Photopolymerization without Light – Polymerization of Acrylates Using Oxalate Esters and Hydrogen Peroxide

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Supporting Information

Synthesis of Model Peroxides

The syntheses were done according to the procedure of Lahti et. al. [1] with some modifications. Commercially available 90% water solution of *tert*-butyl hydroperoxide (10 ml) was dissolved in 50 ml of pentane and dried over Na_2SO_4. The solution was filtered and pentane was removed at reduced pressure at 0°C. During all next steps precautions were taken to keep the reaction mixtures and products at 0°C and at the absence of a daylight at all time – syntheses and work-up were carried out at illumination by reduced intensity tungsten lamp. Authors of [1] also do not recommend to carry these reactions out on significantly larger scales.

tert-Butylperoxyoxalyl Chloride solution.

The solution of oxalyl chloride (13.42 g, 105.7 mmol) in 35 ml of pentane was cooled to 0°C under atmosphere of dry argon. A solution of previously dried tert-butyl hydroperoxide (2.3 g, 25.6 mmol) in 40 ml of pentane was added dropwise over 30 min via syringe and the reaction mixture was stirred at 0°C for 30 min followed by removal of pentane and excess of oxalyl chloride under reduced pressure at 0°C. After removal was

complete, the flask was purged by dry argon and 35 ml of cold dry diethyl ether was added. The resulting solution was immediately used in the next step.

Phenoxyoxalyl tert-Butyl Peroxide.

To the solution of *tert*-Butylperoxyoxalyl Chloride obtained from the previous step the solution of phenol (2.4 g, 25.6 mmol) and pyridine (2.02 g, 25.6 mmol) in 15 ml of dry diethyl ether was slowly added via syringe under atmosphere of dry argon at 0°C. The reaction mixture was stirred for 30 min at 0°C, then filtered and washed consequently with cold aqueous solutions of 10% H_2SO_4, 10% $NaHCO_3$, and water. The resulting ether solution was dried over Na_2SO_4. The diethyl ether was removed under reduced pressure at 0°C, the residue was dissolved in pentane and filtered through 2 cm layer of silica. The pentane was removed under reduced pressure at 0°C to yield 1.3 g (21%) of colorless oil. This product was free of phenol and contained only traces of di-*tert*-Butylperoxalate. The compound is stable when stored in the dark at -18°C. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm: 7.47-7.38 (m, 2H, 3-Ar*H* + 5-Ar*H*), 7.34-7.27 (m, 1H, 4-Ar*H*), 7.24-7.16 (m, 2H, 2-Ar*H* + 6-Ar*H*), 1.42 (s, 9H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm: 155.5 (1C, PhO-*CO*), 154.4 (1C, *CO*-OO), 149.7 (1C, *C1*-Ar), 129.7 (2C, *C3*-Ar + *C5*-Ar), 127.0 (1C, *C4*-Ar), 120.8 (2C, *C2*-Ar + *C6*-Ar), 85.7 (1C, $C(CH_3)_3$), 26.0 (3C, CH_3).

2,4,6-Trichlorophenoxyoxalyl tert-Butyl Peroxide.

The synthesis and work-up were similar to those described above. The solution of 2,4,6-Trichlorophenol (4.74 g, 24 mmol) and pyridine (1.90 g, 24 mmol) in 15 ml of dry diethyl ether was used in the synthesis. Yield of 2.5 g (30 %) was obtained with m. p. of the resulted solid being 38-40°C. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm: 7.42 (s, 2H, 3-

Ar*H* + 5-Ar*H*), 1.42 (s, 9H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm: 154.1 (1C, PhO-*CO*), 152.1 (1C, *CO*-OO), 141.6 (1C, *C1*-Ar), 133.4 (1C, *C4*-Ar), 129.0 (2C, *C2*-Ar + *C6*-Ar), 128.9 (2C, *C3*-Ar + *C5*-Ar), 86.0 (1C, $C(CH_3)_3$), 26.0 (3C, CH_3).

