Supporting Information

Mechanistic studies of photoinitiated free radical polymerization using a bi-functional thioxanthone acetic acid derivative as photoinitiator.

Feyza Karasu,[1] Nergis Arsu,[1]* Steffen Jockusch,[2]* Nicholas J. Turro[2]

[1]*Yildiz Technical University, Department of Chemistry, Davutpasa Campus, Istanbul 34210, Turkey*

[2]*Columbia University, Department of Chemistry, 3000 Broadway, New York, NY 10027*

Detection of gaseous CO_2, which is generated by photolysis of TX-Ct and TX-Ma.

1 mL of each solution of TX-Ma and TX-Ct (5 mM) in DMF was placed in a Pyrex tube which was connected to another tube containing an aqueous solution of Na_2CO_3 (0.67 mM) and one drop of phenolphthalein solution (0.025 mM). Under our irradiation conditions (UVA: 12 W/m^2, UVB: 50 W/m^2) the pink color of the phenolphthalein solution disappeared after approximately 1 hour of irradiation of the two photoinitiators, which indicates CO_2 generation.

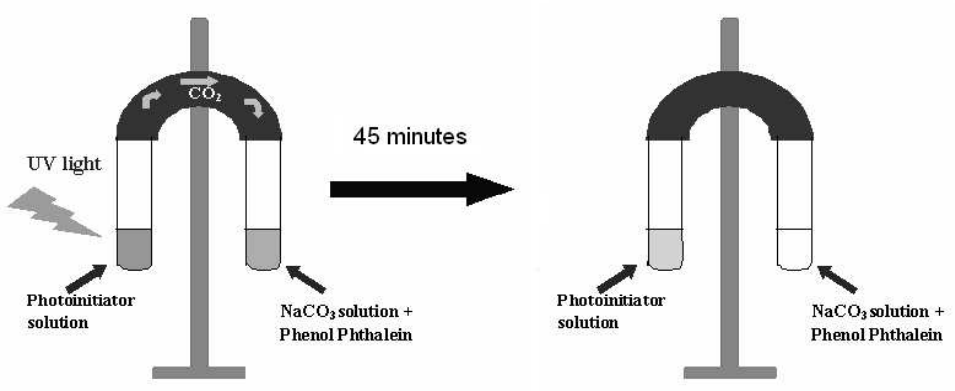

Figure S1: Schematic representation of the apparatus to demonstrate decarboxyation of photoinitiators.

Determination of bi-molecular quenching rate constants by molecular oxygen.

