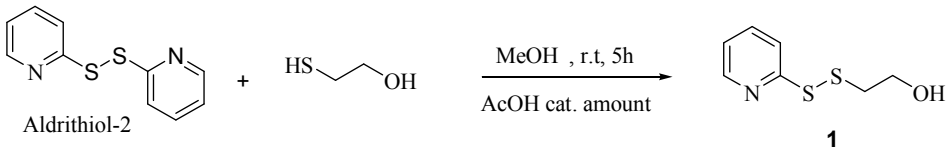
Supporting Information for the article

Exploring versatile sulfhydryl-chemistry in the chain end of a synthetic polylactide

Mijanur Rahaman Molla and Suhrit Ghosh*

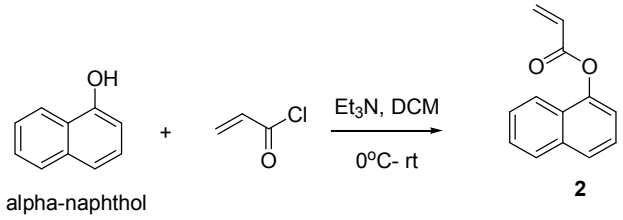
Indian Association for the Cultivation of Science, Polymer Science Unit
2A & 2B Raja S. C. Mullick Road, Kolkata, India-700032
Email: psusg2@iacs.res.in

Synthesis of the initiator: [1]

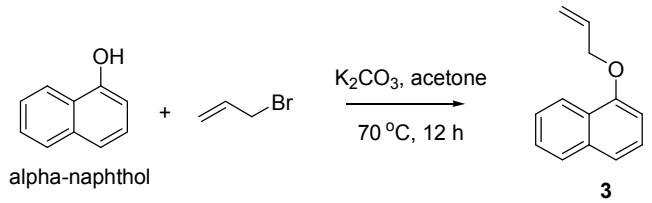


Compound 1: A solution of 2-mercaptoethanol (0.354 gm, 4.53mmol) in MeOH (10 ml) was drop-wise added to a solution of aldrithiol-2 (2 gm, 9.078 mmol) and catalytic amount (0.1 ml) of glacial acetic in MeOH (10 ml) and reaction mixture was stirred at room temperature under N_2 atmosphere for 5 h. Then stirring was stopped and MeOH was evaporated to get crude product as yellow oil. It was purified by column chromatography using silica gel (mesh 60-120) as a stationary phase and pet-ether/ethyl acetate as eluent to obtain the pure product as light green oil in 72% yield. . ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ (ppm) = 8.49-8.45 (m, 1H), 7.67-7.55 (m, 1H), 7.53-7.34 (m, 1H), 7.14-7.10 (m, 1H), 3.80-3.79 (t, 2H), 2.93-2.95 (t, 2H).

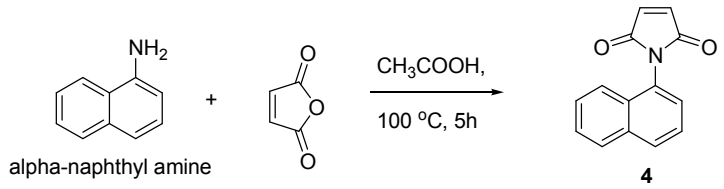
Synthesis of various thiol-reactive and thiol-containing small molecules:



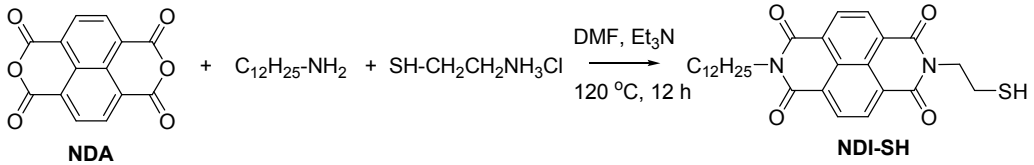
Compound 2: To an ice-cold solution of α-naphthol (500 mg, 3.468 mmol) and triethyl amine (0.55 ml, 6.96 mmol) in dry DCM (5 ml), a solution of acryloyl chloride (377 mg, 4.16 mmol) in dry DCM (5 ml) was added drop-wise and the reaction mixture was stirred at rt under inert atmosphere for 12 h. Stirring was stopped and it was washed with H_2O (3 x 30 ml), brine (1 x 30 ml) and saturated $NaHCO_3$ solution (30 ml) and then the organic layer was dried over anhydrous Na_2SO_4 and solvent was evaporated to get the crude product as light brown oil. It was purified by column chromatography using silica gel (60-120 mesh) as stationary phase and DCM as eluent to get the pure product as colorless oil in 85 % yield. . ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ (ppm) = 7.89-7.88 (m, 2H), 7.80-7.77 (m, 1H), 7.52-7.42 (m, 3H), 7.21-7.30 (m, 1H), 6.76-6.73 (m, 1H), 6.50-6.47 (m, 1H) 6.13-6.10 (m, 1H).