Literature:

[1] Lahti, P. M.; Modarelli, D. A.; Rossitto, F. C.; Inceli, A. L.; Ichimura, A. S.; Ivatury, S. // Aryl Oxalate Derivatives as Convenient Precursors for Generation of Aryloxyl Radicals // *J. Org. Chem.* **1996.** *61*(5), 1730-1738.

Synthesis of NPPG

The solution of benzoylformic acid (3.0 g, 20.0 mmol) and N,N-dimethylformamide (25 mg - catalyst) in 30 ml of dry dichloromethane was cooled to 0°C under atmosphere of dry argon. The oxalyl chloride (3.99 g, 31.4 mmol) was added dropwise via syringe at stirring, the reaction mixture was stirred overnight. During this time the reaction mixture has reached the temperature of 25°C. Dichloromethane and excess of oxalyl chloride were removed under reduced pressure at 25°C, the flask was purged with dry argon, the residue was dissolved in 30 ml of dry dichloromethane and dry pyridine (0.47 g, 6 mmol) was added. The reaction mixture was cooled to 0°C under atmosphere of dry argon and a solution of 2,4-dinitrophenol (3.52 g, 19 mmol) and dry pyridine (2.37 g, 30 mmol) in 30 ml of dry dichloromethane was added via syringe. The reaction mixture was left overnight at stirring allowing the reaction mixture to reach the temperature of 25°C. After that, the reaction mixture was washed consequently with cold solutions of 10% H_2SO_4 (2 times), 5% $NaHCO_3$ (2 times), and water (1 time), dried over Na_2SO_4 and filtered through 2 cm layer of silica. Removing the solvent under reduced pressure gave yellow solid, which was found to be an 1:1 molar mixture of target ester

and 2,4-dinitrophenol. The recrystallization from dichloromethane – hexane yielded 1.7 g (28%) of pale-yellow crystals (m.p. 128 – 129°C). ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm: 9.06 (d, *J* = 2.7 Hz, 1H, 3-Ar$(NO_2)_2$*H*), 8.62 (dd, J_1 = 8.7 Hz, J_2 = 2.7 Hz, 1H, 5-Ar$(NO_2)_2$*H*), 8.23-8.13 (m, 2H, 2-Ar*H* + 6-Ar*H*), 7.79-7.71 (m, 1H, 4-Ar*H*), 7.69 (d, *J* = 8.7 Hz, 1H, 6-Ar$(NO_2)_2$*H*), 7.64-7.54 (m, 2H, 3-Ar*H* + 5-Ar*H*). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm: 182.5 (1C, Ph-*CO*), 159.2 (1C, *CO*-O), 147.7 (1C, *C1*-Ar$(NO_2)_2$), 145.9 (1C, *C4*-Ar$(NO_2)_2$), 141.6 (1C, *C2*-Ar$(NO_2)_2$), 135.9 (1C, *C4*-Ar), 131.7 (1C, *C1*-Ar), 130.5 (2C, *C2*-Ar + *C6*-Ar), 129.4 (1C, *C5*-Ar$(NO_2)_2$), 129.2 (2C, *C3*-Ar + *C5*-Ar), 126.7 (1C, *C6*-Ar$(NO_2)_2$), 122.0 (1C, *C3*-Ar$(NO_2)_2$).

Purification of DNPO

Purification has been done by extracting the sample with CHCl3 in Soxhlet apparatus for three days. Crystallization of the solution obtained gave the product having m.p. 191-193^{o}C (lit.: 189-190^{o}C).

