Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

A Straightforward Approach for the One-pot Synthesis of Cyclic Polymer from RAFT Polymer *via* Thiol-Michael Addition

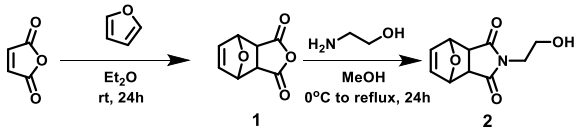
Junfei Zhao, Yanyan Zhou, Yu Zhou, Nianchen Zhou, Xiangqiang Pan, Zhengbiao Zhang* and Xiulin Zhu

Suzhou key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, China. Tel/Fax: 86-512-6588-2787.

*To whom correspondence should be addressed. E-mail: zhangzhengbiao@suda.edu.cn

Synthetic procedures

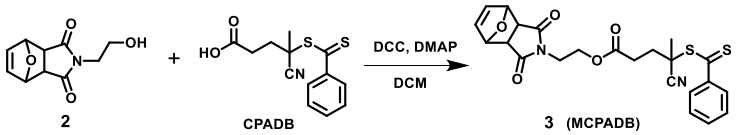
Synthesis of 4-(2-Hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione[1]



4,10-Dioxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (1): Maleic anhydride (40.0 g, 408 mmol) was completely dissolved in 350 mL of anhydrous ether at room temperature. Furan (44.2 mL, 612 mmol) was added and the clear solution stirred for 24 h. The mixture was variable turbidity, and the resulting white crystals were collected by filtration and washed with 3 × 30 mL of anhydrous ether. Obtained was 57.5 g as white powder, Yiled: 85%.[1]H NMR (300 MHz, $CDCl_3$, 298 K, ppm, δ): 3.18 (s, 2H, -C<u>H</u>-), 5.46 (s, 2H, -C<u>H</u>O-), 6.58 (s, 2H, CHvinyl).

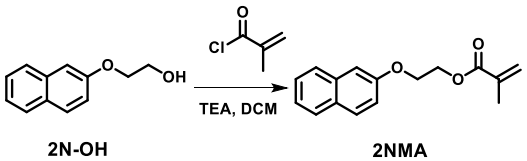
4-(2-Hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (2): The compound 1 (10.00 g, 60.0 mmol) suspended in anhydrous MeOH (150 mL) was added into a 250 mL round-bottomed flask equipped with a magnetic stirrer, and the mixture was cooled to 0 ℃. A solution of ethanolamine (3.6 mL, 60.0 mmol) in MeOH (20 mL) was added dropwise to the above mixture, the resulting clear solution was stirred for additional 10 min at 0 ℃, then an hour at ambient temperature, and finally refluxed at 70 ℃ overnight and the solution turned orange. After the mixture was cooled to ambient temperature and product began to crystallize, white crystals were collected by filtration and washed with 3 × 10 mL of cold anhydrous MeOH to give **2** (1.81 g, 73% yield) as a white solid. [1]H NMR (300 MHz, $CDCl_3$, 298 K, ppm, δ): 2.23 (bs, 1H, -O<u>H</u>), 2.90 (s, 2H, -C<u>H</u>-), 3.69-3.72 (m, 2H, -NC<u>H_2</u>-), 3.75-3.78 (m, 2H, -C<u>H_2</u>OH), 5.29 (s, 2H, -C<u>H</u>O-), 6.53 (s, 2H, CHvinyl), and the result accordant with literature cite.

