Supporting Information

Quantum Amplified Isomerization in Polymers based on Triplet Chain Reactions

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	<u>Page</u>
Instrumentation	S2
Materials	S2
References	S2
¹ H NMR spectra	\$3-\$11

Instrumentation. NMR measurements were performed at 300 MHz for ¹H and 75 MHz for 13 C. HPLC analysis was carried out using reverse phase methods with linear solvent gradients from 90% Solvent A/10% Solvent B to 100% Solvent B over 10 min. Method 1: Hypersil BDS-C18 column (5 µm × 3 mm × 50 mm); Solvent A was 0.1 M aq. ammonium acetate, Solvent B was 1:1 acetonitrile:isopropanol; flow rate was 2.0 mL/min. Method 2: YMC ODS-AQ 120A column (5 µm × 3 mm × 100 mm); Solvent A was 0.1 M aq. ammonium acetate, Solvent B was acetonitrile; flow rate was 1.0 mL/min. GC/MS analysis was carried out using a Restek RTX-5MS column (30 m \times 0.25 mm \times 0.25 µm) using a temperatures ramp starting at 50 °C (hold 2 min) and increasing at 15 °C/min to 320 °C (hold 3 min). Differential Scanning Calorimetry (DSC) was performed under nitrogen at a heating rate of 10 °C/min. The T_g was determined as the midpoint of the transition on the second heating scan (i.e., after heating above T_{g} during the first scan and quenching). Size-exclusion chromatography (SEC) with viscometry detection was carried out in uninhibited THF using three Polymer Laboratories Plgel mixed-C columns. Absolute molecular weights were calculated from the viscosity data and a universal calibration curve constructed from narrow-molecular weight distribution polystyrene standards between 580 (log M = 2.76) and 2,300,000 (log M = 6.36). Distributions and molecular weight averages were corrected for axial dispersion assuming a Gaussian band-broadening function.

Materials. Crude porcine liver esterase (24 units/mg) was obtained from Aldrich. Buffer was made from potassium phosphate (0.1 M) and adjusted to pH 7.8 with 10% HCl. Most co-sensitizers were obtained through commerical sources or were gifts from Kodak Research Laboratories. DB2 and DB3 were synthesized as previously reported.^{S1,S2}

S1. Dopper, J. H.; Greijdanus, B.; Oudman, D.; Wynberg, H. *Tetrahedron Lett.* 1975, 4297.
S2. Koster, J. B.; Timmermans, G. J.; van Bekkum, H. *Synthesis* 1971, 139.

















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P5