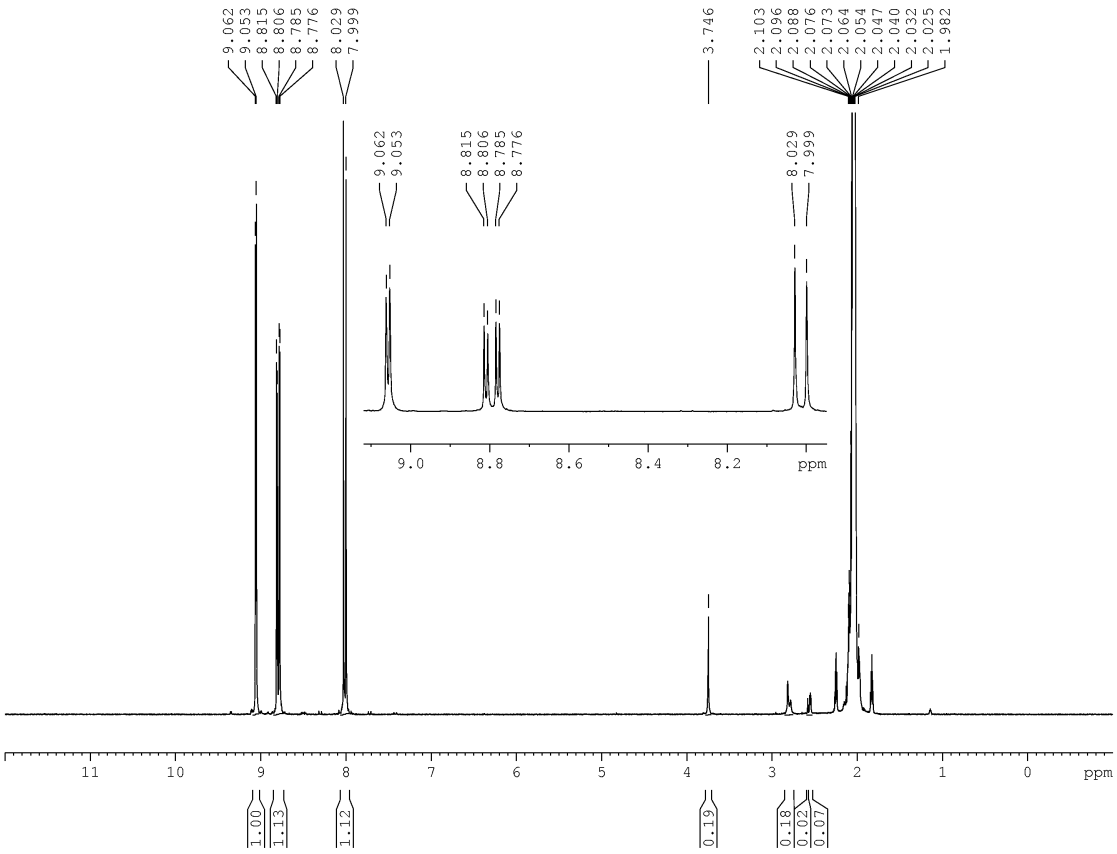

Figure S1. ^{1}H NMR of purified DNPO.

