chain-extension of PMMA Opened to Air

The typical process for chain-extension of PMMA is as follows: MMA (0.283 g, 2.83 mmol), PMMA (0.110 g, 0.007 mmol), $\text{Zn}_{0.64}\text{Fe}_{2.36}\text{O}_4$ (1 mg, 0.0042 mmol), DMSO (0.5 mL) were added to a dry ampoule bottle. The ampoule bottle was not sealed and allowed to be completely open to air. Then, the ampoule bottle was irradiated by exposure to 2.5 mW/cm² simulated sunlight. At the designed time, the mixture was diluted with 2 mL of THF and precipitated into 250 mL of cool methanol (0°C). The product was obtained by filtration and dried to constant weight under vacuum. The conversion of MMA was calculated by gravimetric method.

Photopolymerization Procedure of MMA in the Absence of Air

Photopolymerization of MMA was carried out in a 5 mL dry ampoule bottle containing MMA (0.472 g, 4.71 mmol), CPDN (3.2 mg, 0.0118 mmol), DMSO (0.5 mL). The reaction mixture was bubbled with nitrogen for 15 min to remove oxygen. Then, the ampoule bottle was flame-sealed under nitrogen atmosphere. Subsequently, the polymerization was conducted under the irradiation of simulated sunlight (2.5

mW/cm²). At the designed time, the mixture was diluted with 2 mL of THF and precipitated into 250 mL of cool methanol (0 °C). The product was obtained by filtration and dried to keep constant weight under vacuum. The conversion of MMA was calculated by gravimetric method.

Photopolymerization Procedure of MA in the Absence of Air

Photopolymerization of MA was carried out in a 5 mL dry ampoule bottle containing MA (0.475 g, 5.52 mmol), CPADB (3.8 mg, 0.0136 mmol), DMSO (0.5 mL). The reaction mixture was bubbled with nitrogen for 15 min to remove oxygen. Then, the ampoule bottle was flame-sealed under nitrogen atmosphere and the polymerization was conducted under the irradiation of simulated sunlight (2.5 mW/cm²). At the designed time, the mixture was diluted with 2 mL of THF and precipitated into 250 mL of diethyl ether. The product was obtained by filtration and dried to keep constant weight under vacuum. The conversion of MA was calculated by gravimetric method.

Photopolymerization Procedure of VAc in the Absence of Air

Photopolymerization of VAc was carried out in a 5 mL dry ampoule bottle in the presence of VAc (0.465 g, 5.40 mmol), EXEP (3 mg, 0.0135 mmol), DMSO (0.5 mL). The reaction mixture was bubbled with nitrogen for 15 min to remove oxygen. Then, the ampoule bottle was flame-sealed under nitrogen atmosphere. Next, the polymerization was conducted under the irradiation of simulated sunlight (2.5 mW/cm²). At the designed time, the mixture was freeze-dried to obtain the polymer. The conversion of VAc was calculated gravimetrically.

Photopolymerization Procedure of NIPAAm in the Absence of Air

The process for the photopolymerization of NIPAAm is as follows: NIPAAm (0.3 g, 2.651 mmol), AMP (2.7 mg, 0.0065 mmol), DMSO (0.5mL) were added to a 5 mL dry ampoule bottle. The reaction mixture was bubbled with nitrogen for 15 min to remove oxygen and the ampoule bottle was flame-sealed under nitrogen atmosphere. Then, the polymerization was conducted under the irradiation of simulated sunlight (2.5 mW/cm²). At the designed time, the mixture was diluted with 2 mL of THF and

precipitated into 250 mL of diethyl ether. The product was obtained by filtration and dried to constant weight under vacuum. The conversion of NIPAAm was calculated by gravimetric method.

