Supporting Information

Coil-to-rod transition of conjugated polymers prepared by cyclopolymerization of 1,6-heptadiynes

Eun-Hye Kang and Tae-Lim Choi*

Department of Chemistry, Seoul National University, Seoul 151-747, Korea

E-mail: tlc@snu.ac.kr

Experimental

Characterization

^{1}H NMR was recorded by Varian/Oxford As-500 (500 MHz for ^{1}H and ^{13}C) spectrometer and Agilent 400-MR (400 MHz for ^{1}H). UV–vis spectra were measured by Jasco Inc. UV/vis-Spectrometer V-550. Gel permeation chromatography (GPC) for the polymer analysis was carried out with Waters system (1515 pump, 2414 refractive index detector) and Shodex GPC LF-804 column on samples diluted in 0.001-0.003 wt% by THF (GPC grade, J. T. Baker®) and filtered with a 0.20-μm PTFE filter. Flow rate was 1.0 mL/min and temperature of column was maintained at 35 °C. For the MALLS-VIS-RI analysis (obtaining Mark-Houwink-Sakurada plot and shape parameter α), Wyatt triple detector, Dawn 8+ / Viscostar®II / Optilab®T-rEX were used. Dynamic Light Scattering (DLS) data were obtained in 1 g/L THF solution by Malvern Zetasizer Nano-S.

Materials

All reagents which are commercially available from Sigma-Aldrich® and Alfa Aesar®, without additional notes, were used without further purification. All of the monomers and Grubbs 3rd generation catalyst were prepared following the reported literature.[1] THF for the polymerization was distilled over sodium and benzophenone, and degassed by Ar bubbling for 10 minutes before using. For aging and GPC analysis, BHT-contained (104 ppm) GPC grade THF was purchased from J. T. Baker®. NMR solvent (THF-d_8, 99.50% D, 0.75 mL) was purchased from euriso-top® and used without further purification.

General polymerization procedure

A 5-mL sized screw-cap vial with septum was charged with monomer and a magnetic bar. The vial was purged with argon four times, and degassed THF was added ($[M]_0$= 0.5 M). The solution of initiator was added at once under vigorous stirring. The reaction was quenched by excess ethyl vinyl ether after desired reaction time, and precipitated in methanol. Obtained solid was filtered and dried *in vacuo*. (Caution: Do not dissolve the polymer after precipitation, because the isomerization can occur.)

Aging procedure and UV–vis spectra measurement of polymer solutions

After dissolving the polymers in various organic solvents (generally 0.2 g/l), it was left on the laboratory bench under fluorescent light. All of the UV–vis absorption spectra were obtained in THF with proper concentration.

In order to compare three data (^{1}H NMR, Huang-Rhys factor *S*, shape parameter α) in real-time, we followed this special procedure: (a) Prepare PDHDPM in THF-d_8 following the polymerization procedure (0.1 mmol of DHDPM in 0.2 mL of THF-d_8, M/I ratio=100). (b) After the monomer was fully converted to the polymer, dilute the solution (0.2 mL of reaction mixture + 0.5 mL of THF-d_8) for NMR measurement, and transfer it into sealed NMR tube. (c) Obtain initial ^{1}H NMR spectrum, and take 30 µl of the solution from the NMR tube by using micro-syringe. The extract was dried *in vacuo* and its *S* and α values were obtained from UV–vis absorption spectrum and viscosity analysis (see Figure S5 for the change of *S*). (d) Age the remaining polymer solution under irradiation of LED (blue, green) on NMR tube, and repeat (c) after 1, 2, 3, 5, and 8 hours. Control experiment (dark) was performed as same manner but the NMR tube was stored under the dark.

Light source	M_n (MALLS)	PDI (MALLS)
Blue LED	41.2 k	1.68
Green LED	47.8 k	1.42
Dark	37.3 k	1.81

Table S1. Characterization of PDHDPM prepared in THF-d_8 for the experiment of light irradiation