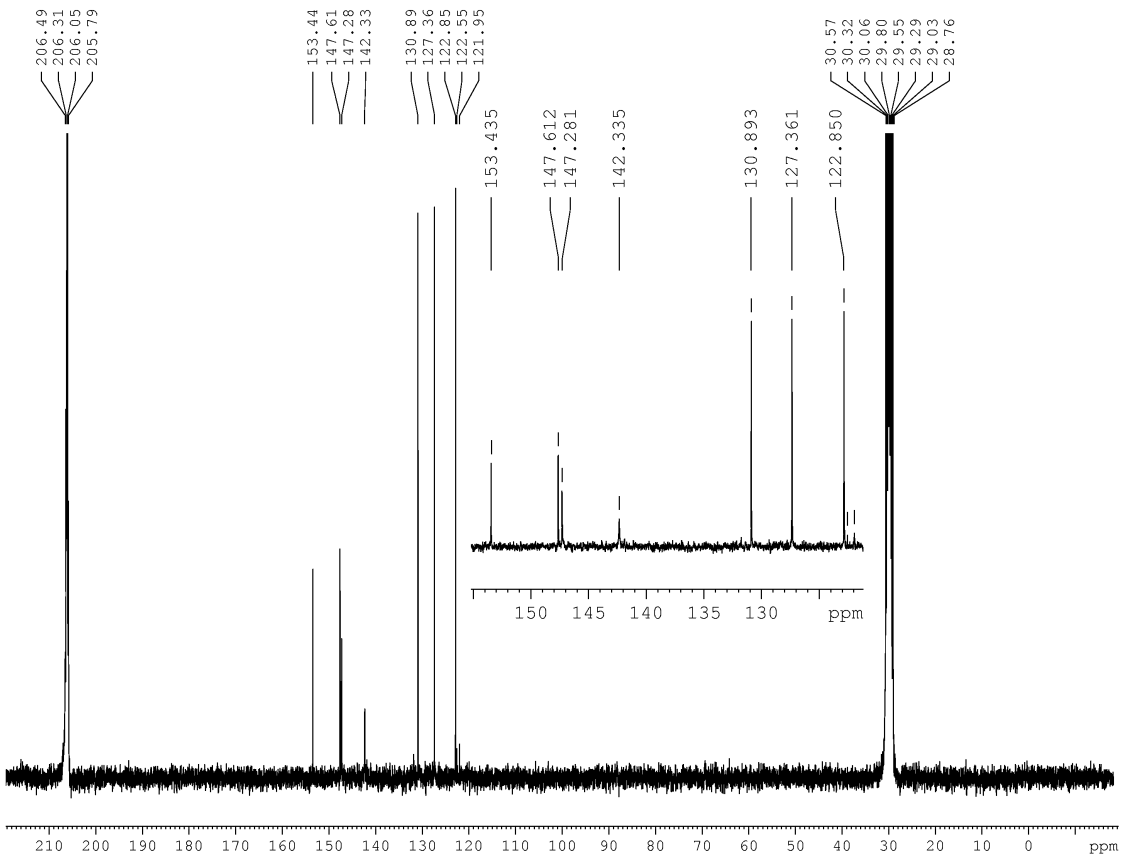

Figure S2. ^{13}C NMR of purified DNPO.

Additional Double Bond Conversion Curves

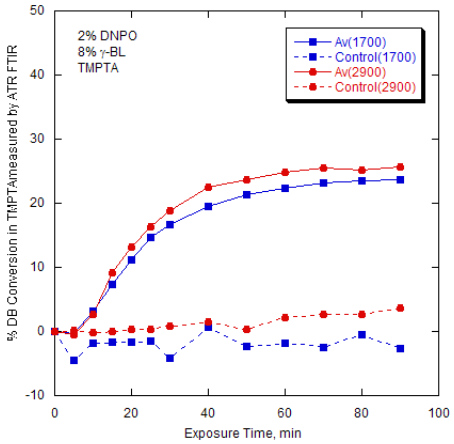

Figure S3. Comparison of DB conversion profiles for TMPTA obtained using carbonyl and CH stretch fundamentals.

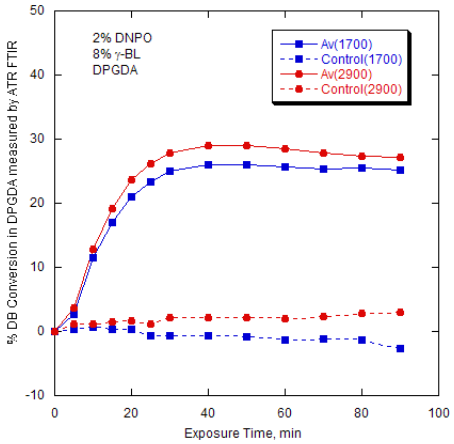

Figure S4. Comparison of DB conversion profiles for DPGDA obtained using carbonyl and CH stretch fundamentals.