Table S1. Molecular Weight Parameters of Polymers Prepared Under Different Light Source

Entry	Light Source	Time (h)	Conv (%)	$M_{n, GPC}$ (g/mol)	M_w/M_n
MMA/CPDN ^a	UV-light	20	---	---	---
MMA ^b	UV-light	20	---	---	---
MMA/CPDN ^a	sunlight	20	52	25500	1.12
MMA ^b	sunlight	20	---	---	---
MMA/CPDN ^a	dark	20	---	---	---

a: [MMA]/ [CPDN] = 400 : 1, MMA = 0.5 mL, DMSO = 0.5 mL;

b: MMA = 0.5mL, DMSO = 0.5 mL.

The polymerizations were conducted under the irradiation of simulated sunlight in the absence of air. The average intensity of simulated sunlight is 2.5 mW/cm².

Table S2. Molecular Weight Parameters of Polymers Prepared Via Different RAFT Agents

Monomer	RAFT Agent	Time (h)	Conv (%)	$M_{n, GPC}$ (g/mol)	M_w/M_n
MMA ¹	CPDN	20	52	25500	1.12
MA ²	CPADB	22	71	59600	1.31
VAc ³	EXEP	27	28	11700	1.13
NIPAAm ⁴	AMP	15	46	32400	1.24

1: [MMA]/[CPDN] = 400 : 1, MMA = 0.5 mL, DMSO = 0.5 mL;

2: [MA]/[CPADB] = 400 : 1, MA = 0.5 mL, DMSO = 0.5 mL;

3: [VAc]/[EXEP] = 400 : 1, VAc = 0.5 mL, DMSO = 0.5 mL;

4: [NIPAAm]/[AMP] = 400 : 1, NIPAAm = 0.3 g, DMSO = 0.5 mL.

The polymerizations were conducted under the irradiation of simulated sunlight in the absence of air. The average intensity of simulated sunlight is 2.5 mW/cm².

Table S3. Molecular Weight Parameters of Polymers Prepared in the Presence of Air or N₂

Entry	Atmosphere	Time (h)	Conv (%)	$M_{n, GPC}$ (g/mol)	M_w/M_n
MMA/CPDN ^a	air	24	58	29500	1.42
MMA/CPDN ^b	N ₂	20	52	25500	1.12
MMA ^c	N ₂	30	-	-	-

a: [MMA]/[CPDN] = 400 : 1, MMA = 0.5 mL, Zn_{0.64}Fe_{2.36}O₄ = 1 mg, DMSO = 0.5 mL;

b: [MMA]/[CPDN] = 400 : 1, MMA = 0.5 mL, DMSO = 0.5 mL;

c: MMA = 0.5 mL, Zn_{0.64}Fe_{2.36}O₄ = 1 mg, DMSO = 0.5 mL;

The average intensity of simulated sunlight is 2.5 mW/cm².

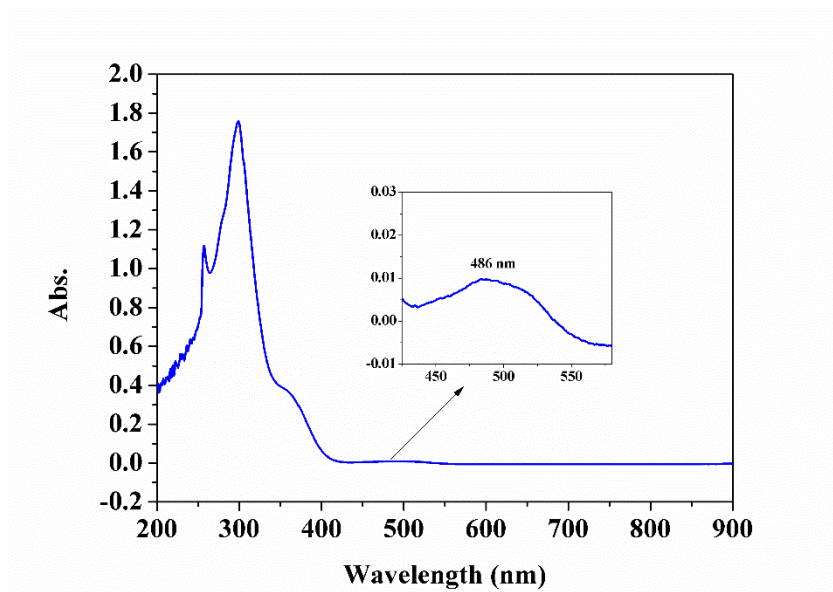


Figure S1. UV-vis absorption spectrum of CPDN in DMSO at 0.2 mM.

