Supporting information

Photoswitchable ring-opening polymerization of lactide catalyzed by azobenzene-based thiourea

Zhongran Dai, Yaqin Cui, Changjuan Chen, and Jincai Wu*

Experimental

Materials and Methods

PMDETA and BnOH were distilled from CaH_2; *L*-lactide and *rac*-lactide were purchased from Daigang BIO Engineer Limited Co. of China and recrystallized from toluene; ^{1}H NMR were recorded on a JNM_ECS 400 MHz, ^{1}H NMR chemical shifts are reported in ppm versus residual protons in deuterated solvents as follows: δ 7.26 ppm for chloroform-d. The molecular weights (M_n and M_w) and the molecular mass distributions (M_w/M_n) of the polymer samples were measured by gel permeation chromatography (GPC) at 25 ^{o}C using THF as the solvent, an eluent flow rate of 1 mL/min, and narrow polystyrene standards as reference samples. The measurements were performed using a Waters 1525 binary system that was equipped with a Waters 2414 RI detector using two Styragel columns (10^2-10^6 kg/mol). Each reported value is the average of two independent measurements and was corrected using a factor of 0.58 for polylactide according to the literature. Photoisomerization of UV/Vis samples was accomplished by irradiation with a 40 W black light lamp (λ = 330-400 nm, λ_{max} = 365 nm).

Synthesis of **1**: The synthesis of **1** was according to the literature,[1] 3,5-Bis(trifluoromethyl)phenyl isothiocyanate (288 μl, 1.58 mmol) was added under Ar atmosphere to a solution of (*E*)-3-((3-Nitrophenyl)diazenyl)aniline (0.35 g, 1.43 mmol) in dry DCM (7.2 mL) and the mixture was stirred 4 h. Then, the solvent was evaporated under reduced pressure and the crude mixture was purified by flash chromatography (from hexane/EtOAc 90:10 to hexane/EtOAc 70:30) to afford compound **1** in 59 % yield (0.43 g, 0.85 mmol). Characterization matched the literature. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (t, *J* = 2.0 Hz, 1H), 8.37 (ddd, *J* = 8.0, 2.0, 0.8 Hz, 1H), 8.27 (m, 2H), 8.01-7.99 (m, 3H), 7.93 (t, *J* = 2.0 Hz, 1H), 7.84 (s, 1H), 7.76-7.68 (m, 3 H), 7.53 (ddd, *J* = 8.0, 2.0, 0.8 Hz, 1H).

Typical polymerization of *L*-lactide (entry 1, table 1)

Under an inert atmosphere, *L*-Lactide (0.144 g, 1.0 mmol) was added to a solution of

1 (0.015 g, 0.02 mmol), PMDETA (4.2 μl, 0.02 mmol), and BnOH (2.0 μl, 0.02 mmol) in $CDCl_3$ (1 mL). After 24 h, the reaction was then quenched by the addition of benzoic acid (2 mol equivalents to base). Then the solution was concentrated under vacuum, and the polymer was recrystallized from dichloromethane and methanol. The final polymer was then dried under vacuum to constant weight.

Polymerization of *rac*-lactide in UV light

Under an inert atmosphere, compound **1** (0.02 mmol. 10.2 mg), PMDETA (0.02 mmol, 4.2 μl), and BnOH (0.02 mmol, 2 μl) were dissolved with 1.0 mL of $CDCl_3$ and placed in an NMR tube, This solution was irradiated at UV light for 3.0 h and then *rac*-LA (1.0 mmol, 0.144 g) was added. The tube was then submitted under continuous irradiation and the conversion was measured by ^1H NMR.