Compound 3[2]**:** α-naphthol (500 mg, 3.468 mmol), distilled allyl bromide (350 µl, 3.9 mmol) and anhydrous K_2CO_3 (495 mg, 3.5 mmol) were taken together in a reaction vessel along with dry acetone (10 ml) and the reaction mixture was refluxed under inert atmosphere for 5 h. Heating was stopped, acetone was evaporated and H_2O was added to the reaction vessel and the product was extracted with DCM and the combined organic layer was dried over anhydrous Na_2SO_4 and solvent was removed to produce the crude product as light brown oil. It was purified by column chromatography using silica gel (60-120 mesh) as stationary phase and petroleum ether as eluent and the pure product was isolated as pale yellow oil in 97% yield. . ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ (ppm) = 8.34 (d, 1H), 7.80 (d, 1H), 7.52-7.33 (m, 4H), 6.80 (d, 1H), 6.16-6.23 (m, 1H), 5.56-5.52 (m, 1H), 5.37-5.34 (m, 1H), 4.52 (d. 2H).



Compound 4[3]**:** α-naphthyl amine (500 mg, 3.49 mmol) and maleic anhydride (410 mg, 4.19 mmol) were mixed with 15 ml glacial acetic acid and the reaction mixture was stirred at 100 °C for 5 h. Reaction was stopped, acetic acid was evaporated under reduced pressure and water (20 ml) was added to the reaction mixture. The organic compound was extracted with DCM (2 x 20 ml) and the combined organic layer was washed with saturated $NaHCO_3$ solution (2 x 30 ml), 1N HCl (1 x 30 ml) solution and brine (1 x 30 ml). Organic extract was then dried over anhydrous Na_2SO_4 and solvent was evaporated to produce the desired product as brown solid in almost quantitative yield. As from TLC and ^{1}H NMR it was found to be pure enough, it was used for polymer functionalization without any further purification. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ (ppm) = 7.97-7.92 (m, 2H), 7.50-7.57 (m, 2H), 7.30 (d, 1H), 6.98 (s, 2H).



NDI-SH: Naphthalene dianhydride (1 gm, 3.72 mmol), cystamine hydrochloride (423 mg, 3.72 mmol), dodecyl amine (690 mg, 3.72 mmol) and triethyl amine (564 mg, 5.58 mmol) were taken in a reaction vessel along with dry DMF (25 ml) and the contents were stirred at 120 °C under inert atmosphere for

12h. During the course of the reaction lots of solid precipitate came out. Heating was stopped after 12 h and contents were cooled to rt and solid precipitate was filtered and washed with MeOH. It was then purified by column chromatography using silica gel (60-120 mesh) as stationary phase and dichloromethane as eluent to get the desired product as pale yellow solid in only 5 % yield. Very low yield in this case can be attributed to possible dimmerization of cystamine hydrochloride by oxidation of the thiol group which in principle can react with NDA to produce oligomers/polymers which might have been precipitated out during the reaction. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ (ppm) = 8.75 (s, 4H), 4.59 (t, 2H), 4.17 (t, 2H), 3.15 (t, 2H), 1.72 (m, 2H), 1.35-1.20 (m, 18H), 0.87 (t, 3H).