Synthesis of protected-maleimide RAFT agent (MCPADB)



Protected maleimide alcohol (0.50 g, 2.4 mmol), 4-Cyanopentanoic Acid Dithiobenzoate (CPADB, 0.55 g, 2.0 mmol) which was synthetized according to the literature[2], DMAP (49 mg, 0.4 mmol) mixing with anhydrous CH_2Cl_2 (DCM, 30 mL) were added into a 100 mL round-bottomed flask equipped with a magnetic stirrer at room temperature. Then DCC (0.41 g, 2.0 mmol) was dissolved in DCM (10 mL) and added dropwise to the above mixture, which was stirred for 12 hours subsequently at ambient temperature and the white precipitate byproduct was filtered off, the filtrate was washed with brine and water, the combined organic phase was dried with anhydrous Na_2SO_4, after the solvent was removed by rotary evaporation, the crude product was chromatographed on a silica gel column. Eluting with a mixed solvent of hexane/EA (v/v = 2/1) afforded the pure compound **3** (MCPADB) as a pink oil. Yiled: 70%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm, δ): 7.91 (t, 2H, -Ar), 7.58 (t, 1H, -Ar), 7.40 (t, 2H, -Ar), 6.50 (t, 2H, CHvinyl), 5.24 (t, 2H, -C<u>H</u>O-), 4.27 (t, 2H, -C<u>H$_2$</u>O-), 3.76 (t, 2H, -NC<u>H$_2$</u>-), 2.87 (m, 2H, -C<u>H</u>-), 2.35-2.64 (m, 4H, -COC<u>H$_2$</u>C<u>H$_2$</u>-), 1.91 (s, 3H, -C<u>H$_3$</u>). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, ppm, δ): 222.37, 176.06, 171.23, 144.56, 136.54, 133.03, 128.58, 126.71, 118.49, 80.95, 61.13, 47.49, 45.73, 37.70, 33.16, 29.64, 24.07. (**Figure S1**.)

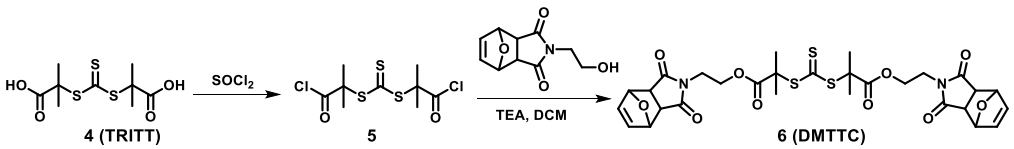
Synthesis of functional monomer with naphthol (2NMA)



2-(Naphthalen-2-yloxy) ethanol (2N-OH, 3.00 g, 15.9 mmol) which was synthesized according to the literature[3] dissolved in 25 mL of DCM were added in a 50 mL round-bottomed flask equipped with a magnetic stirrer, and TEA (3.31 mL, 23.9 mmol) was added to the mixture and cooled to 0 ℃. Methacryloyl

chloride (2.50 g, 23.9 mmol) in 10 mL of DCM was added dropwise within 30 min. The reaction mixture was stirred at 0 ℃ for another 1 h, then it was placed in room temperature with stirring for 4 hours. After filtration, the mixture was washed with saturated aq. $NaHCO_3$. The aqueous phase was again extracted with DCM, and the combined organic phase was dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography over silica gel eluting with hexane/ethyl acetate (15/1) to give white solid (yield = 3.46 g, 85%).^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm, δ): 7.80 (m, 3H, naphthalene), 7.49-7.34 (m, 2H, naphthalene), 7.22-7.16 (m, 2H, naphthalene), 6.20 (m, 1H, CHvinyl), 5.62 (m, 1H, CHvinyl), 4.60 (t, 2H, -OC$\underline{H}_2$CH_2O-), 4.36 (t, 2H, -OCH_2C$\underline{H}_2$O-), 2.00 (t, 3H, -C$\underline{H}_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, ppm, δ):167.39, 156.57, 136.05, 134.48, 129.57, 129.17, 127.70, 126.81, 126.50, 126.12, 123.86, 118.89, 106.93, 65.99, 63.12, 18.35. (**Figure S7**)

Synthesis of protected-maleimide RAFT agent (DMTTC)

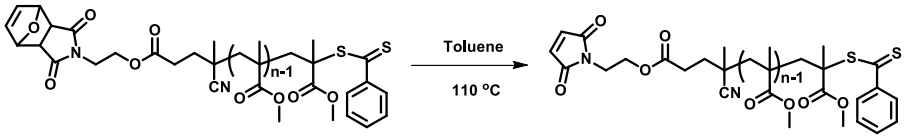


S,S'-Bis(α, α'-dimethyl-α''-acetic acid)-trithiocarbonate (TRITT, 2.0 g, 7.08 mmol) which was synthesized according to the literature[4], and $SOCl_2$ (20 mL) were added in a 50 mL round-bottomed flask equipped with a magnetic stirrer. Then the mixture was refluxed (70 ℃) with stirring for 4 hours. The reaction mixture was cooled to room temperature and removed the excess $SOCl_2$ to get the crude product (**5**), which was used for the next step without further purification.