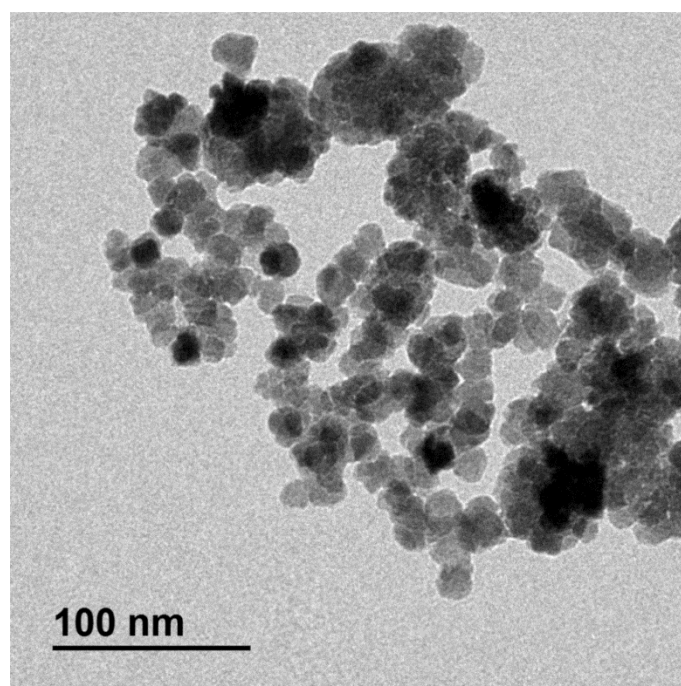


Figure S2. TEM image of the zinc ferrite nanoparticle ($\text{Zn}_{0.64}\text{Fe}_{2.36}\text{O}_4$).

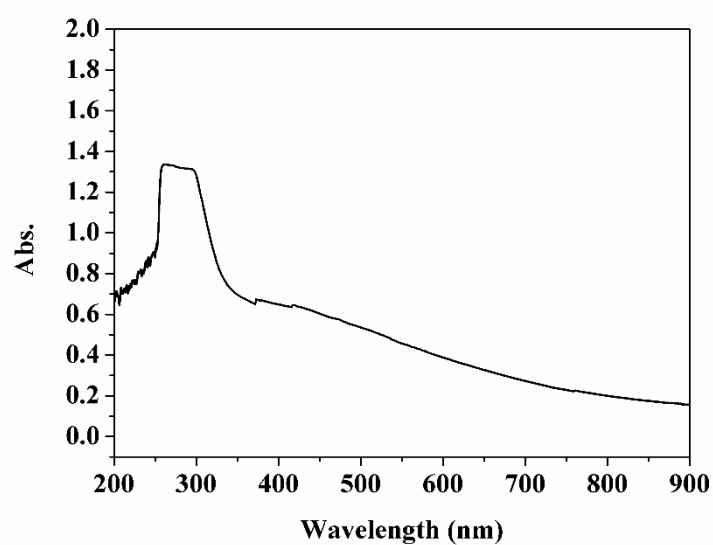


Figure S3. UV-vis absorption spectrum of zinc ferrite nanoparticles (NPs) in DMSO at 0.2 mM.

Table S4. Molecular Weight Parameters of Polymers Prepared in the Presence of Different Amount of Zinc Ferrite Nanoparticles (NPs).