Additional figures:

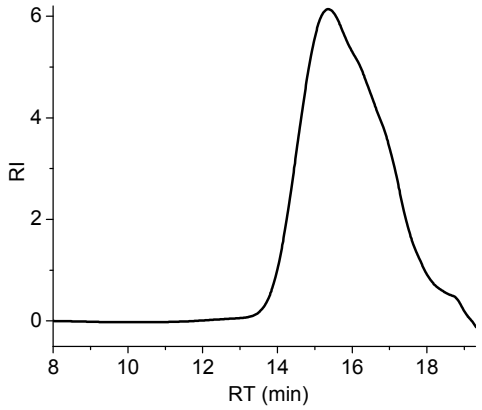


Figure S1: GPC traces of the **P1** in THF. Molecular weight and PDI were calculated with respect to PMMA standards. M = 7200 and PDI = 1.2

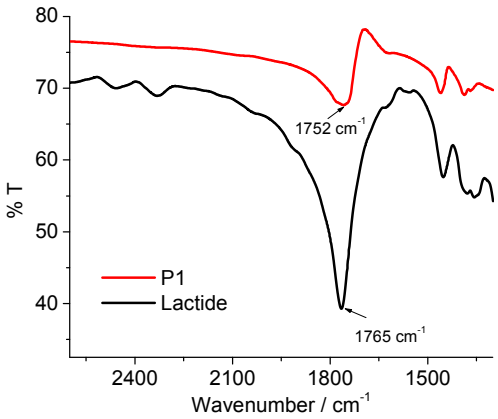


Figure S2: FT-IR spectra of the lactide monomer and **P1**in KBR pellet

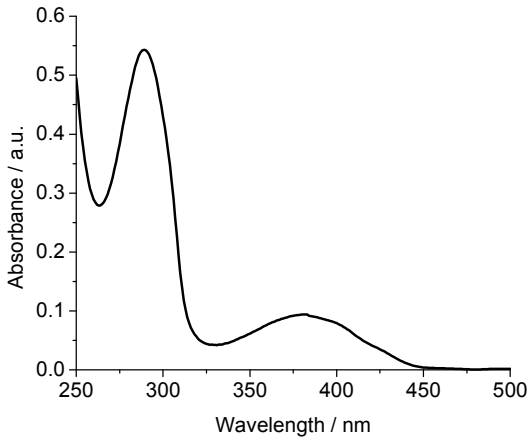


Figure S3: UV/ Vis spectrum of 2- pyridothione in THF. Concentration = 0.1 mM, Temperature = 25°C, path length of cuvette = 1cm

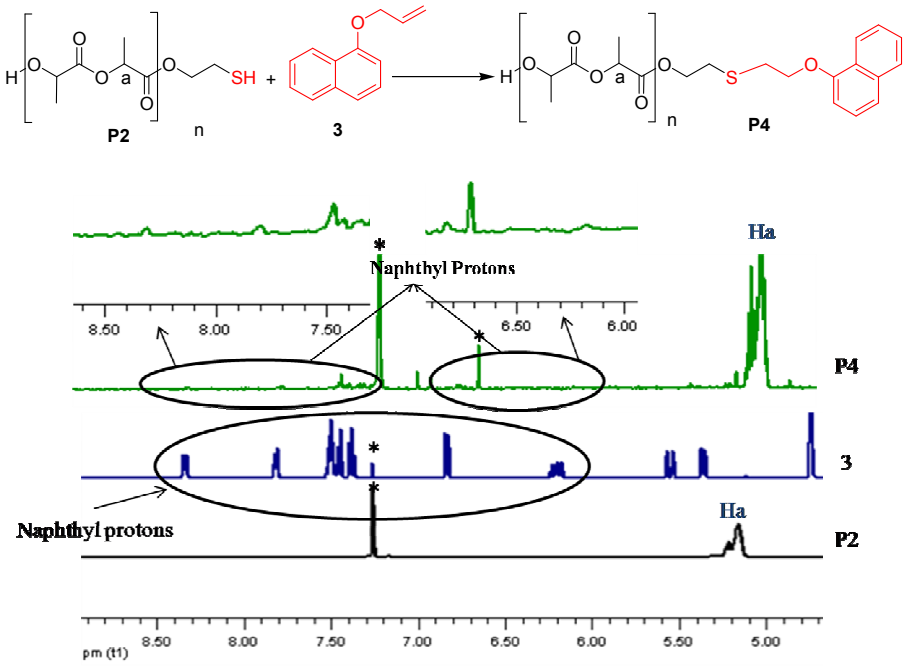


Figure S4: Selected region of ^{1}H NMR spectra of **P2, 3** and **P4** in $CDCl_3$ (* indicates peaks coming from the solvent)