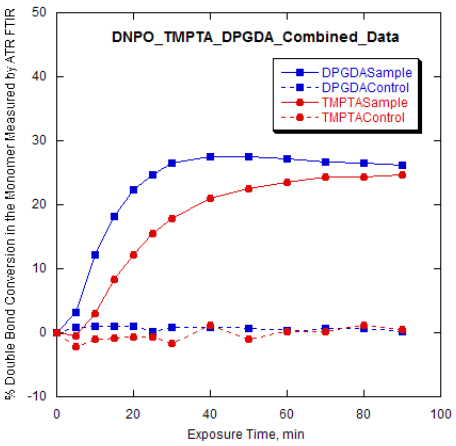

Figure S5. Combined data for TMPTA and DPGDA obtained by averaging data from C=O and CH internal references.

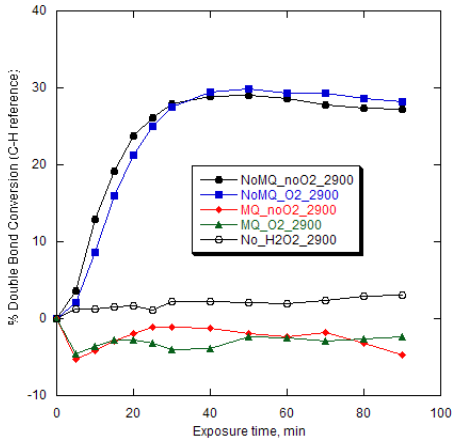

Figure S6. Control experiments investigating the effect of various factors on RC activity for CH internal reference.

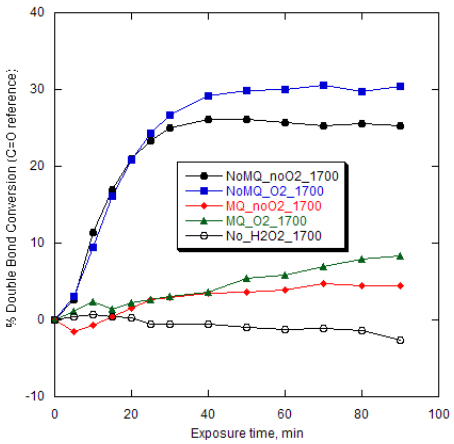

Figure S7. Control experiments investigating the effect of various factors on RC activity for C=O internal reference.

LFP Studies

<u>308 nm excitation</u>

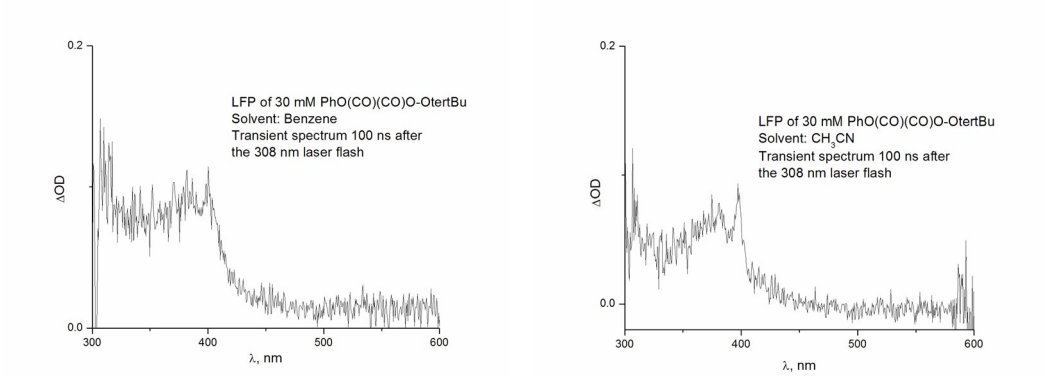

Figure S8. Transient spectra obtained 100 ns after 308 nm excimer laser excitation of 30 mM of Phenoxyoxalyl *tert*-Butyl Peroxide in benzene (left) and CH_3CN (right). Two maxima characteristical of phenoxyl radical are observed in the 380 – 405 nm interval for both solvents.