Entry	Time (h)	NPs (mg)	Conv (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
a	22	0.5	69	27500	31000	1.48
b	22	1	72	29100	33200	1.43
c	22	5	70	28300	32700	1.45

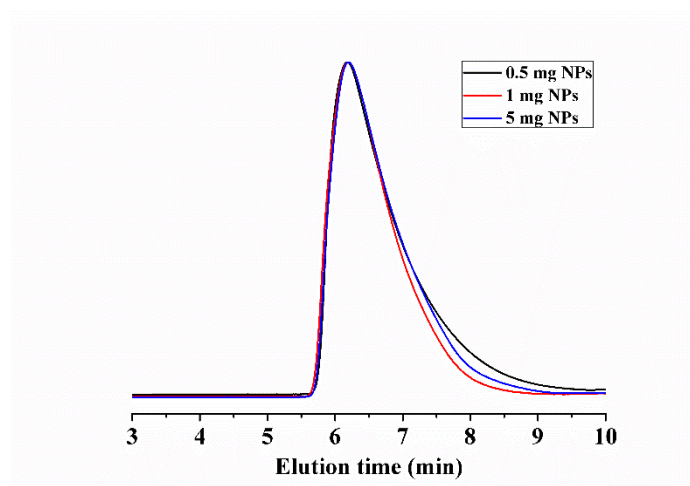


Figure S4. GPC curves of PMMA obtained in the presence of different amount of zinc ferrite nanoparticles (NPs).

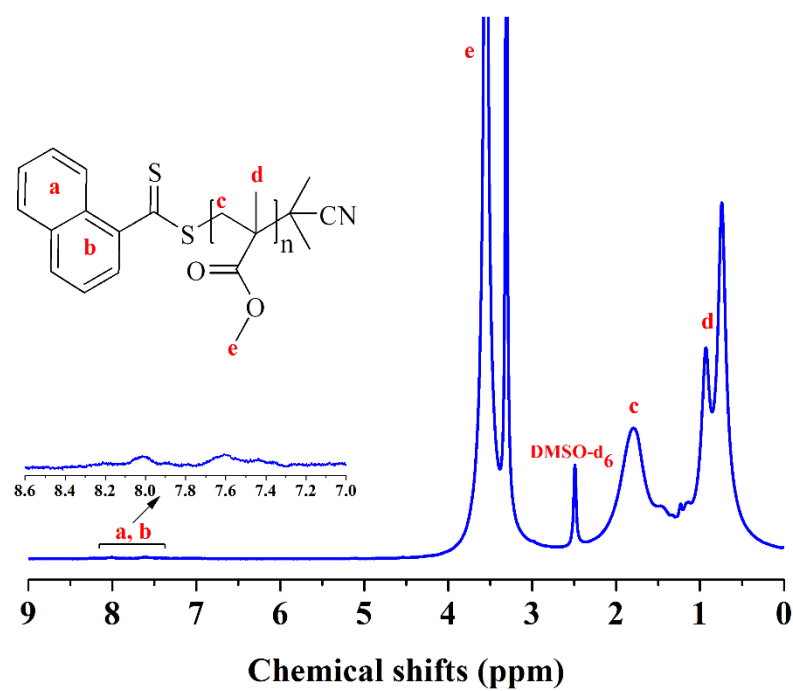


Figure S5. ^1H -NMR spectrum of PMMA prepared in the presence of air.