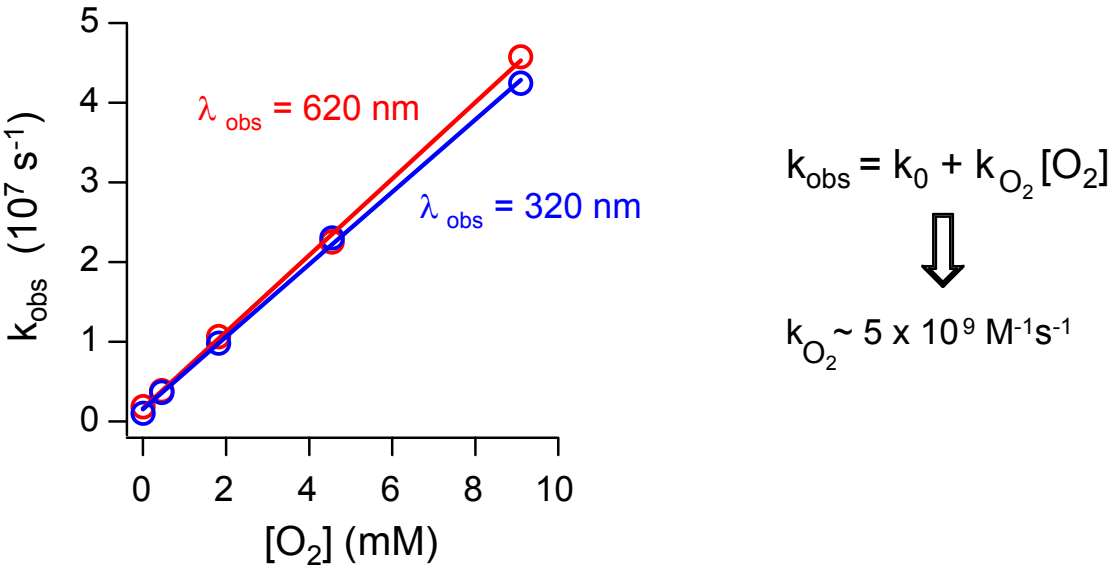

Figure S2: Dependence of the pseudo-first-order rate constant of the transient absorption decays at 320 nm and 620 nm on the concentration of dissolved molecular oxygen in acetonitrile. The transients were generated by pulsed laser excitation (355 nm, 5 ns) of acetonitrile solutions of TX-Ma. Varying oxygen concentrations were achieved by bubbling the sample solutions with different O_2/N_2 mixtures. Saturation concentration of acetonitrile after bubbling with O_2 at 24°C: [O_2] = 9.1 mM (Clark, W. D. K.; Steel, C. *J. Am. Chem. Soc.* **1971**, *93*, 6347-6355).

UV-Vis analysis of polymer generated by photopolymerization.

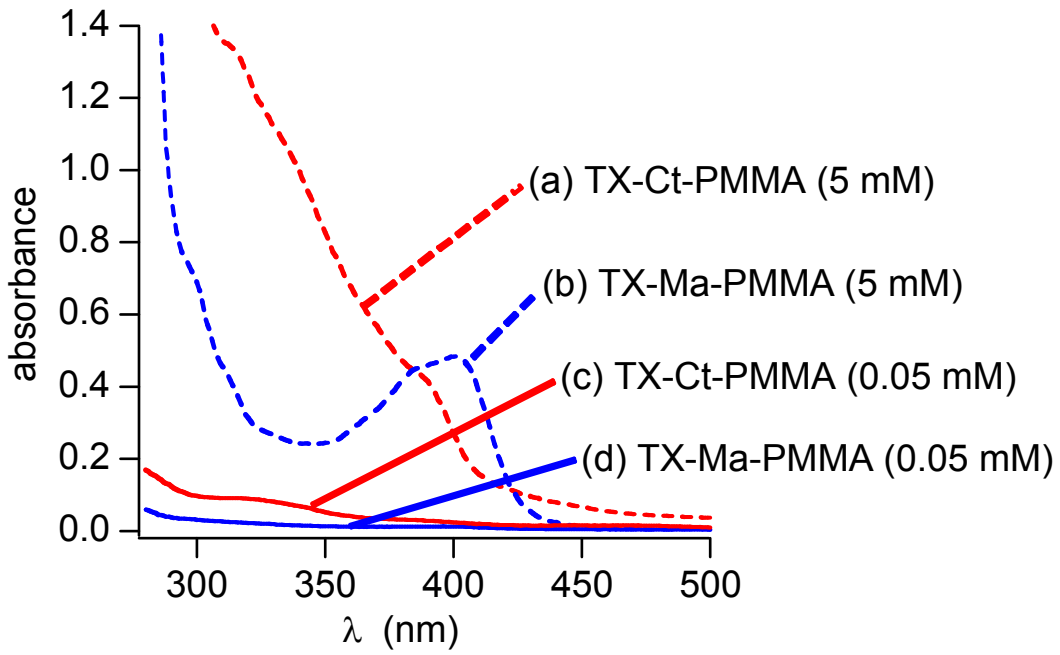

Figure S3: UV absorption spectra of PMMA (5 mg/mL) in DMF obtained by photoinitiated polymerization of MMA under nitrogen with TX-Ct (a) and TX-Ma (b) ([PI] = 5 mM) and TX-Ct (c) and TX-Ma (d) ([PI] = 0.05 mM). The spectra show that at high initiator concentration (5 mM) the TX chromophore is incorporated into the polymers (a,b). However, no absorbance attributed to TX was observed in the case of initiation with a low initiator concentration (0.05 mM) (c,d).