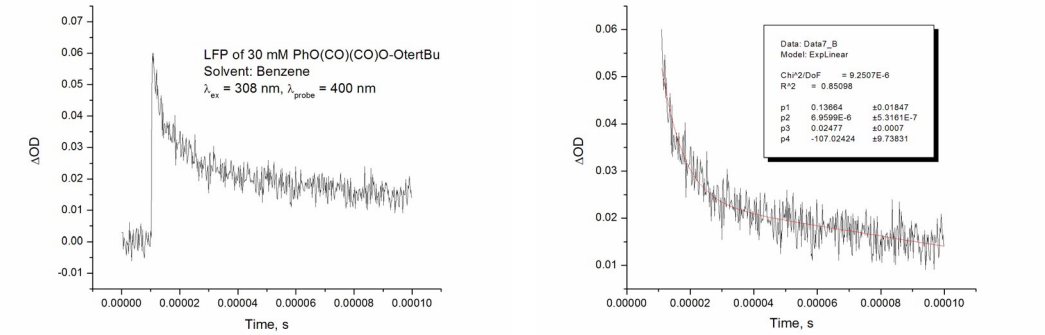

Figure S9. Kinetic trace and its fit obtained by monitoring decay of the PhO• transient signal in benzene at 400 nm. Lifetime of 7.0 μs was obtained using (monoexponential + linear) fit.

The obtained lifetimes for this and other traces are used only to compare transient signals under different conditions and do not represent any kinetic information as PhO• radicals decay via nonexponential pathway.

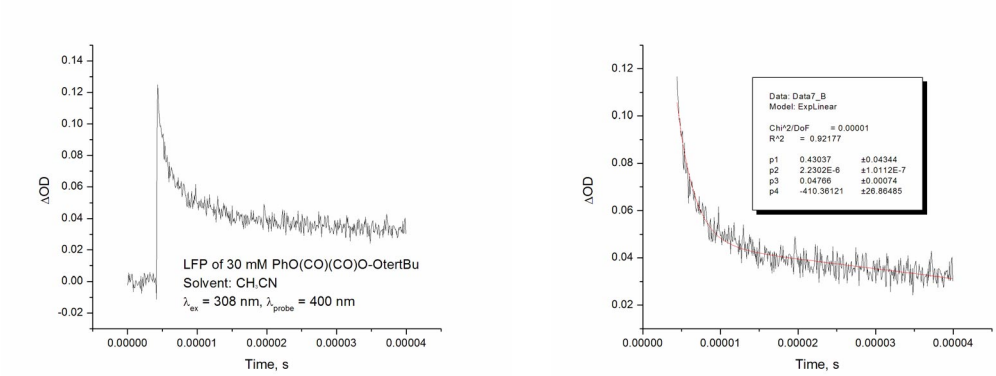

Figure S10. Kinetic trace and its fit obtained by monitoring decay of the PhO• transient signal in acetonitrile at 400 nm. Lifetime of 2.2 μs was obtained.

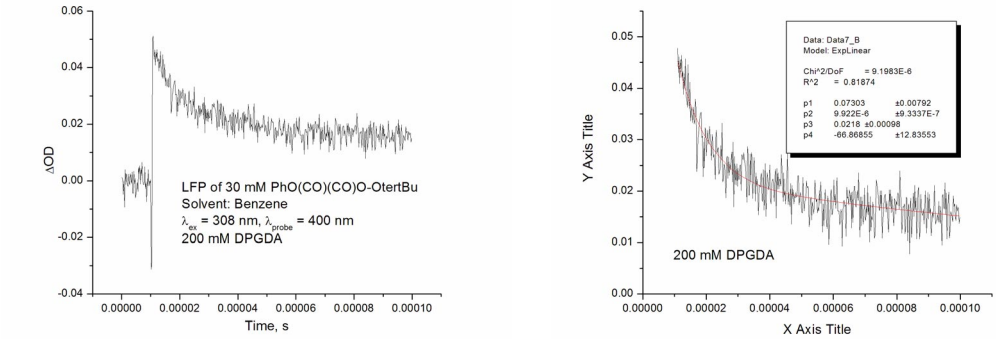

Figure S11. Kinetic trace and its fit obtained by monitoring decay of the PhO• transient signal in benzene at 400 nm with 200 mM of DPGDA monomer added. Lifetime of 9.9 μs was obtained, which is not significantly different from 7.0 ms lifetime of PhO• in the absence of any monomer. This indicates no reactivity between PhO• and DPGDA.