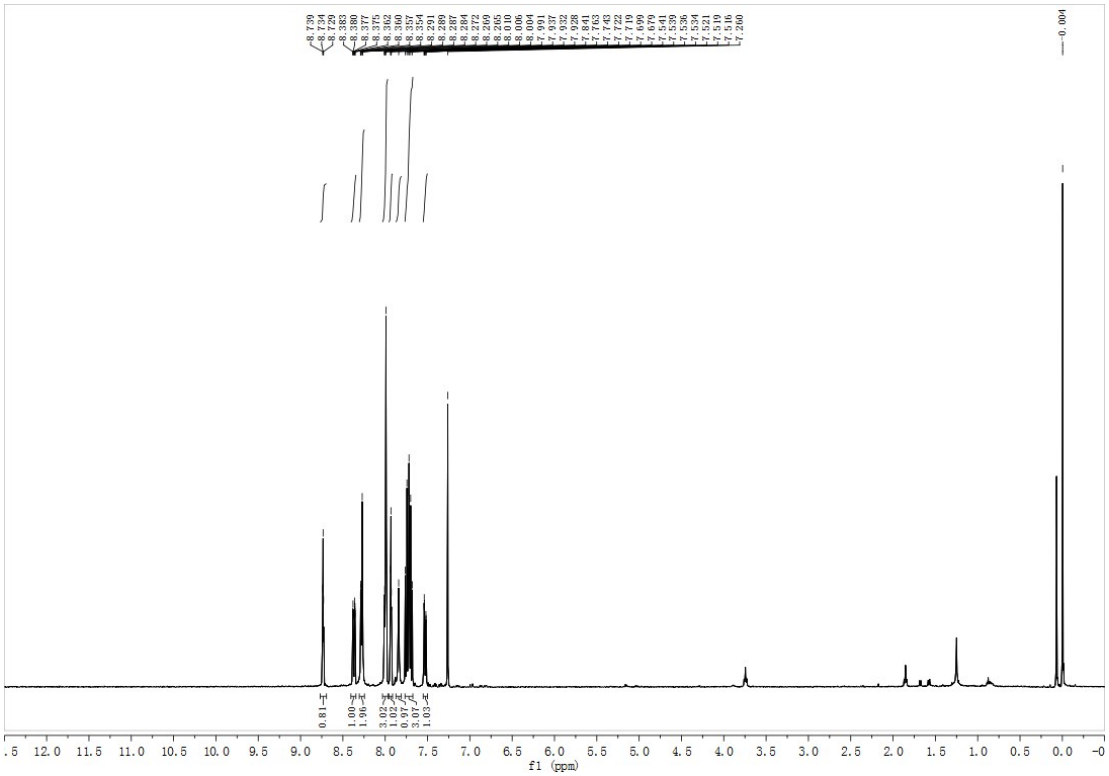

Figure S1 ^{1}H NMR spectrum (300 MHz, chloroform-d, 25 ^{0}C) of **1**.

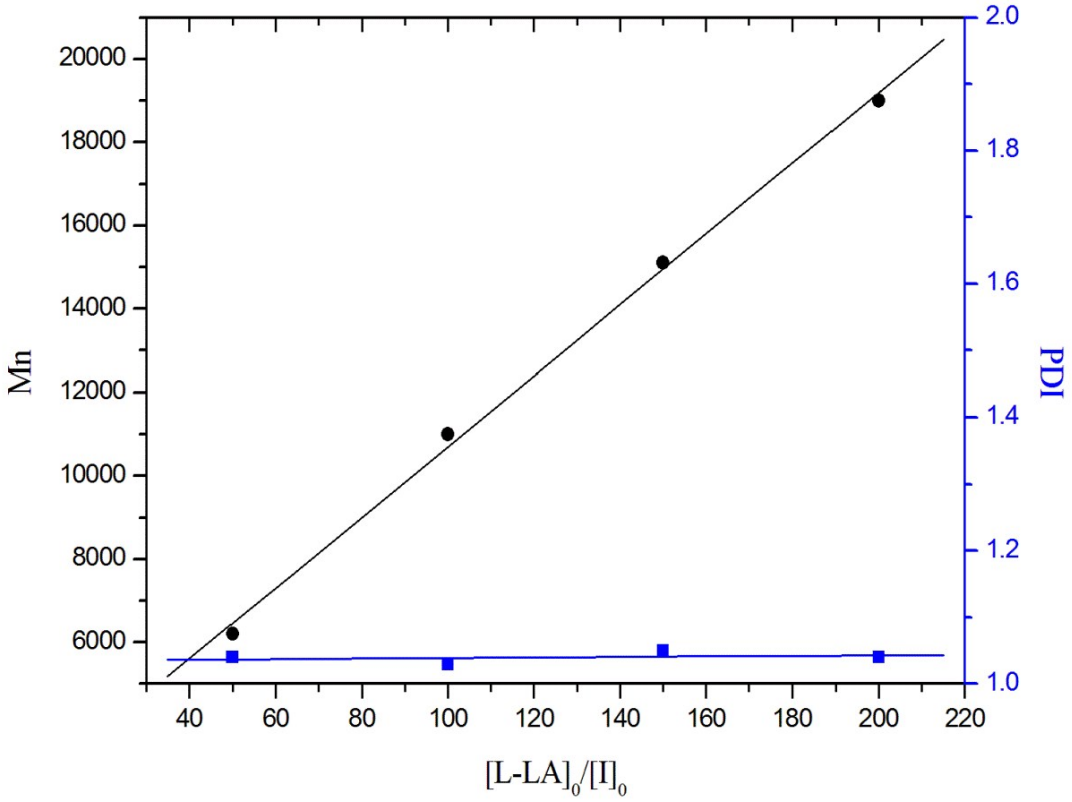

Figure S2 The relationship between the Mn (●) or the PDI value (■) of the polymer and the initial molar ratio $[LA]_0/[BnOH]_0$ is shown (entries 1-4, table 1)