Protected maleimide alcohol (**2**, 3.72 g, 17.7 mmol) and TEA (2.45 mL, 17.7 mmol) were dissolved by DCM (20 mL) in a 50 mL round-bottomed flask. All the compound **5** was dissolved by DCM (20 mL) and added dropwise to the above solution at 0 ℃. Then the mixture was allowed to react at room temperature and stirred overnight. After the reaction mixture was filtered and the filtrate was concentrated, it was washed

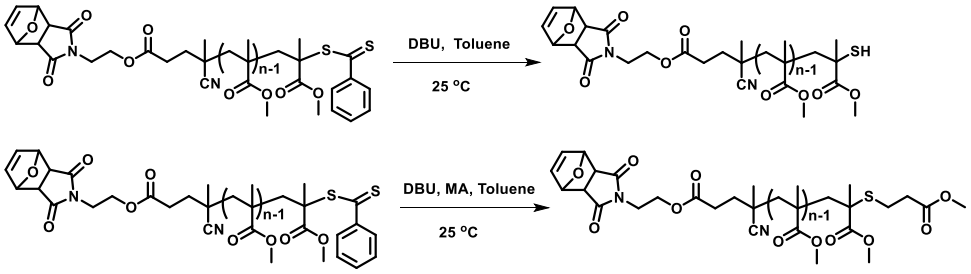
with saturated sodium bicarbonate solution and water respectively, the combined organic phase was dried with anhydrous Na_2SO_4, the crude product was purified by flash column chromatography. Eluting with a mixed solvent of hexane/EA (v/v = 1/2 to 1/4) to afford yellow solid (1.5 g, 32% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, ppm, δ): 6.52 (s, 4H, CHvinyl), 5.26 (s, 4H, -C<u>H</u>O-), 4.22 (t, 4H, -$CH_2C\underline{H}_2$O-), 3.78 (t, 4H, -N$C\underline{H}_2$-), 1.61 (s, 12H, -$C\underline{H}_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, ppm, δ): 218.91, 175.88, 172.35, 136.55, 80.88, 62.18, 56.24, 47.50, 37.55, 24.93. (**Figure S8**)

Model reaction of deprotection of furan-protected maleimide of linear PMMA precursor



50 mg polymer was dissolved in 1 mL toluene and the solution was brought to reflux at 110 ℃ for about 8 hours. After the solvent was removed, the concentrated product was precipitated from an excess of hexane, and dried in vacuum at 25 ℃ to afford the target maleimide-terminated PMMA as a pink powder.

Model reaction of the ammonolysis of thiocarbonylthio group of the linear PMMA precursor



50 mg *l*-PMMA-1, a little amount reducing reagent ($Na_2S_2O_3$), 200 μL DBU, and toluene (1.0 mL) were added into a 5 mL ampoule. The mixture was degassed using three freeze/pump/thaw cycles, the reaction mixture was placed in room temperature and allowed to stir under argon for several hours. The crude mixture was turned from red to pale yellow, and transferred onto a short neutral alumina column to remove salts. After the solvent was removed, the concentrated product was precipitated from an excess of hexane, and dried in vacuo at 25 ℃ to afford the product as a white powder. In order to set up a model for the further

constructions as well as to confirm the activity of the thiol group, a representative thiol-Michael addition reaction was carried out. In the above system, an additional MA (100 μL) was added to the solution. The mixture was degassed using three freeze/pump/thaw cycles and stirred under argon at 25 ℃ for several hours. The mixture was then directly precipitated in hexane, filtered, and dried overnight in a vacuum oven at 25 ℃ to obtain a white solid.