Increase of the hydrodynamic volume

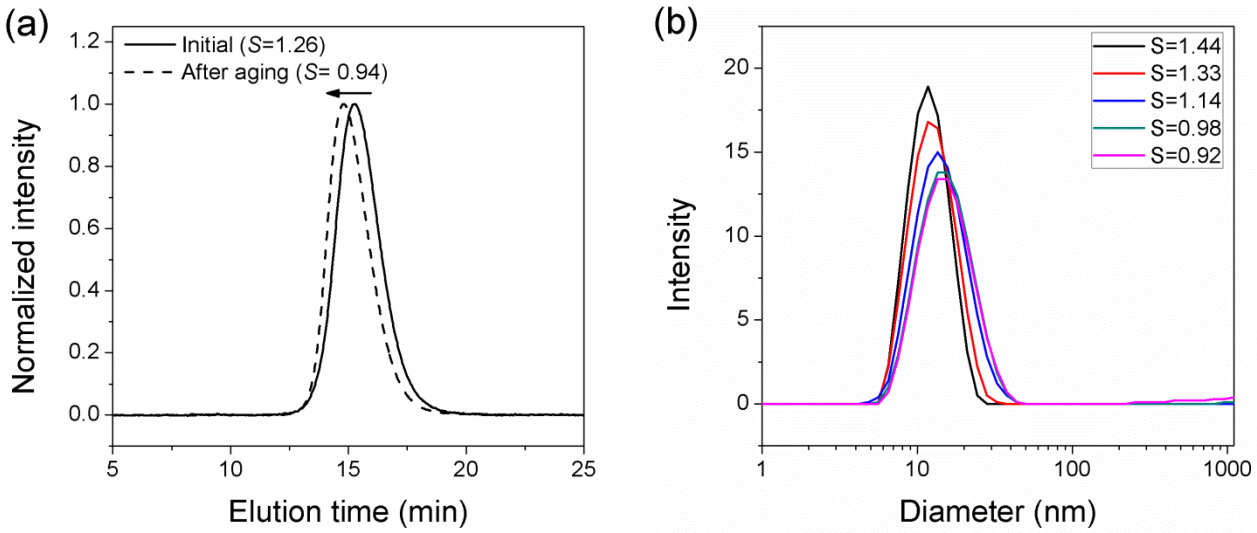


Figure S1. (a) SEC trace shift after aging, which indicates that the hydrodynamic volume of the polymer increased. (b) Hydrodynamic diameter change as *S* decreased.

Isomerization of other polymers

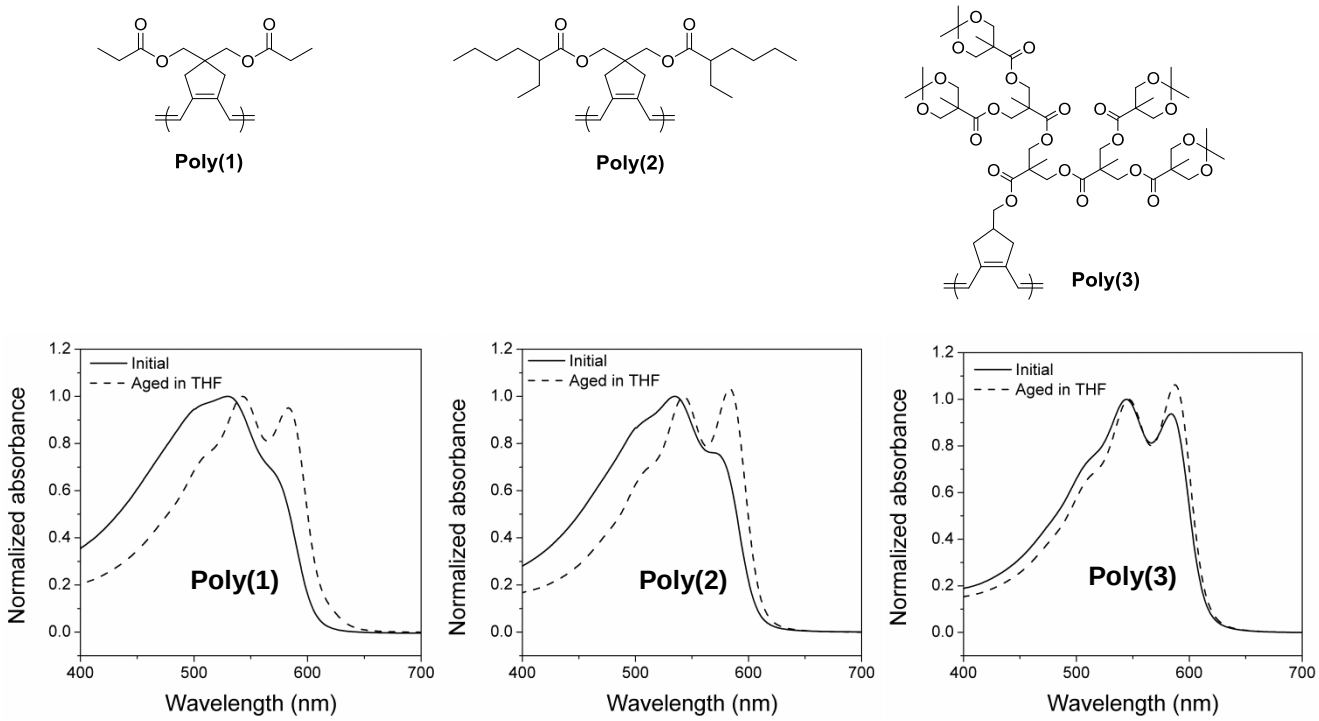
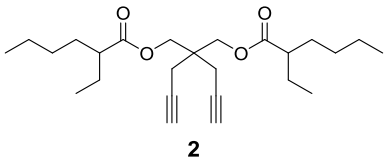


Figure S2. Changes in absorption spectra of substituted PCPVs. The syntheses of **1** and **3** was reported in the previous literature,[1] and **2** was prepared by following procedure.