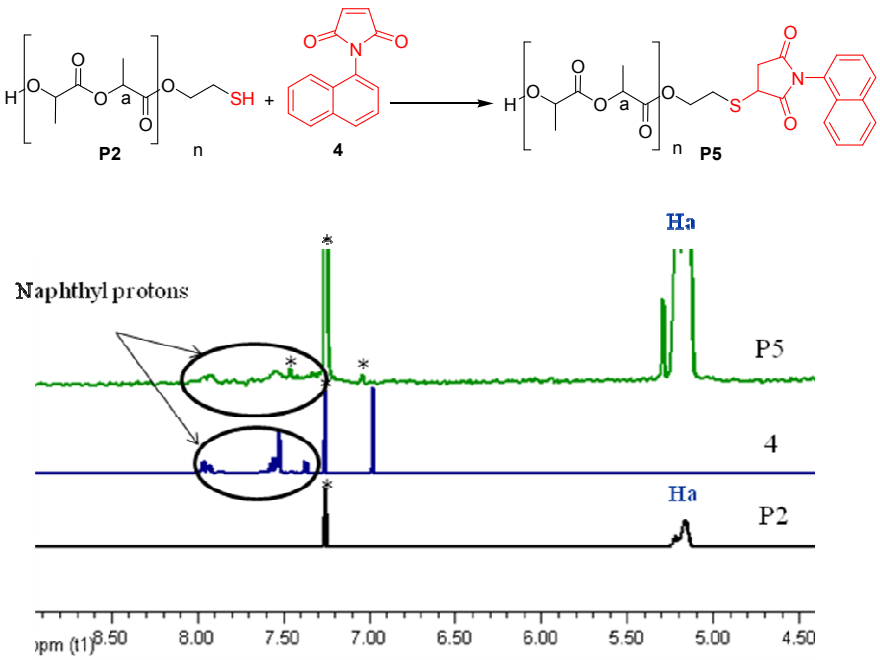


Figure S5: Selected region of ^{1}H NMR spectra of **P2, 4** and **P5** in $CDCl_3$ (* indicates peaks coming from the solvent)

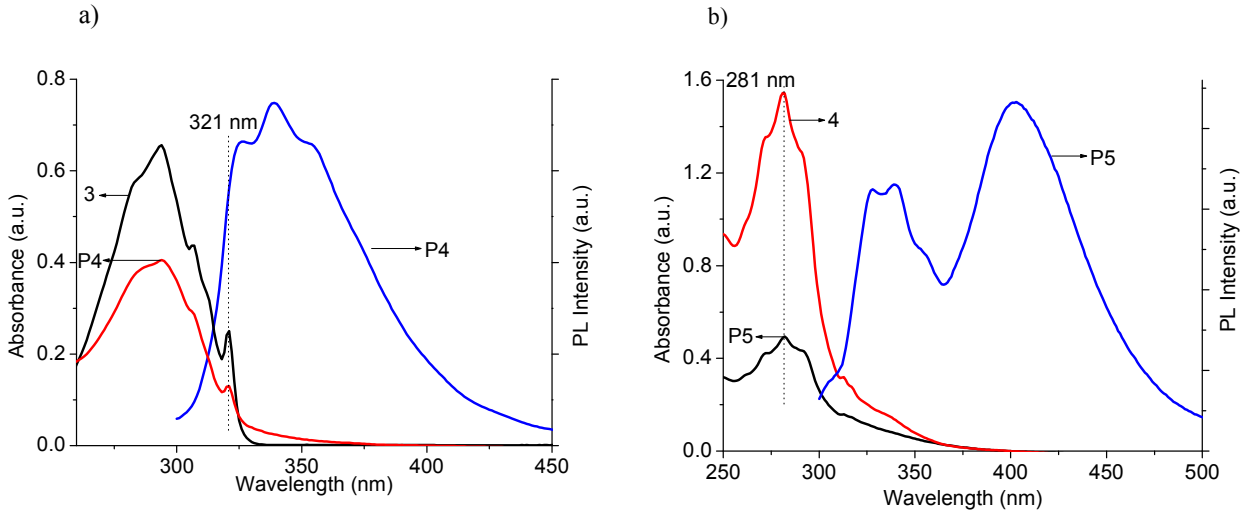


Figure S6: (a) UV/Vis absorption spectra of **P4** (0.5 mg/ mL) and compound **3** (0.1 mM) and photoluminescence spectra of **P3** (0.5 mg/ ml) in THF (λ_{ex} = 290 nm). (b) UV/vis absorption spectra of **P5** (0.5 mg/ ml) and compound **4** (0.1 mM) and photoluminescence spectra of **P5** (0.5 mg/ ml) in THF (λ_{ex} =