Additional figures:

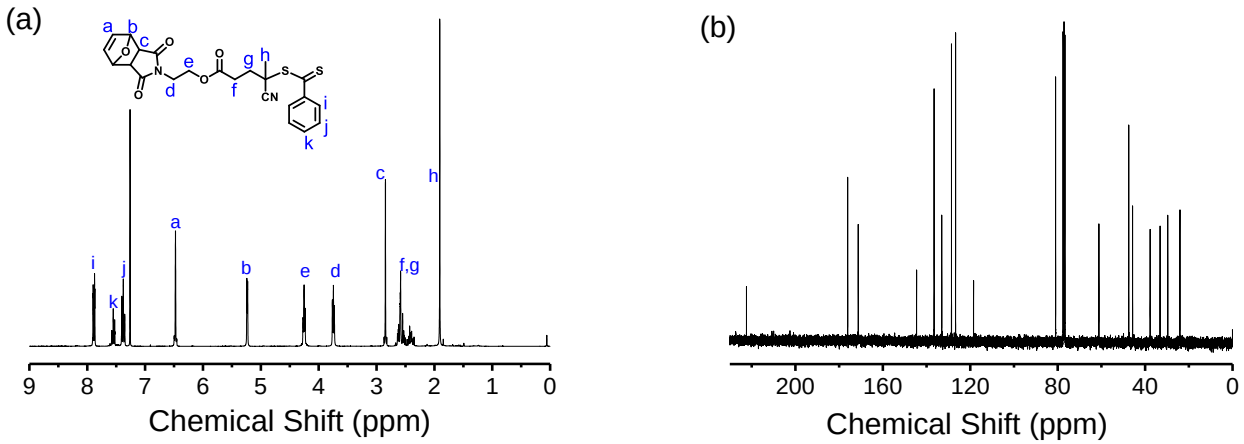


Figure S1. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of RAFT agent **MCPADB**.

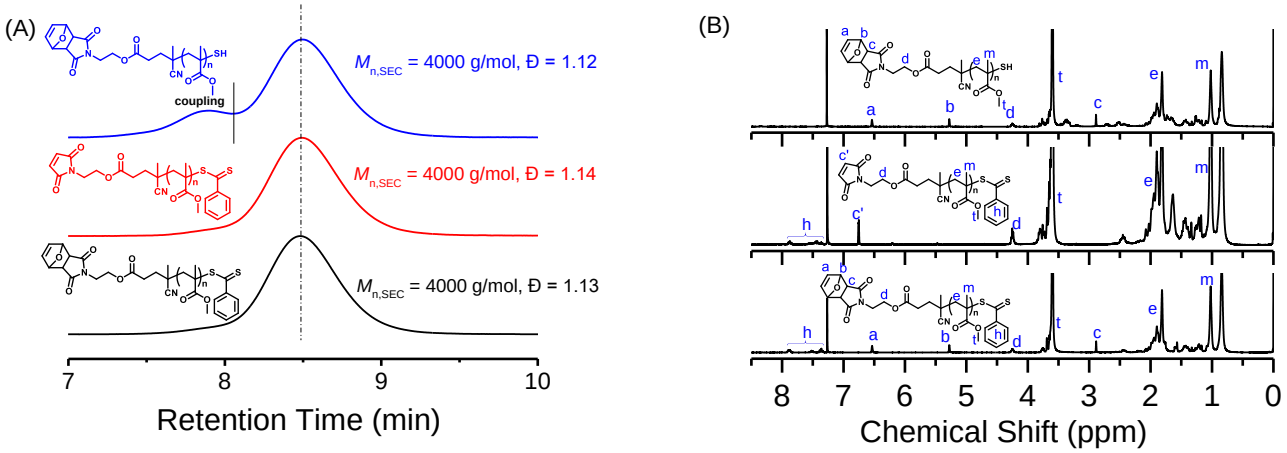


Figure S2. SEC RI traces (A) and ^{1}H NMR spectra (B) of each product from original linear polymer.