Synthesis and characterization of 2



To a mixture solution of 4,4-bis(hydroxymethyl)-1,6-heptadiyne[2] (323.2 mg, 2.12 mmol), triethylamine (1.48 mL, 10.6 mmol) and 4-dimethylaminopyridine (DMAP) (13.0 mg, 0.106 mmol) in dichloromethane (6 mL), ethylhexanoyl chloride (0.80 mL, 4.67 mmol) was added dropwisly at 0 °C. The reaction mixture was stirred overnight at room temperature. The reaction was quenched by adding saturated $NaHCO_3$ aqueous solution and stirred for a few minutes. The mixture was washed with saturated NH_4Cl solution and extracted by ethyl acetate (75 mL*2). The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (ethyl acetate : hexane = 1 : 20, R_f = 0.24) to afford compound **2** as a pale yellow liquid (828.6 mg, 2.05 mmol, 96%). ^{1}H NMR (500 MHz,

$CDCl_3$): δ 0.88 (m, 12 H), 1.21-1.35 (m, 8 H), 1.43-1.66 (m, 8 H), 2.03 (t, 2 H), 2.29 (m, 2 H), 2.41 (d, 4 H), 4.11 (s, 4 H); ^{13}C NMR (125MHz, $CDCl_3$) : δ 11.8, 13.9, 22.1, 22.6, 25.4, 29.5, 31.7, 40.0, 47.4, 64.5, 71.6, 78.7, 175.8; HRMS (EI+): calcd. for $C_{25}H_{40}O_4$, 404.2926, found, 404.2925

Poly(2): ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (br m, 6 H), 1.27 (br m, 8 H), 1.40-1.75 (br m, 8 H), 2.32 (br m, 2 H), 2.40-2.95 (br m, 4H), 3.80-4.40 (br m, 4 H), 6.10-6.80 (br m, 2 H); ^{13}C NMR (125MHz, $CDCl_3$) : δ. 11.9, 14.0, 22.6, 25.5, 29.6, 31.6, 39.8, 43.0, 47.3, 66.9, 123.1, 137.6, 176.0

Solvent dependence on the rate of isomerization

PDHDPM solutions in chloroform, dichloromethane, chlorobenzene, dichloroethane, and THF were prepared (0.2 g/l) and aged under ambient condition. Absorption spectra were obtained after diluting each solution by 20 fold using THF (0.1 mL of mother solution + 1.9 mL of THF).

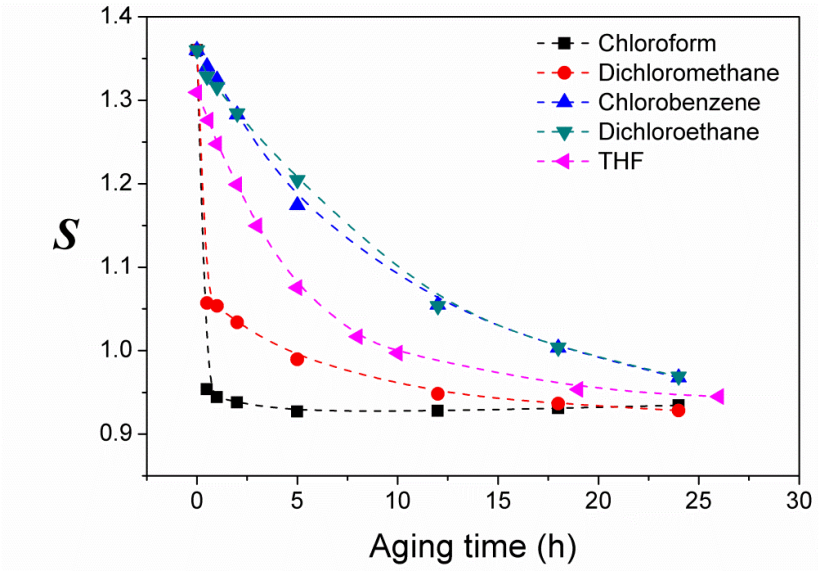


Figure S3. Time-dependent changes of Huang-Rhys factor *S* of PDHDPM in various organic solvents.