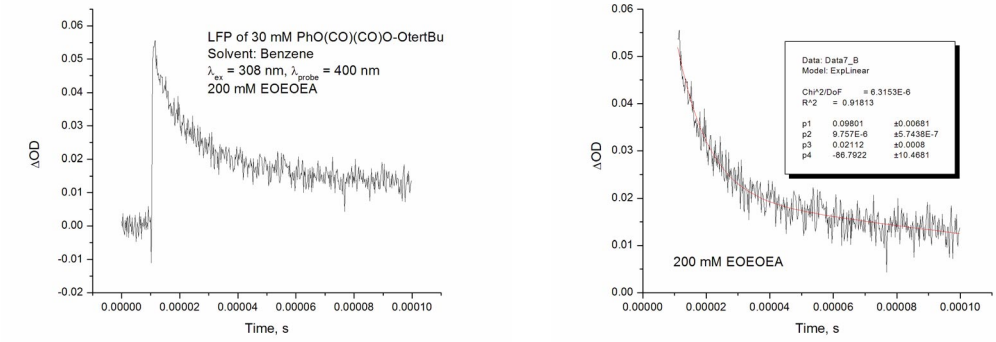

Figure S12. Kinetic trace and its fit obtained by monitoring decay of the PhO• transient signal in benzene at 400 nm with 200 mM of EOEOEA monomer added. Lifetime of 9.8 μs was obtained, which is not significantly different from 7.0 ms lifetime of PhO• in the absence of any monomer. This indicates no reactivity between PhO• and EOEOEA.

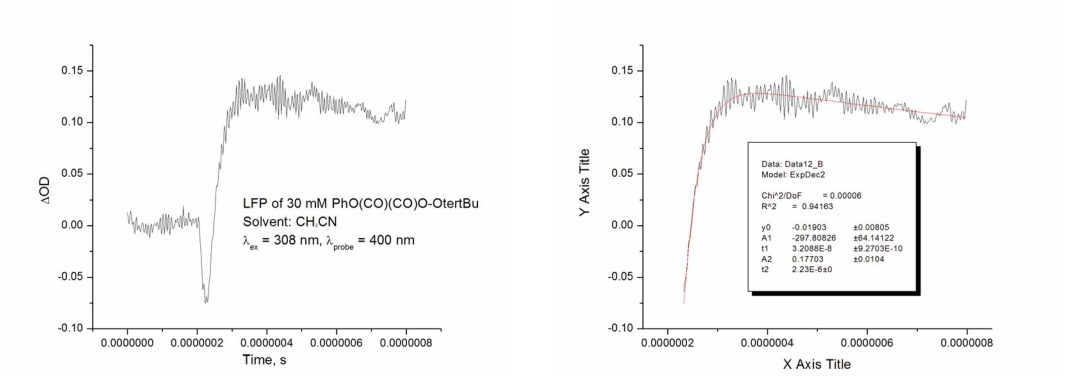

Figure S13. Kinetic trace and its fit obtained by monitoring the growth of the PhO• transient signal in benzene at 400 nm. Growth lifetime of 32 ns was obtained, which corresponds to the response time of the LFP setup. Therefore, the rate of PhO• formation and, hence, the rate of PhO(CO)• decarbonylation is faster than the 32 ns response time of the LFP setup.

355 nm excitation

PhO• radicals were generated according to the procedure reported by Ingold and coworkers (JACS, 1994, 116(21), 9440 – 9447).

Solvent: $(Me_3CO)_2$/benzene 3/1; [PhOH] = 1.4 M.