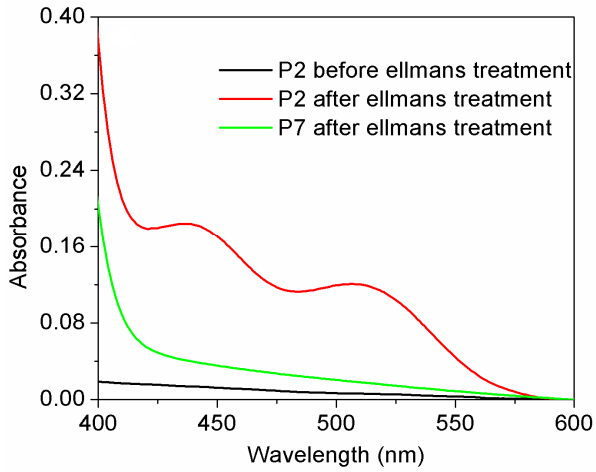


Figure S7: Ellman's test results with various polymers in THF. Concentration of polymer = 0.5 mg/ ml and Ellman's reagent = 2.5 mg/ ml

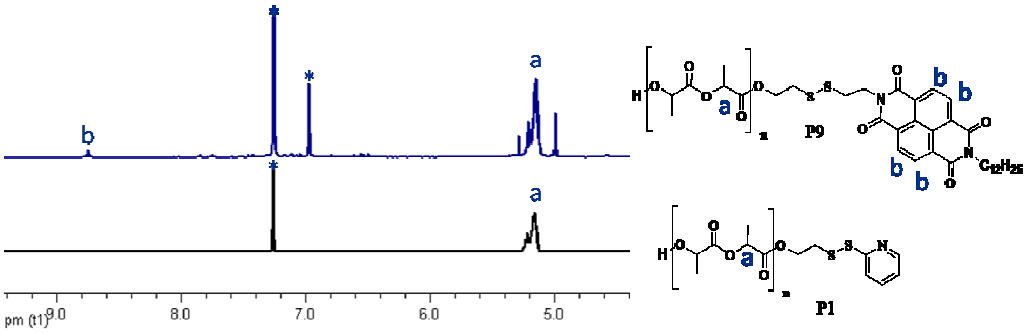


Figure S8: Selected region of ^{1}H NMR spectra of **P1** and **P9** in $CDCl_3$ (* indicates peaks coming from the solvent)

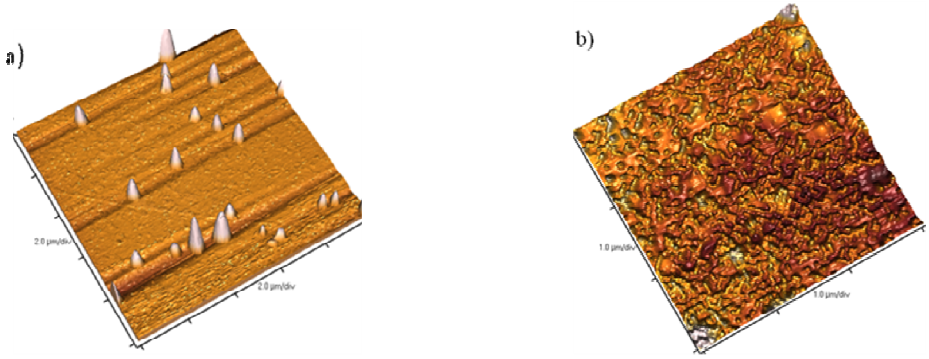


Figure S9: (a) 3D view of the AFM image of (a) **P1** and (b) **P9**. In both cases THF solutions (concentration = 1mg/ ml) were drop casted on a silicon wafer and air dried before images were taken.

References:

1. Ghosh, S.; Basu, S.; Thayumanavan, S. *Macromolecules* **2006**, *39*, 5595-5597.
2. Yoshida, M.; Higuchi, M.; Shishido, K. *Org. Lett*. **2009**, *11*, 4752-4755.
3. Nötha, J.; Frankowski, K. J.; Neuenswanderb, B.; Aubéb, J.; Reisera, O. *J. Comb. Chem*. **2008**, *10*, 456-459.