Concentration dependence on the rate of isomerization

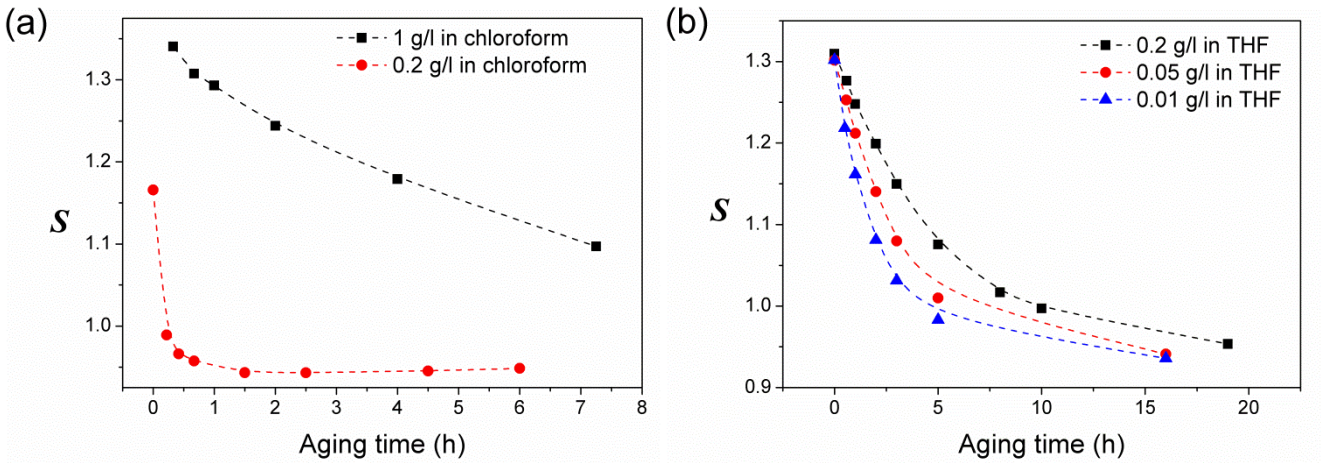


Figure S4. Time-dependent changes of *S* with different concentrations of PDHDPM solution in (a) chloroform and (b) THF.

Light and Temperature dependence on the rate of isomerization

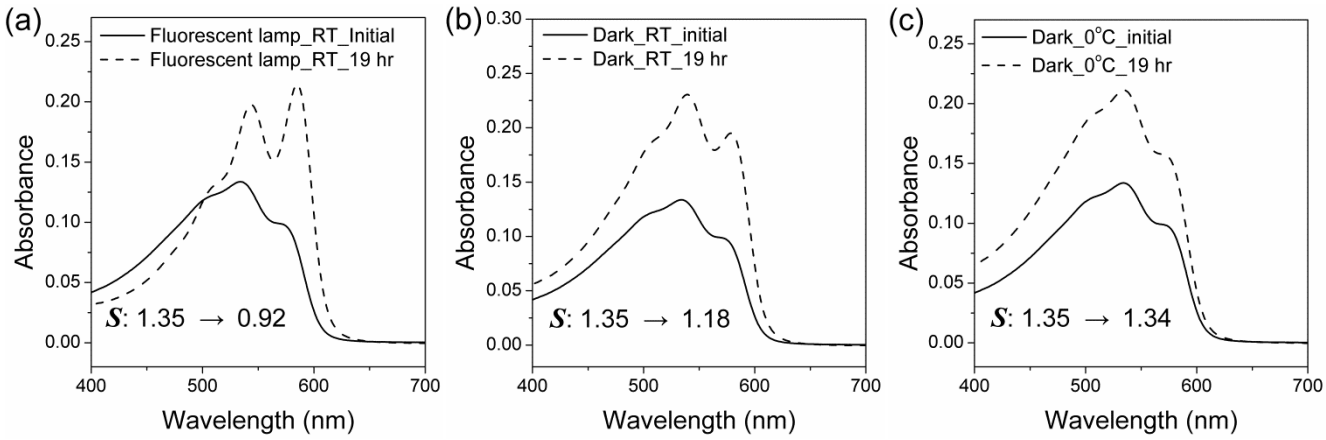


Figure S5. Changes in absorption spectra of PDHDPM solution in THF (0.1 g/l) under light- and temperature-controlled conditions.