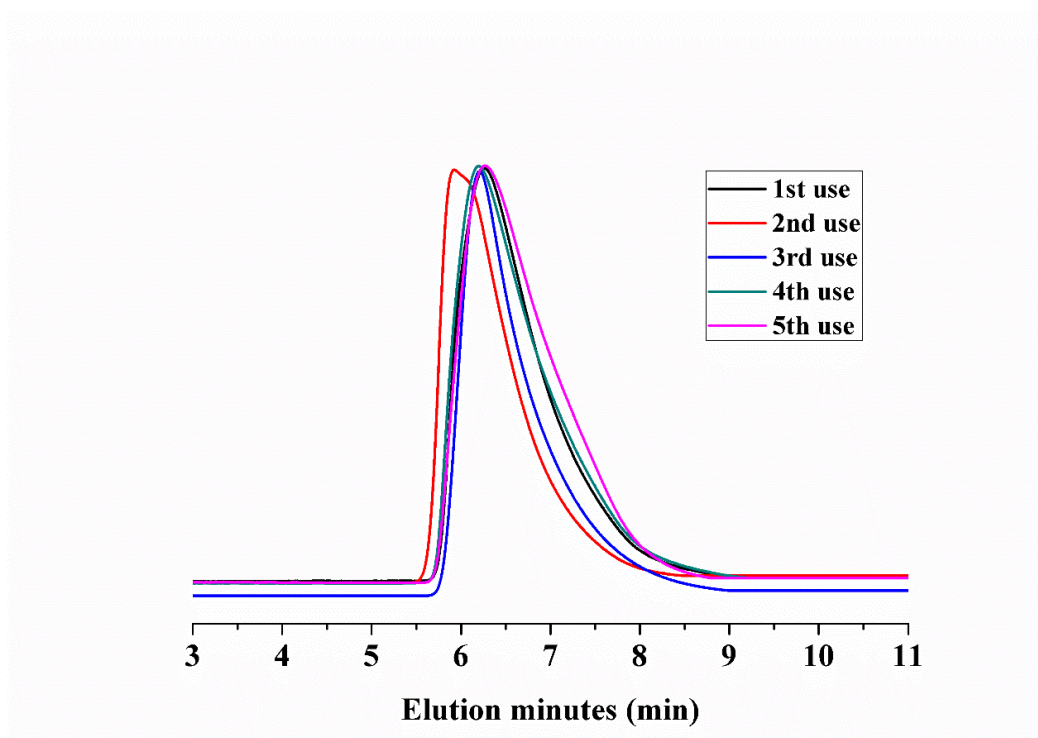


Figure S6. GPC curves of PMMA obtained from zinc ferrite nanoparticle recycling experiments. Polymerization condition: [MMA]/[CPDN] = 400 : 1, MMA = 0.5 mL, $\text{Zn}_{0.64}\text{Fe}_{2.36}\text{O}_4$ = 1 mg, DMSO = 0.5 mL.