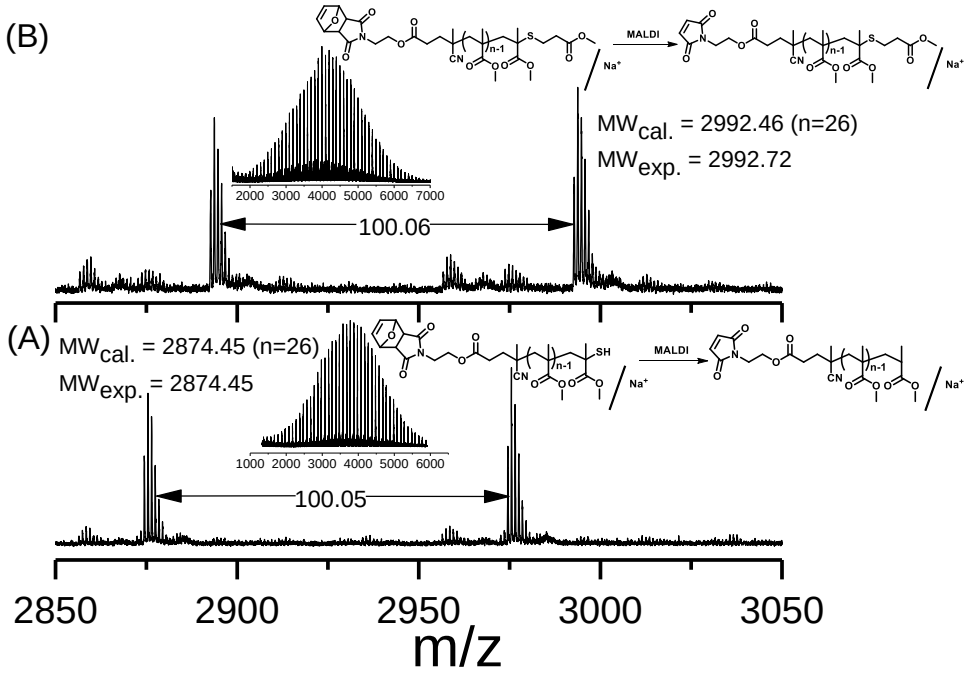


Figure S3. MALDI-TOF mass spectrum of the aminolysis product l-PMMA-1-SH (A) and thiol-Michael addition with MA (B) was acquired in reflection mode by using Na salt as the cationization agent and a DCTB matrix.

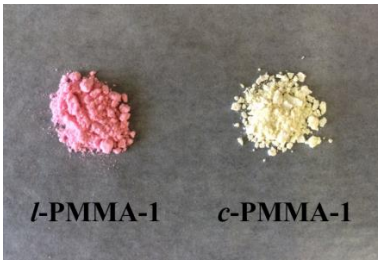


Figure S4. Visual inspection of ***l*-PMMA-1** (pink) and ***c*-PMMA-1** (white) indicating successful removal of dithioester group evidenced in a clear color change.