Mechanism of Formation:

$$Me_3COOCMe_3 \rightarrow 2Me_3CO\bullet \quad (1)$$

$$Me_3CO + PhOH \rightarrow Me_3COH + PhO\bullet \quad (2)$$

Phenoxyl radicals are generated within the time interval of the laser flash (ca. 10 ns) owing to fast time of reactions (1) and (2)

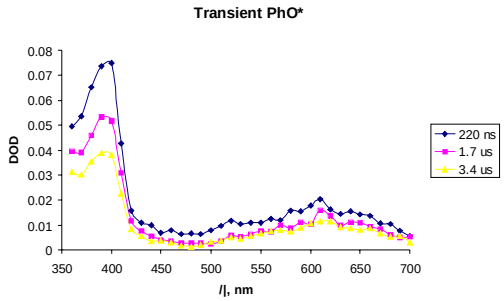

Figure S14. Transient spectra obtained 220, 1700 and 3400 ns after 355 nm Nd:Yag laser excitation of 1.4 M phenol in 3/1 $(Me_3CO)_2$/benzene. In addition to two characteristic maxima in the 380 – 405 nm interval, weaker maximum was observed around 610 nm.

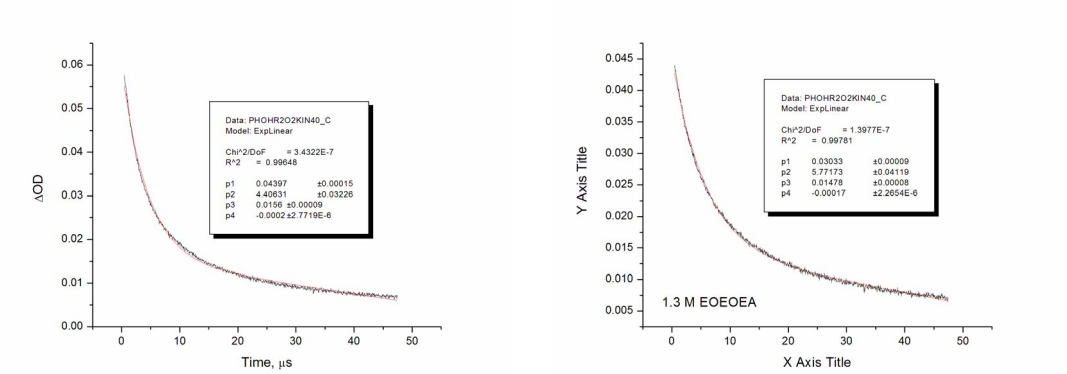

Figure S15. Fitted kinetic traces obtained by monitoring decay of the PhO• transient signal in benzene at 400 nm without monomer (left) and with 1.3 M DPGDA monomer added (right). Lifetimes of 4.4 and 5.8 µs, respectively, were obtained using (monoexponential + linear) fit. This confirms no reactivity between PhO• and DPGDA.

<u>266 nm excitation</u>

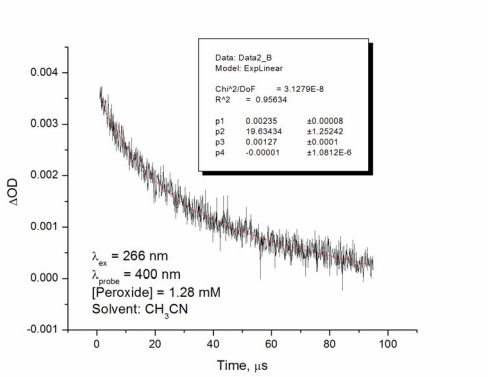

Figure S16. Fitted kinetic trace obtained by monitoring decay of the PhO• transient signal in benzene at 400 nm after 266 nm Nd:Yag laser excitation of 1.28 mM of Phenoxyoxalyl *tert*-Butyl Peroxide.

$\tau_{phenoxyl}$ = 19.6 µs

Addition up to 25 mM of both DPGDA and EOEOEA did not result in significant change of the lifetime

Higher concentrations of monomer could not be used due to own absorbance of acrylates at 266 nm.