Light source dependence on the rate of isomerization

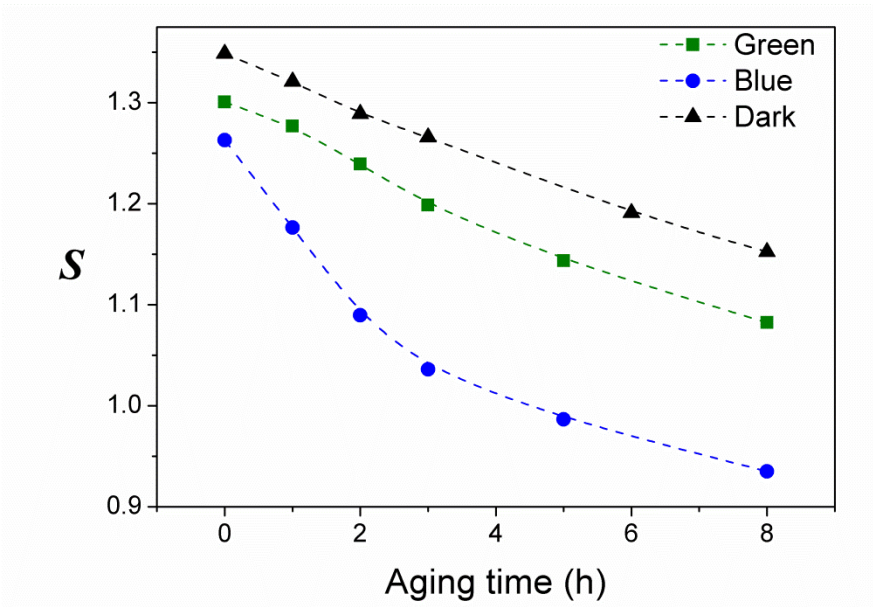
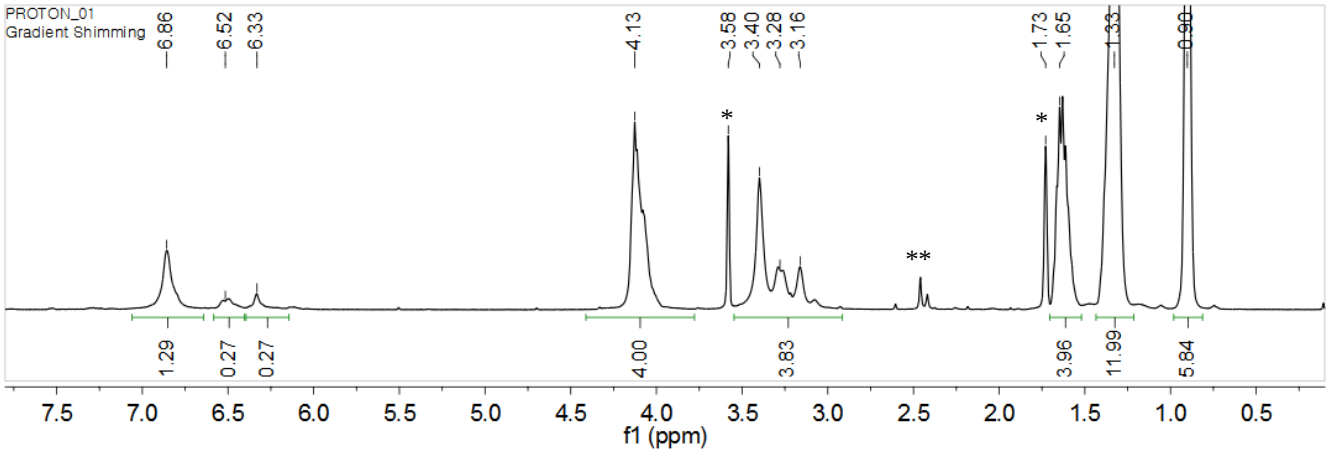


Figure S6. Light source effect on the isomerization of PDHDPM in THF-d_8 (50 g/l).

NMR characterization of polymers in THF-d_8
(*: THF, **: water)

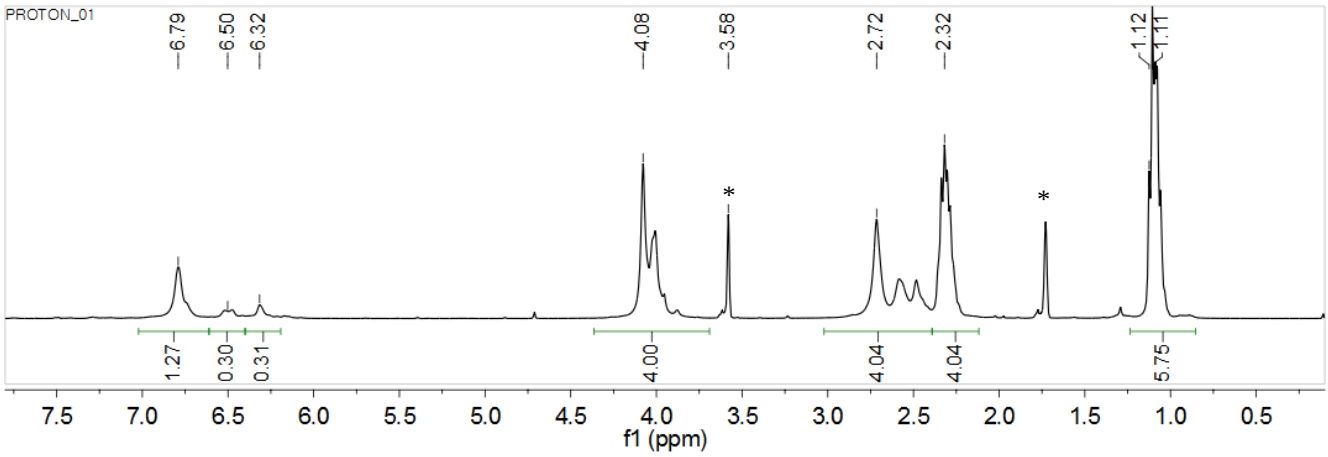
● *cis* : *trans* calculation = (integration of 6.33 ppm) : (integration of 6.86 ppm + 6.52 ppm)