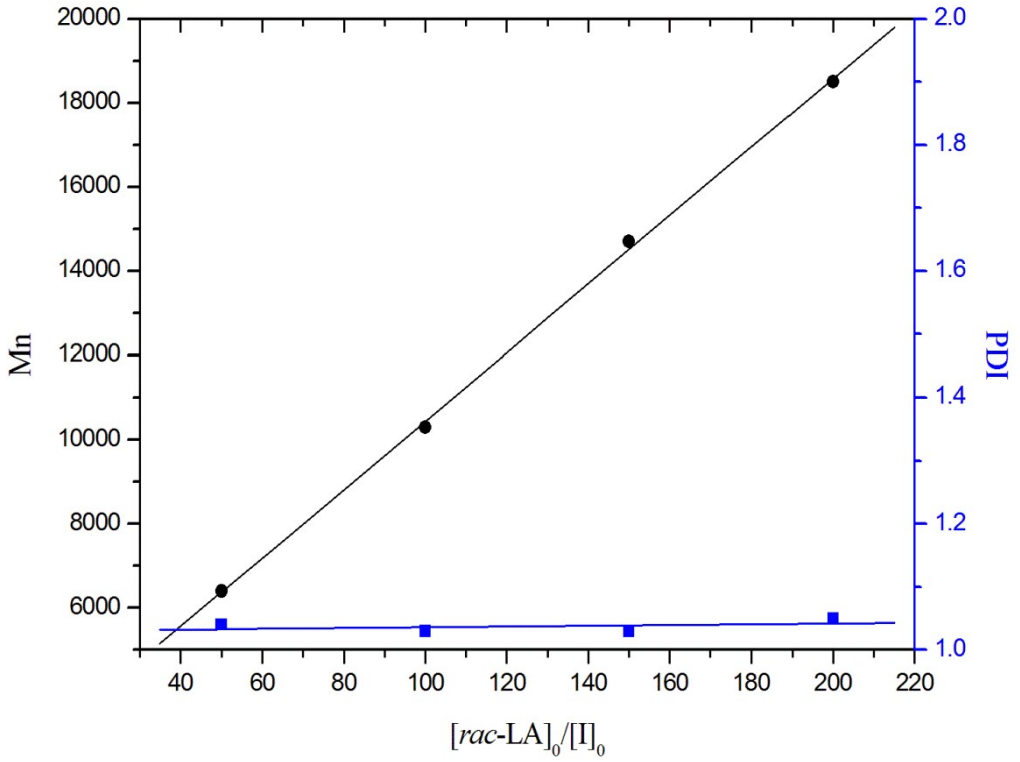

Figure S3 The relationship between the Mn (●) or the PDI value (■) of the polymer and the initial molar ratio $[LA]_0/[BnOH]_0$ is shown (entries 5-8, table 1).