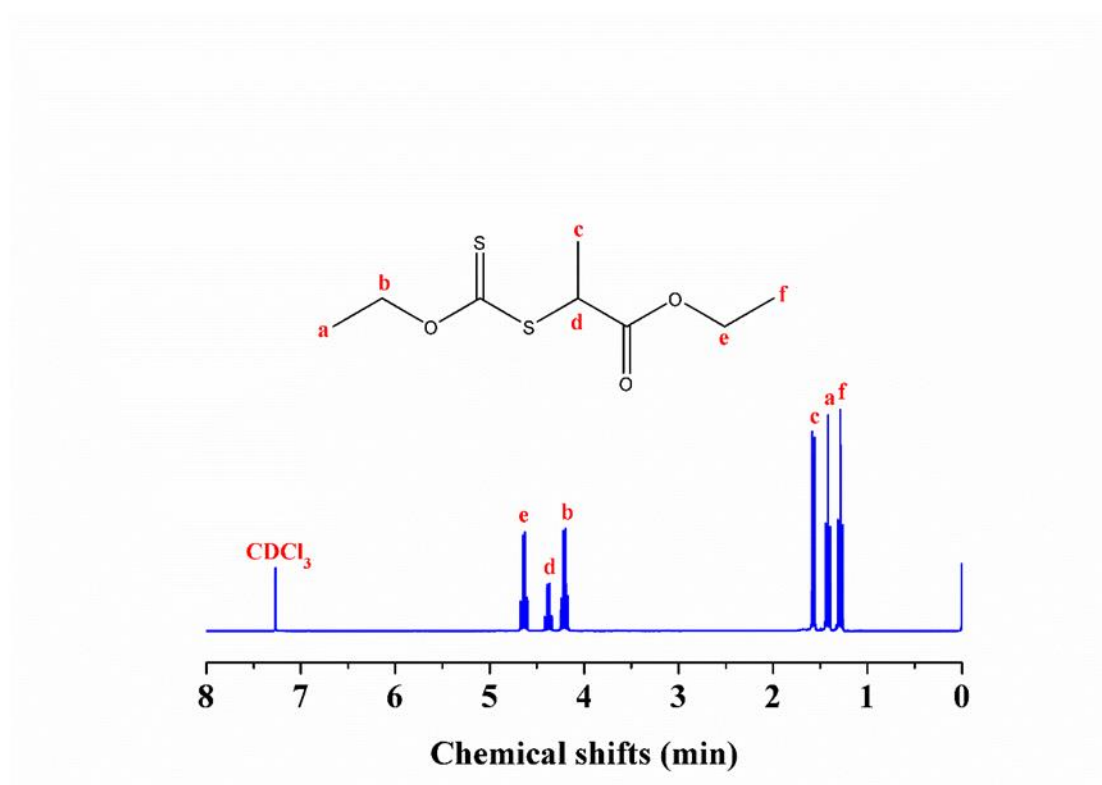


Figure S7. ^1H NMR spectrum of the RAFT agent (EXEP) obtained in CDCl_3 .

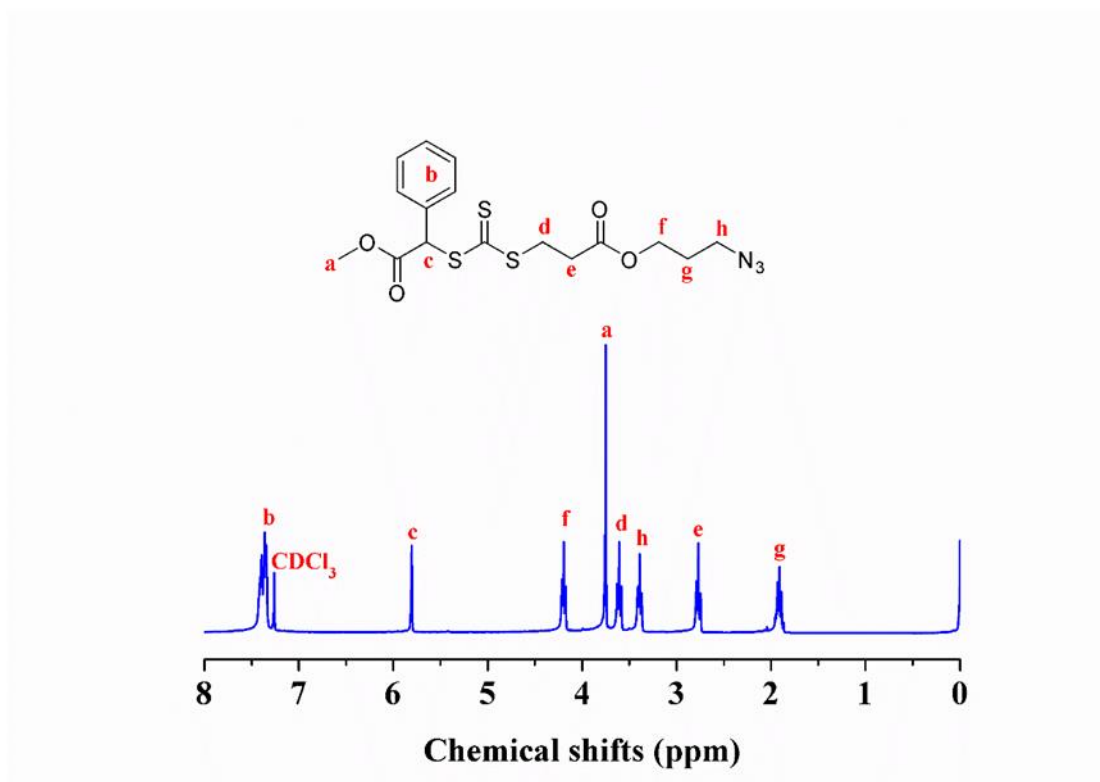


Figure S8. ^1H NMR spectrum of the RAFT agent (AMP) obtained in CDCl_3 .

References

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