Poly(PDHDPM)



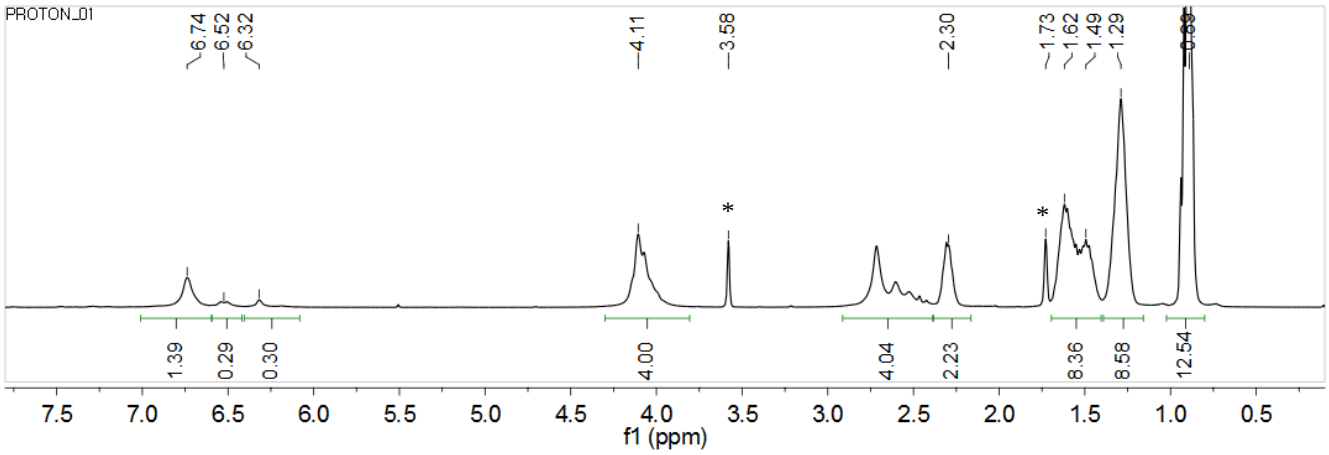
cis : *trans* = (0.27) : (1.29 + 0.27) = 1 : 5.8 (15% of *cis*)

Poly(1)



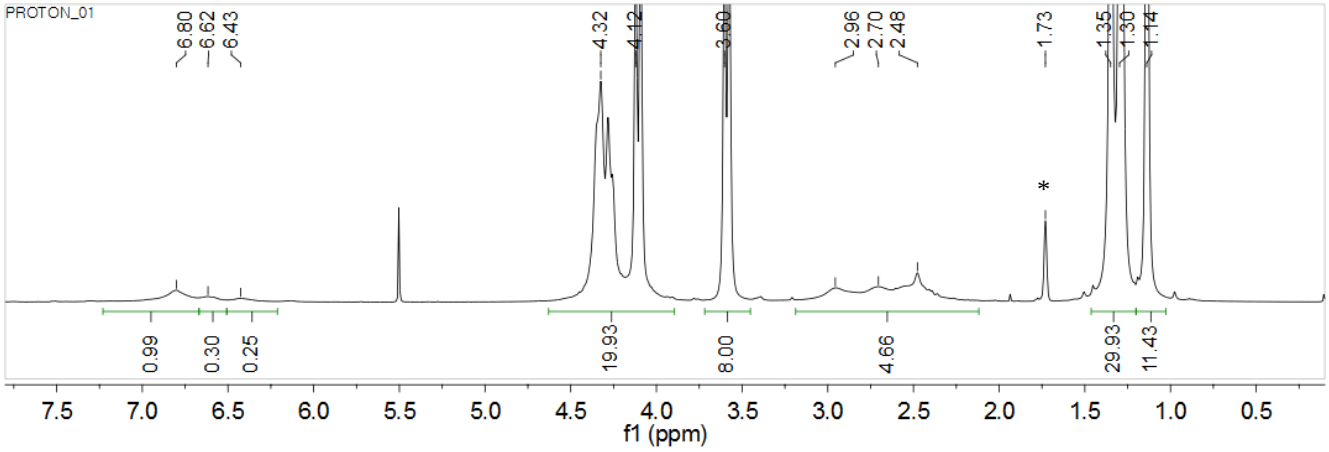
cis : *trans* = (0.31) : (1.27 + 0.30) = 1 : 5.1 (16% of *cis*)

Poly(2)



cis : *trans* = (0.30) : (1.39 + 0.29) = 1 : 5.6 (15% of *cis*)

Poly(3)



cis : *trans* = (0.25) : (0.99 + 0.30) = 1 : 5.2 (16% of *cis*)