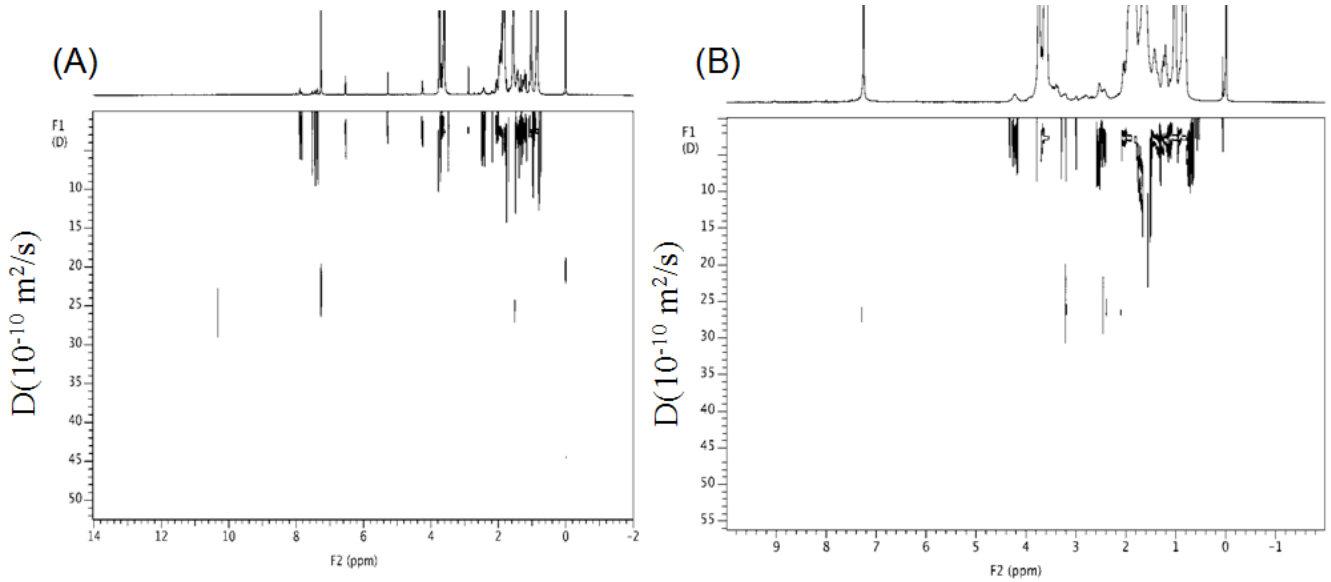


Figure S5. ^{1}H DOSY NMR spectra of linear polymer (*l*-PMMA-1, A) and cyclic polymer (*c*-PMMA-1, B).

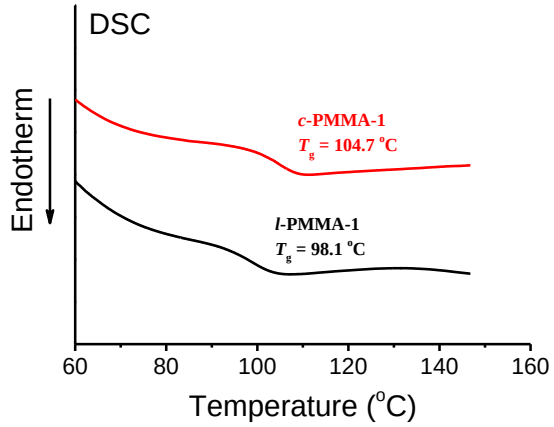


Figure S6. DSC traces for cyclic polymer compared with the linear precursor. Heating rate of 10 ℃ min^{-1}; T_g measured on the third cycle of a heat/cool/heat experiment.