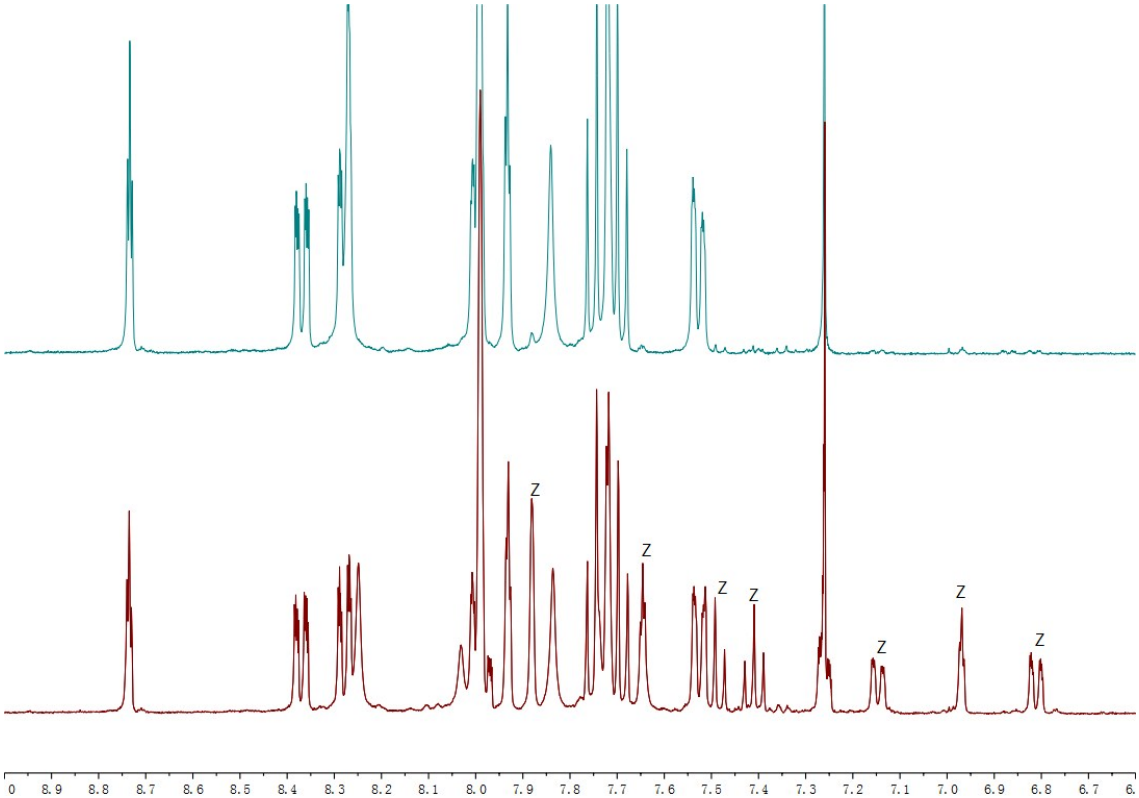

Figure S4 ^{1}H NMR spectra of compound **1** before UV irradiation (green) and after 3 h UV irradiation (red) (PSS = 34:66 *Z*/*E*)

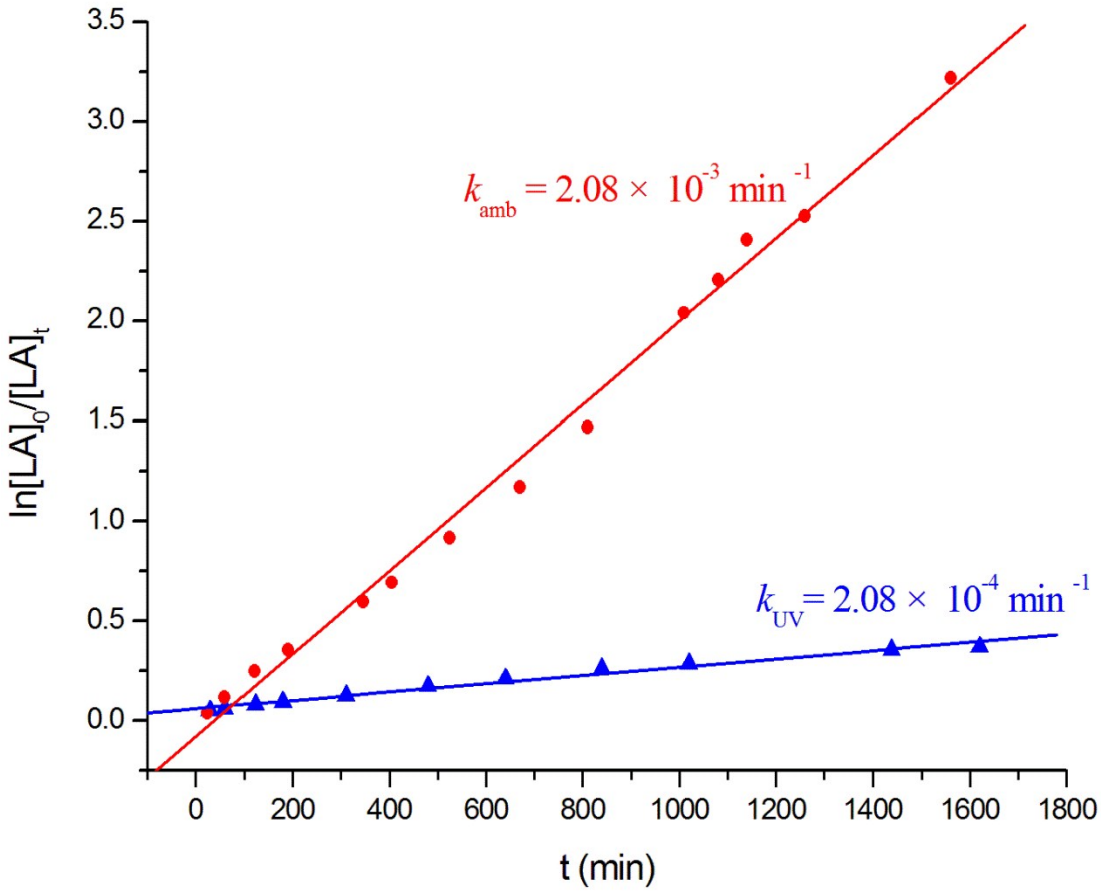

Figure S5 Plot of ln ($[LA]_0/[LA]_t$) vs time (min) for the ring opening polymerization of lactide catalyzed by **1**

References

1. L. Osorio-Planes, C. Rodríguez-Escrich and M. A. Pericas, *Org. Lett.,* 2014, **16**, 1704.