Two dimensional NMR analysis in THF-d_8: COSY and NOESY

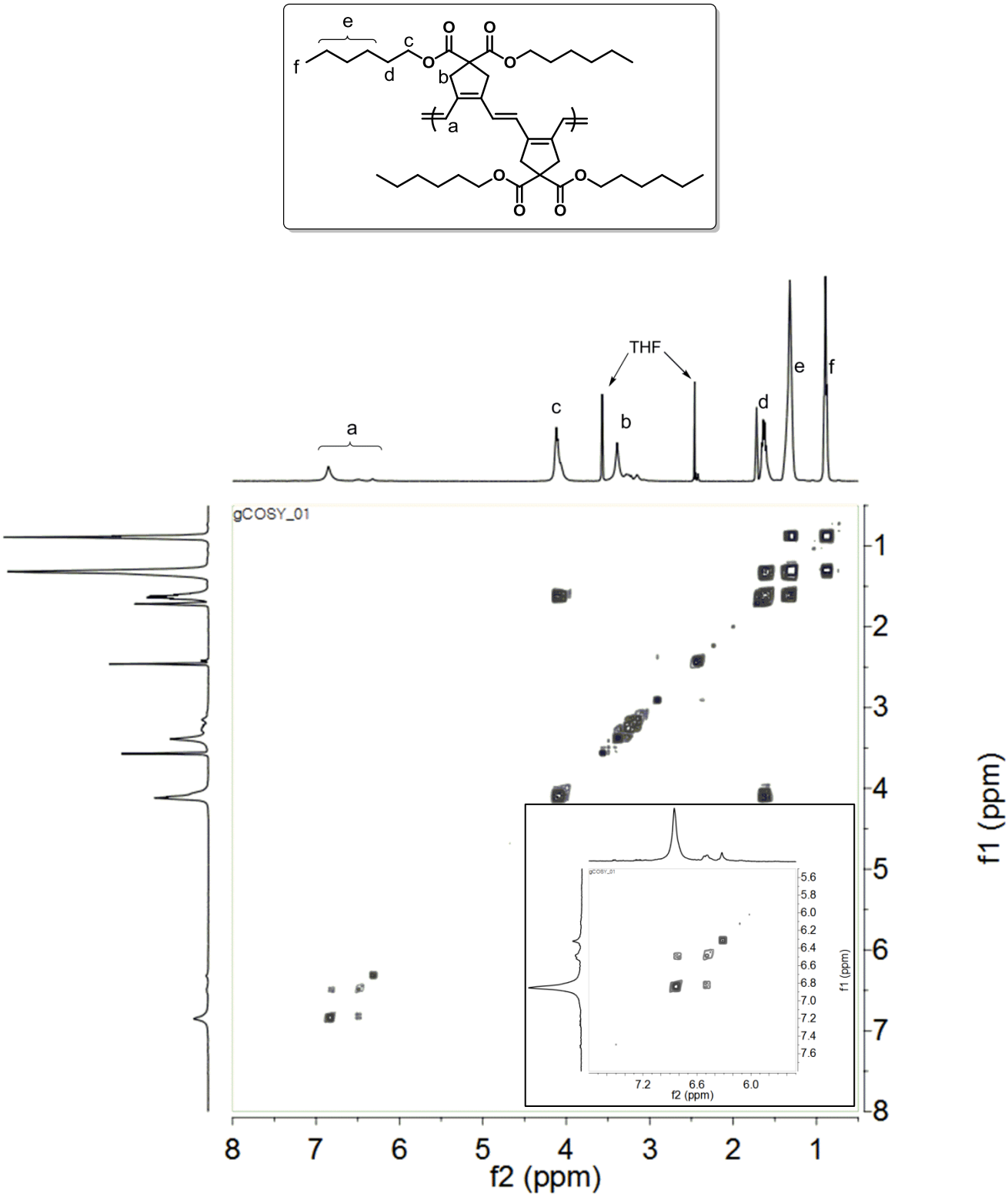


Figure S7. COSY of PDHDPM (inset: conjugated olefin region)