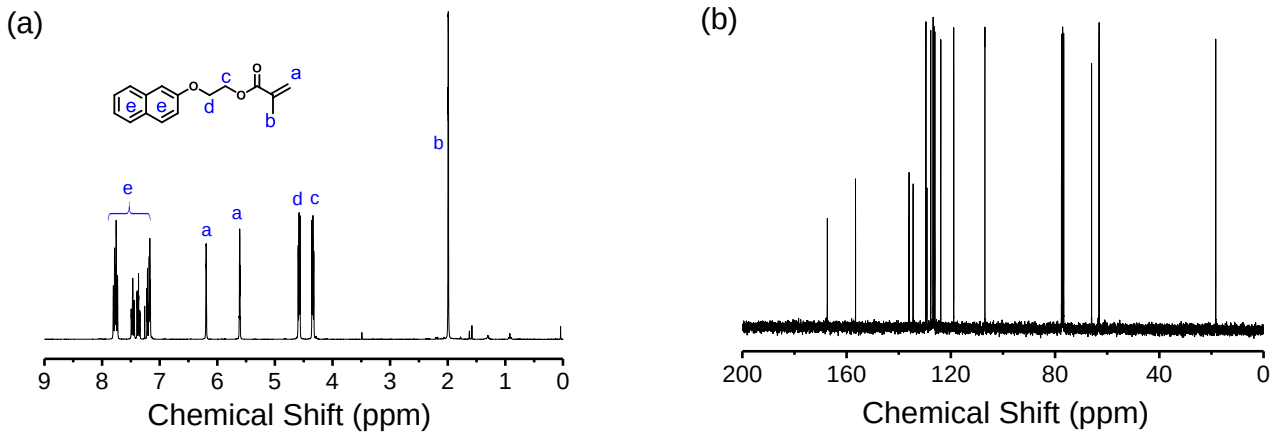


Figure S7. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of functional monomer 2NMA.

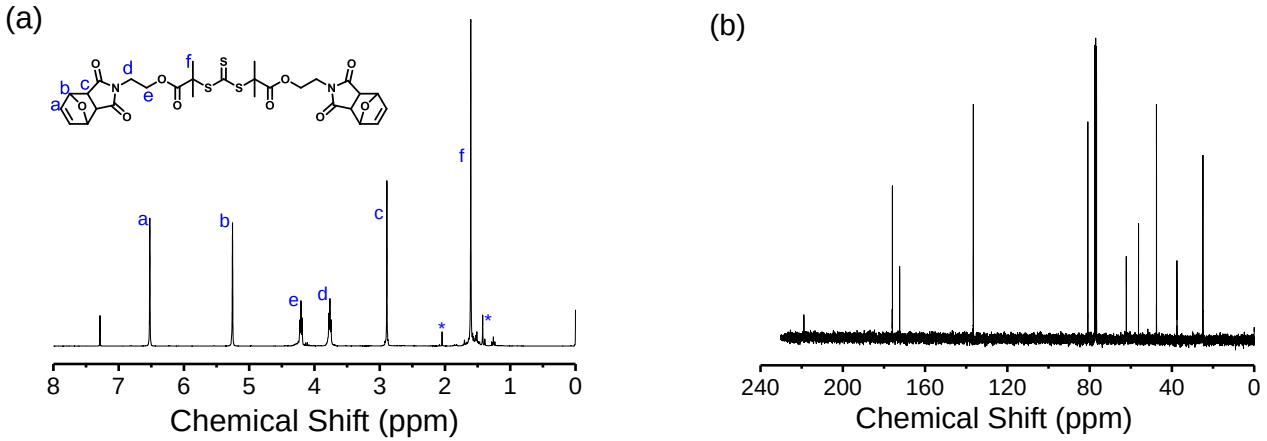


Figure S8. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of RAFT agent **DMTTC**.

Table S1. Summary of molecular characterizations

Sample	representative m/z value	Molecular Formula[a]	M_{Calcd} (Da)[a]	M_{Found} (Da)[a]
l-PMMA-1	M_{26}+Na-Furan-ArCSS[b]	$C_{142}H_{220}N_2NaO_{56}$	2872.43	2872.27
l-PMMA-SH	M_{26}+Na-Furan-S	$C_{142}H_{222}N_2NaO_{56}$	2874.45	2874.45
c-PMMA-1	M_{26}+Na-S	$C_{142}H_{222}N_2NaO_{56}$	2874.45	2874.53

[a] These data are based with a sodium ion ([M +Na]+). [b] ArCSS = thiocarbonylthio.

References

1 G. Mantovani, F. Lecolley, L. Tao, D. M. Haddleton, J. Clerx, J. J. L. M. Cornelissen and K. Velonia, *J. Am. Chem. Soc.* 2005, **127**, 2966-2973.

2 Y. Mitsukami, M. S. Donovan, A. B. Lowe and C. L. McCormick, *Macromolecules* 2001, **34**, 2248-2256.

3 K. Ghosh and I. Saha, *Org. Biomol. Chem.* 2012, **10**, 9383-9392.

4 J. T. Lai, D. Filla and R. Shea, *Macromolecules* 2002, **35**, 6754-6756.