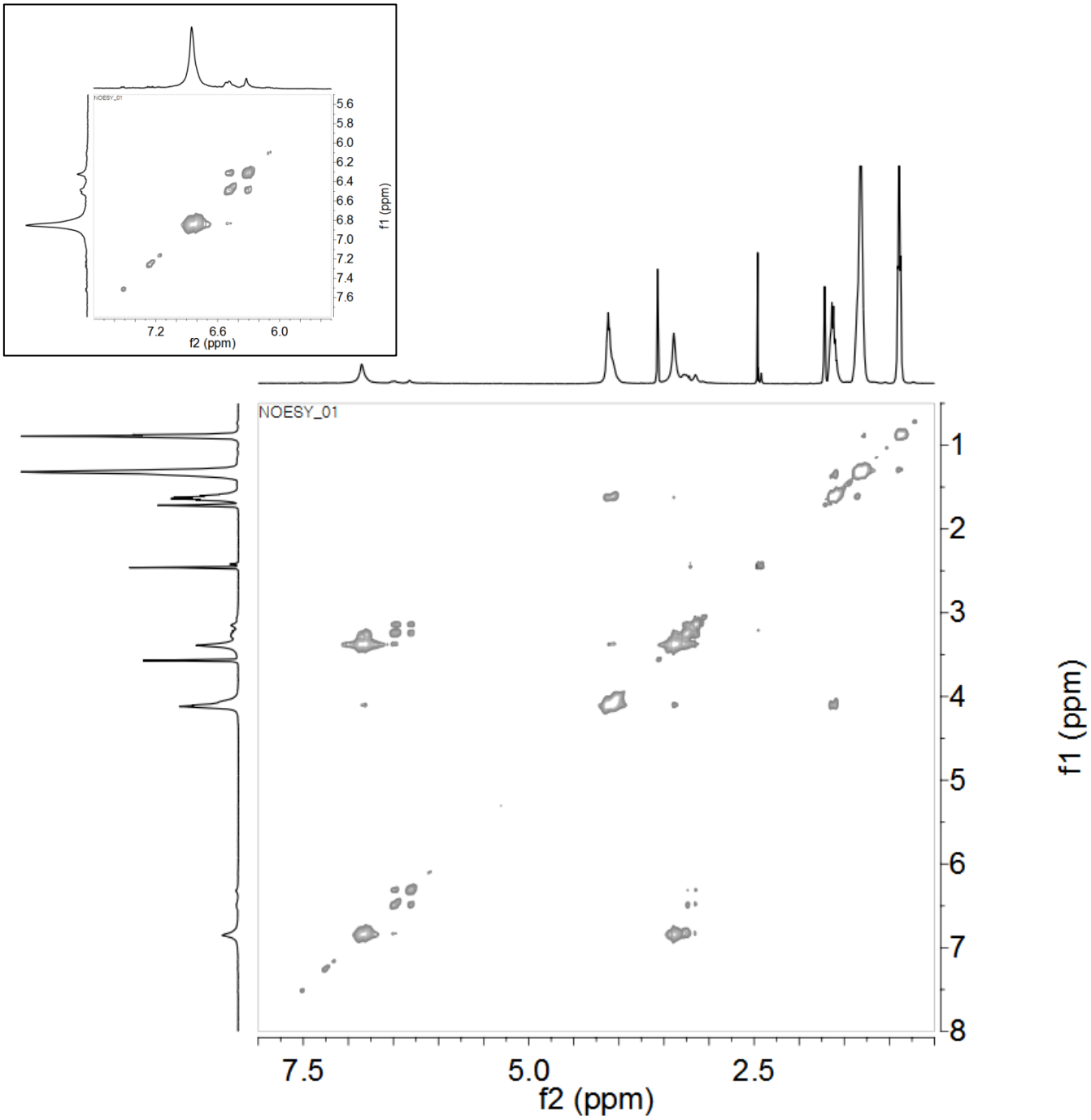


Figure S8. NOESY of PDHDPM (inset: conjugated olefin region)

Retardation of isomerization by TEMPO

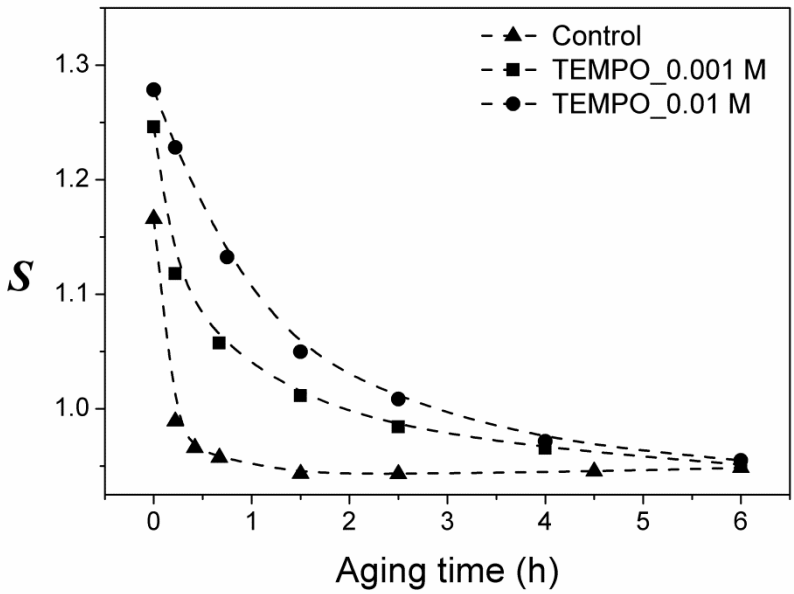


Figure S9. Changes in *S* by addition of TEMPO in chloroform solution.

Reference

1. Kang, E.-H.; Lee, I. S.; Choi, T.-L. *J. Am. Chem. Soc.* **2011**, *113*, 11904.

2. Fox, H. H.; Wolf, M. O.; O'Dell, R.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc*. **1994**, *116*, 2827.